Measurement of Wavefunction Overlap of Phosphorus Donors in Silicon

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Abstract

There are many formidable challenges along the road to building a silicon quantum computer, and perhaps none is more demanding than engineering and measuring the coupling between qubits. In the P donor implementation of a solid state quantum computer, entanglement is mediated via coupling between P donors. The exchange coupling interaction governs the two qubit interactions and the exchange energy sets a limit on the speed of the qubit interactions. Although the interaction has been extensively modelled, there are few techniques that can provide information as to the strength of the interaction.

The study of donor-donor interactions is made difficult by the need to engineer and control the spacing between atoms. This thesis reports a novel approach to the creation of ensembles of pairs of donors using molecular ion implantation. The technique is consistent with the top-down strategy for the creation of qubits via low energy phosphorus ion implantation.

While originally motivated by the measurement of the strength of the exchange coupling between phosphorus donor atoms via a proposal to use electronic Raman scattering, this thesis ended up studying the various components required of the measurement. These included the electronic Raman scattering technique, the accurate measurement of the sample temperature, and the production and analysis of samples containing closely spaced clusters of donors.

The main results of this thesis are as follows:

1. Simulations of the ion implantation process were employed to calculate the expected distributions of the phosphorus donors following ion implantation. Monte Carlo simulations were compared to molecular dynamics simulations for both atomic and molecular dimer implantation. The degree of clustering of P donors into pairs and clusters containing more than two atoms was simulated for both molecular and atomic implantation. The results provide a set of simulation tools that provide a guide to the implantation parameters that are required to produce the required distribution of donors.

2. Electronic Raman scattering of phosphorus donors in silicon was evaluated as a technique to measure the exchange coupling between pairs of donors. Both visible and infra-red excita-
tion was employed. For visible excitation, the electronic Raman transition was not observed due to competition with the much more efficient process of exciton generation and binding to donors. Measurements in the near infra-red revealed the electronic Raman scattering transition from both donors and acceptors in bulk doped silicon, but did not have the sensitivity to measure shallow implanted samples. It was not possible to determine the exchange coupling interaction using the available experimental set-up.

3. The measurement of exchange coupling requires the precise knowledge of the local sample temperature, and as laser heating can be an issue, a technique was required to provide a local temperature probe. The temperature dependence of the TO mode phonon was studied as a local probe of temperature for the cryogenically cooled samples. An anomalous shift in the temperature dependence of the frequency of the phonon was observed and reported for the first time.

4. Low temperature photoluminescence was used to evaluate the quality of the sample substrate and impurities introduced during sample processing. Photoluminescence measurements of the phosphorus ion implanted samples revealed a peak originating from clusters of phosphorus donors which shifted in energy with the density of phosphorus atoms. The behaviour of the peak was modelled using two donor interaction, but it was the many-particle process of band gap narrowing and the formation of a dopant band which fully explained the peak behaviour.
Declaration

This is to certify that:

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

(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 tables, maps, bibliographies and appendices.

......................
Nikolas Stavrias.
Preface

The work presented in this thesis which was performed in collaboration with the following people:

- The near infra-red spectrometer was built in collaboration with P. Spizzirri.
- FT-photoluminescence spectra were obtained with the aid of M. Thewalt.
- Implantation of samples at ANU were performed by J. McCallum.
- Electron paramagnetic resonance measurements were performed by W. Huchison.
- Molecular dynamics simulations on phosphorus ion implants into silicon performed by H. F. Wilson.
- My contribution to the work on NV-centres in diamond was the implanted ion distribution simulations.
- In work published on the chemistry of copper luminescent centres in $^{28}\text{Si}$, the natural copper in natural silicon samples were produced by me and I participated in the measurements.

At certain points in this thesis, figures have been used that are not my own, but which have been taken from other sources. In these situations, a reference at the end of the figure caption has been used to denote and acknowledge the source of these figures.
I would like to thank the following people for their help and support during my candidature: my supervisors Steven Prawer, Paul Spizzirri, and Andy Martin; Jeff McCallum, David Jamieson, Chris Pakes, Eric Gauja, Wayne Hutchison, Cam Wellard, Andrew Greentree, Lloyd Hollenburg, Alberto Cimmino, Greg Tamanyan, Roland Szyszanski, Wayne Powrie, Paolo Olivero, Brett Johnson, the Hox, and the many many more in MARC and the CQCT; can’t forget Bob Clarke – where would we be without him.

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Shout out to all my friends who inhabit the world outside of the physics building. Coburgistan crew in the house.

Finally, a heartfelt thanks to my family for all their love and support, Mum, Dad, George and Lambros, Pappou and Yiayia, and all the extended family.
List of Publications

Refereed Publications


Conference Presentations


N. Stavrias, P.G. Spizzirri, S. Prawer, J.C. McCallum, D.N. Jameson, A. Cimmino, M.L.W. The-


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Chapter 1

Introduction

1.1 Context

The development of the theory of quantum mechanics beginning in the early part of the twentieth century has led to one of the most successful theories in physics. Talk of exploiting the quantum mechanical properties of systems to perform calculations didn’t begin until the early 1980’s, with Feynman’s suggestion [1] that quantum mechanics may be used to simulate quantum systems. Such a computer would open up a class of problems which could be computed faster on a quantum computer than a classical computer [2], with the most famous of these, Shor’s algorithm [3] for finding the prime factors of numbers and Grover’s search algorithm [4] generating much interest in the practical implementation of a quantum computer (QC). For example, Shor’s algorithm could perform the factorising task exponentially faster on a quantum computer than the fastest known classical algorithm on a classical computer. As one of the most widely used forms of electronic data security, the Rivest-Shamir-Adleman (RSA) encryption protocols [5], relies on the difficulty classical computers have in factoring large numbers, an implementation of Shor’s algorithm will have huge implications for cryptography.

A qubit is the logical unit of quantum information processing. A qubit can be in one of two states $|1\rangle$ or $|0\rangle$ (like the classical bit, 1 or 0, on or off), but also in a superposition state $\alpha|0\rangle + \beta|1\rangle$. Entanglement between a number of these qubits gives a quantum computer its exponential computational advantage. The possibility of being in all the coupled states at once, where an action on one element affects every superposed state, allows for operations on a superposition of $2^N$ different states to be performed simultaneously for an $N$ qubit system, an exponential increase in computing power.

The realisation of a practical implementation of quantum information processing involves the precise knowledge and control of the physical systems the quantum devices are based on and the
ability to construct a large number of interacting qubits. Potential candidates for use as qubits are any two level system that can physically be encoded, such as a spin state in a magnetic field, the polarisation of a photon or the ground and excited state of an electron. This opens up many possibilities for physical implementation, however the proposal must meet certain criteria [6] to form the basis of a useful device. These include: the ability to operate on individual qubits, to form quantum logic gates by coupling qubits, to read-out the states of the qubits, to make logical operations faster than environmental decoherence, and to be scaleable. Scalability is the ability for a quantum computer system to increase in size so as to perform larger and more complicated calculations. For example, to break RSA encryption, numbers of 4096 bits length require factorising. A quantum computer operating at 100 MHz and containing 24,484 qubits has been estimated at taking approximately 5 hours to complete the task [7].

Many systems have been proposed as candidates for building a working quantum computer, the most notable include those based on: liquid state NMR [8], ion traps [9, 10], optical systems [11, 12], superconductors [13–15], and semiconductors [16–18]. Each implementation has advantages and disadvantages. For example the liquid state NMR and ion trap quantum computers have been able to perform quantum algorithms on a handful of qubits, as both have good readout and encoding. However, the scalability of these systems is an issue as the difficulty of controllably adding another qubit increases with each qubit. Semiconductor systems offer the best candidates for scalable quantum computing.

The Centre for Quantum Computer Technology, based at various universities around Australia, has taken the approach of implementing a silicon based quantum computation device [19]. The key advantage in using the semiconductor silicon to build the quantum computation device is the prospect of scalability, where the knowledge accumulated by the silicon electronics industry in building large numbers of integrated nano-scale devices on a single chip can be utilised to build large numbers of qubits. Two dimensional architectures addressing scale up have been proposed [20], with regards to addressing states, readout, interactions of qubits and transporting states. Research into two types of devices is being conducted by the Centre, on the Kane type quantum computer and the charge qubit type which are described below.

### 1.1.1 Silicon Quantum Computing

Work in silicon quantum computation began with the proposal by Kane [21], where the nuclear spins of phosphorus atoms in a spin free $^{28}\text{Si}$ lattice, in a magnetic field, act as the qubits, see Figure 1.1 (a). The qubit is encoded in the spin by either aligning or anti-aligning the spin with the magnetic field. Applying a rotating magnetic field precesses the spins. The donor electrons mediate single and coupled two qubit interactions through the contact hyperfine interaction (with the nuclear spins), and the exchange interaction (with other electron spins).
CHAPTER 1. INTRODUCTION

Figure 1.1: Implementation of quantum computing in silicon: (a) Kane type, with the phosphorus nuclear spin state as the qubit and (b) charge type, with electron position in the double well of the two phosphorus atoms acting as the qubit. [19]

The P atom qubits are 20 nm apart and placed approximately 20 nm below the silicon surface. A set of electronic gates are present on the thin dielectric film at the surface, with the $A$ gates directly above the phosphorus atom qubits, and the $J$ gates between them. Voltages applied to the $A$ gates control the resonant frequency of the nuclear spin through the hyperfine interaction. The $J$ gate controls two qubit operations by attracting the wavefunctions of the neighbouring donor electrons, increasing their overlap and exchange coupling the spins. This produces a two qubit coupled electron-nuclear spin system. The fundamentals of this exchange interactions will be discussed in Chapter 2. The coupled electrons can form singlet or triplet spin states with an energy difference proportional to the wavefunction overlap. So applying a voltage to the $J$ gate couples the nuclear spins of the neighbouring donors and allows for two qubit interactions. One of the processes available here is the “swap gate” where the $J$ gate is applied for a certain amount of time and the nuclear spins swap states. Read out of the spin state of a phosphorus spin qubit can be performed through spin to charge conversion via a single electron transistor.

Another advantage of the solid state scheme over many others is the long spin coherence of the nuclear spin states of the phosphorus atoms in silicon. The spins are well isolated from their environment with spin-spin dephasing times $T_2$ of 25 s at room temperatures [22] and spin-lattice $T_1$ times of 10 hours at 1 K [23]. This allows for a large number of gate operations to be performed before the spins dephase, and the qubit states decohere.

The electron spins in silicon also have relatively long decoherence times (in relation to gate times), which has led to the proposal of a charge based P/P$^+$ quantum computer [24], see Fig-
1.2. RATIONALE, MOTIVATION AND RESEARCH DIRECTION

ure 1.1 (b). Two ionised phosphorus atoms and a single electron act as the qubit, forming a $\text{P}_2^+$ molecule in the solid state. The logical states of the qubit are the position of the electron on either of the donors, which can be read out through single electron transistors placed on the surface. The P atoms can be set 50 nm apart which makes for easier implementation in the short term than the nuclear spin counterpart.

1.1.2 Fabrication of Silicon Quantum Computer

The most challenging aspects of building the phosphorus in silicon quantum computer are the placement of single phosphorus atoms, their subsequent incorporation into the lattice, placing the electronics in the right place to address the qubits, and keeping the environment defect free. Two approaches have been taken towards the placement of the single atoms [19]: ‘bottom-up’, using scanning tunnelling microscopy (STM) lithography, and ‘top-down’ using single ion implantation.

While STM lithography of a clean hydrogenated silicon surface has the potential for atomic scale placement of the P atoms the implantation of single ions is a faster route to test devices. The STM tip makes holes in the hydrogenated silicon surface where the P atoms, introduction via $\text{PH}_3$ gas, can bond to the underlying substrate [25]. Low temperature epitaxial overgrowth of silicon incorporates these dopants into the crystal. From there a dielectric and metal gates can be placed above the overgrown silicon to control the state of the qubit. Low temperature processing is required so as to minimise the diffusion of the P atoms.

The ‘top-down’ approach involves the use of single ion implantation of phosphorus into silicon through holes made in a PMMA resist capping layer. Holes into the PMMA layer are made using electron beam lithography, providing the positioning for the qubits. A detector built into the substrate detects the ionisation from the ion strike [26], allowing for the controllable implantation of single ions. An alternative method to accurately place ions into substrates involves the use of a nano-aperture in a scanning probe cantilever [27]. The probe can find the correct position for the implantation via an atomic force scan of the surface, and act as a beam block to allow for the single ion implantation through the nano-aperture. A rapid thermal anneal is used to activate the phosphorus, and repair the damage from the ion strike. The electronics are then placed above with alignment to the implanted qubits provided by markers placed on the surface. The straggle (uncertainty in position due to statistical ion stopping) of the implanted ions reduces the accuracy of the atom placement, but allows for faster fabrication of test devices.

1.2 Rationale, Motivation and Research Direction

To build a working quantum computer device requires a good understanding of the qubit as a physical system. This includes both controllable interactions, where computations are performed
CHAPTER 1. INTRODUCTION

with the system, and unintended interactions which lead to decoherence pathways.

The most important interaction in the two-qubit gates of a Kane-type device (between neighbouring qubits), is the exchange coupling interaction. The strength of this interaction determines the gate times and thus the speed on the calculations. The methods pursued to place the phosphorus atom qubits in the device have some inherent uncertainty in the final position of the qubit. As the strength of the exchange coupling interaction is strongly dependent on the separation and orientation of neighbouring qubits, the effect of this on a working QC device is still unknown. With a working device, the strength of the exchange coupling interaction can be inferred by taking measurements on the system, but since we don’t have a working device another diagnostic tool is required. Optical tools could prove beneficial in measuring the exchange coupling between neighbouring donors.

Koiller et al. [28] recently proposed a method to measure the strength of the exchange coupling interaction between phosphorus donors in silicon. The proposal involved the use of electronic Raman scattering spectroscopy to measure a ground state transition in the phosphorus donor. An estimate of the exchange coupling strength would be provided by measuring the change in intensity with temperature of the split singlet and triplet lines of the coupled pair system. Sensitivity to few donors would be provided by exploiting a resonance condition in the scattering equation. Experimentally this proposal would require: an excitation source to exploit the resonance, a spectrometer which can resolve the split components of the line, cryogenics with temperature control, and the accurate measurement of the local sample temperature, as well as samples containing coupled pairs of donors. This technique has the potential to identify phosphorus atoms interacting with other defects by monitoring differences in the donor ground state.

While the original motivation for this work was the measurement of the strength of the exchange coupling between phosphorus donors in silicon, the final thesis took the form of an investigation into the components required to achieve this measurement. The sensitivity to few donors proved problematic. The investigation focused on the following: the fabrication and characterisation of samples containing coupled pairs, the electronic Raman scattering technique on bulk samples, the accurate measurement of the sample temperature, and the measurement of ensembles of interacting donors using other spectroscopic techniques. The experimental techniques of photoluminescence and electron spin resonance were used to aid in the characterisation of the samples, as they had previously shown sensitivity to donor interactions [29, 30]. Focusing the study on optical techniques also had the advantage of simple sample preparation.

While further work would be required to achieve the measurement of the exchange coupling strength, the methods discussed in this thesis could assist in the future optical readout of solid state qubits [31–34]. As well as the field of quantum computing, the potential exists for more general study of molecular systems in the solid state.
1.3 Thesis Outline

This thesis continues, in Chapter 2, with a discussion of the background and theory. The topics introduced are: the material properties of silicon, the electronic states of donors, and the exchange coupling interaction between donor pairs in silicon. Raman scattering theory, electron paramagnetic resonance and photoluminescence spectroscopy are introduced. The proposals to measure interactions between donors using these techniques are also explained.

The materials used to produce the samples, and the experimental methods employed in this thesis will be discussed in Chapter 3. The sample fabrication process included the choice of silicon substrate, the ion implantation process and equipment, subsequent thermal processing, and sample characterisation. The experimental methods and instrumentation related to the Raman and photoluminescence spectroscopy are discussed, as well as the cryogenics used to cool the samples. Electron paramagnetic resonance characterisation of the silicon samples will also be discussed, and results from the experiments presented.

Silicon samples containing isolated and interacting phosphorus atoms and pairs of atoms were produced via ion implantation of atomic and molecular phosphorus ions. Chapter 4 considers the modelling of the distributions of the implanted ions. This involves a discussion of ion-solid interactions, simulations of the range and straggle of ions in silicon, the final separation of the molecular implanted ions, and the distribution of atoms in realistic large area implants. Simulations of molecular ion implants in silicon will also be discussed, leading to the selection of the sample processing parameters and revealing the conditions required for the production of isolated coupled pairs of donors. The simulations also provided insights into the statistics of the possible number of donors interacting in the samples, which proved valuable when analysing the experimental data.

The experimental results from the electronic Raman scattering experiments of donors in cryogenically cooled silicon with both the visible and near infra-red spectrometry instruments are examined in Chapter 5. Electronic Raman scattering was observed from donors and acceptors in bulk doped silicon samples using near infra-red Raman spectroscopy, but was not observed from the implanted donor samples, and thus exchange coupling between coupled pairs of donors could not be measured. The experimental trends observed from the bulk samples, the sample heating due to the laser, and issues with the use of above band gap excitation for electronic Raman scattering will be discussed.

The proposal to measure the the exchange coupling between two donors requires the precise knowledge of the local sample temperature. Laser based measurements can also suffer from laser heating of the sample. The use of a physical property of the system, the silicon Raman active TO mode phonon, will be discussed in Chapter 6 as a local probe of the sample temperature. New
results on the temperature dependence of the phonon frequency will be presented.

The photoluminescence spectroscopy experiments on donors in silicon will be discussed in Chapter 7. Results will be presented on the doping density of the silicon substrate, the presence of impurities in the silicon due to sample processing, the electrical activation of implanted phosphorus, and the interactions between implanted phosphorus atoms. Trends to changes in the luminescence spectra due to many donor interactions were analysed with the aid of the implantation simulations and donor interaction models. The implantation range of interest had not previously been investigated using photoluminescence.

The thesis finishes in Chapter 8 with the conclusions, and a discussion on possible future work.
Chapter 2

Background and Theory

The search for a scalable implementation for quantum computing has led researchers in the direction of solid state and semiconductor systems, in particular silicon. In this chapter the material properties of silicon and their relevance to the understanding of this thesis will be discussed. The theory of shallow donor state in silicon and exchange coupling of donor electrons in silicon will also be discussed. The various theoretical proposals for measuring exchange coupling and interactions between donors will be examined including an explanation of the experimental techniques used.

2.1 Silicon

The electronic levels of phosphorus in silicon can be thought of as hydrogen like, but as they are housed in the silicon lattice an understanding of the properties of silicon is required to fully understand the donor states. Also, any interaction with the phosphorus donor electron is mediated by the properties of the silicon crystal, which can themselves be affected by these interactions.

Silicon is a Group-IV element in the periodic table with unique electrical properties which have led to its dominance of the electronics industry over the past few decades. A description of these properties follows. Of relevance to this work are the structural, thermal, electronic and optical properties of silicon.

2.1.1 Silicon Structure

Crystalline silicon binds covalently to its nearest neighbours through four valence band electrons. These electrons form tetrahedral bonds resulting in a crystal with a diamond lattice structure, as shown in Figure 2.1. This figure shows the silicon unit cell, with a characteristic lattice parameter of $a = 0.543$ nm. The temperature variation of this parameter, and thus the length of the crystal,
2.1. SILICON

Figure 2.1: The diamond type lattice of crystalline silicon. Coloured lines show the tetrahedral covalent bonds of the central silicon atom [35].

![Diamond lattice of crystalline silicon](image)

Figure 2.2: Thermal expansion coefficient of the silicon lattice [36].

![Thermal expansion coefficient](image)

shown in Figure 2.2. Interestingly silicon undergoes a negative thermal expansion between 30 K and 120 K due to soft phonon modes.

Silicon has two acoustic and two optic phonon branches, longitudinal and transverse. The phonon dispersion and density of states is shown in Figure 2.3. Phonons can scatter light and thus be observed in Raman scattering experiments (to be discussed further in Chapter 6 in light of their temperature behaviour). They also contribute to photoluminescence by aiding in the conservation of crystal momentum in excitonic processes.

Phonons also carry heat through the crystal. The thermal properties of silicon are shown in Figure 2.4. The heat capacity of silicon drops by several orders of magnitude as the temperature
Figure 2.3: (a) Phonon dispersion and (b) density of states at 300 K for silicon. Labels of phonon modes in figure (a) are: TA - transverse acoustic, TO - transverse optic, LA - longitudinal acoustic and LO - longitudinal optic [37].

Figure 2.4: (a) The specific heat at constant pressure of silicon [38]. (b) The thermal conductivity of silicon at various temperatures [39].

decreases from room temperature to liquid helium temperature (4 K), and the thermal conductivity of silicon has a maximum at around 50 K. During laser based measurements, dissipation of heat is important in maintaining sample temperature. Laser based measurements on silicon at liquid helium temperatures have to contend with sample heating issues as the heat capacity and thermal conductivity are both small.

Crystalline silicon has three stable isotopes $^{28}\text{Si}$, $^{29}\text{Si}$ and $^{30}\text{Si}$ whose natural abundance and nuclear spin state are presented in Table 2.1. The isotopic composition of the crystal affects the
2.1. SILICON

width of the bound exciton photoluminescence lines in silicon, and the phosphorus nuclear spin
decoherence times. Recently work into isotopic enrichment of silicon to remove most of the $^{29}\text{Si}$
isotopes (nuclear spin 1/2) from the crystal has produced samples with an almost nuclear spin free
environment [40]. Isotopic enrichment also reduces the linewidth of optical transitions such as
photoluminescence lines [41].

<table>
<thead>
<tr>
<th>Isotope Mass</th>
<th>Nuclear Spin</th>
<th>Natural Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{28}\text{Si}$</td>
<td>0</td>
<td>92.22 %</td>
</tr>
<tr>
<td>$^{29}\text{Si}$</td>
<td>$+1/2$</td>
<td>4.69 %</td>
</tr>
<tr>
<td>$^{30}\text{Si}$</td>
<td>0</td>
<td>3.09 %</td>
</tr>
</tbody>
</table>

Table 2.1: Table of stable isotopes in silicon, including the isotope mass, nuclear spin and natural abundance.

2.1.2 Silicon Electrical Properties

The electrons bound to the phosphorus atoms in silicon are affected by the silicon potential and in-
teract with the electronic structure of silicon. The electrical properties of silicon can be understood
through the band structure theory of solids. Figure 2.5 shows the formation of bands from $N$
electrons. The proximity of electrons in neighbouring atoms split the quantised energy levels of elec-
trons orbiting other nuclei. As the electrons obey the Pauli exclusion principle, and as the atoms
sit closer together, the quantised energy levels overlap and form bands. Solving the Schrödinger
equation in a periodic potential yields similar results, and will be used when discussing shallow
donor states. The conduction and valence bands are separated by $E_g$, the forbidden energy gap.
For silicon this gap is an indirect gap, the top of the valence band is not at the same point in crystal
momentum ($k$) space as the bottom of the conduction band, which sits 85 % along the [001] axis
direction, see Figure 2.6. There are six of these minima, one along each of the equivalent [001]
directions. The band gap changes with temperature, from $E_g = 1.12 \text{ eV}$ at room temperature to
1.17 eV at 0 K, see Figure 2.7. The energy of optical transitions between valence band and con-
duction band states change with temperature as the bang gap changes, and so do their spectral line
positions. Also, the Nd:YAG laser used in the Raman experiments (Chapter 5) has an energy of
1.165 eV, which is above or below the band gap depending on the temperature of the sample.

Conduction in intrinsic silicon occurs with electrons thermally excited from the valence band
to the conduction band, leaving a ‘hole’ in the valence band. Applying an electric field gives the
electrons and holes kinetic energy producing a current. At $T = 0 \text{ K}$ silicon is an insulator. The
electrical properties of silicon can be modified by doping the substrate with Group III and Group
V elements. Figure 2.8 shows the substitution of a silicon atom with boron and arsenic. Boron has
CHAPTER 2. BACKGROUND AND THEORY

Figure 2.5: Formation of semiconductor bands [35].

Figure 2.6: (a) Schematic of band structure of silicon. Note indirect band gap. [35]. (b) Electron dispersion of silicon showing full band structure [37]. The 0 point in (a) is the Γ point in (b) with the [100] direction towards the X point.
2.1. SILICON

Figure 2.7: Temperature dependence of indirect band gap of crystalline silicon [42].

Figure 2.8: Doping of a silicon semiconductor. (a) Donors form covalent bonds to four neighbouring silicon atoms, leaving one electron free. (b) Acceptors form four covalent bonds with neighbouring silicon atoms, leaving a hole in a bond which can be involved in conduction [35].
three valence electrons that result in a hole in one of the covalent bonds. Arsenic has five valence electrons, with four bonding to the silicon leaving one free to take part in electrical conductivity. The donor electron has an energy level close to the conduction band and the acceptor hole level is close to the valence band. Thus, less thermal excitation is required to excite a particle for conduction. At low temperatures these particles are bound to the dopants with discrete electronic levels, to be discussed in more detail in a subsequent section. As the doping of the semiconductor is increased the Fermi level moves from the mid gap level towards the bands, and at a doping level of about $3 \times 10^{18} \text{ cm}^{-3}$ conduction becomes metallic due to the formation of an impurity band. As with the previous discussion on the formation of the silicon band, an increase in density of the impurity atoms changes the discrete donor electron energy levels into a continuum. The impurity band is metallic even at $T = 0 \text{ K}$.

### 2.1.3 Silicon Optical Properties

The band structure of silicon also determines various optical properties. Important to laser based measurements is the absorption of light, the amount of light absorbed by silicon at different wavelengths, as this relates to the penetration depth of the laser as well as the local heating of the sample. Absorption can be regarded as an interaction of light with the electrons in the crystal.

![Optical absorption coefficient (α) of silicon at 300 K as a function of the energy of light](image_url)

**Figure 2.9:** Optical absorption coefficient ($\alpha$) of silicon at 300 K as a function of the energy of light [43].
2.2 SHALLOW DOPANTS IN SILICON

At low temperatures, unpaired electrons bound to donors and holes bound to acceptors form discrete energy levels within the silicon band. These can be thought of as a hydrogenic system of a single charged particle attached to an ionic core, with the silicon as a dielectric screening medium, forming Bohr orbitals. Far infra-red absorption measurements of phosphorus doped silicon have provided a ground state energy of 45.5 meV below the conduction band edge with a Bohr radius of 2.5 nm [44]. Figure 2.10 shows the energy levels of the bound phosphorus electron. Of note are the three energy levels with $1s$ symmetry. A calculation of the energy levels using the Bohr model does not reproduce these experimental results.

The periodic potential of the silicon lattice affects the bound donor electron wavefunctions. This is treated theoretically by taking the effective mass approximation, where the effect of the

\[ \begin{array}{c|c|c}
\text{(meV)} & \text{CB} & 3p_{\pm} \\
-3.1 & \hline \\
-6.3 & \hline \\
-11.4 & \hline \\
\text{1s(E)} & \text{1s(T2)} & \text{1s(A1)} \\
-32.6 & \hline \\
-33.9 & \hline \\
-45.5 & \hline \\
\end{array} \]

Figure 2.10: Energy levels of the phosphorus electron in silicon. Taking the bottom of the conduction band as the \( E = 0 \). Values from Ref. [45].
silicon potential is to change the mass of the electron from that of the free electron $m$ to an effective mass $m^*$, and the periodicity is treated by expanding the donor electron wavefunction by the periodic Bloch functions for silicon [46]. Applying the effective mass approximation, the calculated energy levels of the excited states match those of the experiments. The calculation leaves a sixfold degenerate ground state whereas optical absorption experiments [44] show this degeneracy as lifted. The splitting of this ground state into the $1s(A_1)$ singlet, $1s(E)$ doublet, and $1s(T_1)$ triplet states is due to the presence of the donor atom in the crystal breaking the crystal symmetry, and lifting the six-fold degeneracy of the ground state. This process is called the valley-orbit coupling. The labels of these states indicate their symmetry. Transitions between the $1s$ states are one photon forbidden but can be involved in inelastic scattering events, two photon transitions. The theory matches experiments when the valley-orbit coupling is included [45].

The wavefunctions of the ground state bound donor electrons are shown in Figure 2.11. The wavefunctions oscillate in intensity with distance from the core. The shape of this interference is different along different directions in the crystal. These oscillations are due to the periodicity of the silicon lattice and mixing between the six different conduction band minima.

### 2.2.1 Exchange Coupling

The exchange interaction involves the behaviour of the wavefunction of a two indistinguishable particle system with respect to the exchange of the position of the two particles. This is the symmetrization requirement for the two particle system [48]. Considering an electron in state $a$ at position $1$, $\psi_a(r_1)$ and another in state $b$ at position $2$, $\psi_b(r_2)$, as both are fermions with spin-1/2, the wavefunction is antisymmetric under the exchange of the particles:

$$\psi(r_1, r_2) = -\psi(r_2, r_1).$$  \hspace{1cm} (2.1)
2.2. SHALLOW DOPANTS IN SILICON

The electrons \(a\) and \(b\) form a coupled spin system, producing a singlet state with total spin \(S = 0\) and triplet states with \(S = 1\):

\[
S = 1 \begin{cases} 
|\uparrow\uparrow\rangle \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\
|\downarrow\downarrow\rangle 
\end{cases} \quad (2.2)
\]

\[
S = 0 
\frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (2.3)
\]

The singlet state is antisymmetric under exchange and the triplet states are symmetric. The electron wavefunctions include both position \((\psi_r)\) and spin \((\chi_s)\), and as they are fermions the total state, \(\psi_r\chi_s\) must be antisymmetric. For this to occur, one component of the total wavefunction must be antisymmetric and the other symmetric. So the antisymmetric spin singlet state must form a spatially symmetric state, and the symmetric triplet spin state forms a spatially antisymmetric state.

Spatially antisymmetric states are anti-bonding states, where the electrons sit further apart on average, and the spatially symmetric states are bonding states, where the electrons sit closer together on average. The region of wavefunction overlap is directly between the two particles, leading to larger wavefunction overlap for the singlet spin state than the triplet, and a lowering of the energy for the singlet-spin state in relation to the triplet. This difference in energy is the exchange energy \(J\) and is directly proportional to the wave function overlap. So an exchange coupled singlet spin state will have a ground state energy with a magnitude \(J\) lower than the equivalent triplet spin state.

The interactions between qubits in the silicon quantum computer, either electron spin or nuclear spin, are mediated through the coupling of neighbouring donor electrons. This is possible through the exchange interaction or the dipole interaction, whose strength sets the possible gate times on devices. The dipole interaction is long ranged and has the form \(D(R) \sim R^{-3}\), but is weaker than the exchange interaction for donor separations less than 30 nm. The exchange interaction, for hydrogenic states, has the form \([21]\):

\[
J(R) \sim \frac{R}{a^*} \exp \left( \frac{-2R}{a^*} \right) \quad (2.4)
\]

for separation \(R\) and where \(a^*\) is the Bohr radius of the electron.

More accurate representations of the exchange interaction for donor electrons in silicon, which include the interference effects in the wavefunctions, have been calculated using the Kohn-Luttinger formalism \([47]\) and shown as the solid lines in Figure 2.12, and using the Heitler-London formalism \([49]\) the dotted lines in Figure 2.12. Both these methods give similar results, where the
oscillations in the wavefunctions produce oscillations in the exchange energy in terms of donor separation and direction, but with the trend still following an exponential decay (the dot-dashed line in the figure). A change in the separation by only a lattice spacing changes the exchange energy drastically. Donor atoms in substitutional lattice positions are indicated on the figure by dots, showing that for separations along the [100] directions the exchange energy is not affected by the oscillations whereas along other directions the oscillations play a significant part in the strength of the coupling. The large variations in exchange coupling strength seen here indicate the importance of both the accurate donor qubit positioning, and the measurement of the actual exchange energy between qubit atoms in devices.

2.3 Experimental Measures of Phosphorus Interactions

Methods to experimentally measure the exchange coupling between bound donor electrons in silicon are required. As was mentioned in Chapter 1, the exchange interaction is used to couple the phosphorus nuclear spins to perform two-qubit operations, and its strength sets the speed of these operations. Experimental probes are required to gain a better understanding of the interaction in physical devices. One method proposed was to use electronic Raman scattering spectroscopy, where theoretical work has shown it to offer a direct measure of the strength of the exchange coupling [28]. Other methods sensitive to the interactions between donors include electron paramagnetic resonance and photoluminescence spectroscopy. These techniques and how they can be applied to measure donor interactions will be explained in this section.

Figure 2.12: Exchange energy as a function of inter-donor distance along high symmetry directions of the silicon lattice. Solid lines are calculations from Ref. [47], dotted lines from Ref. [49], and the dashed lines the simple hydrogenic calculations. The circles indicate phosphorus atoms taking up substitutional positions in the lattice [47].
2.3. EXPERIMENTAL MEASURES OF PHOSPHORUS INTERACTIONS

2.3.1 Raman Scattering

Raman scattering is a two photon inelastic process, a second order interaction of light with matter. The proposal to measure the strength of the exchange coupling of phosphorus in silicon relies on such a transition between two donor electronic states. An incident photon with an energy $\hbar \omega_L$, polarisation direction $\vec{\eta}_L$, and wave vector $\vec{k}_L$ scatters off an electronic (or vibronic) state with an initial energy $E_0$, energy is transferred in the inelastic collision ($0 \neq f$) leaving the final state with energy $E_f$. The outgoing photon is scattered to a state with: $\hbar \omega_R$, $\vec{\eta}_R$ and $\vec{k}_R$. Energy conservation results in the difference in energy ($\hbar \omega$) of the initial and final electronic state equalling the difference in energy of the incoming and outgoing photons via:

$$\hbar (\omega_L - \omega_R) = E_f - E_0 = \pm \hbar \omega.$$  \hfill (2.5)

The positive energy difference is referred to as the Stokes line, where some of the energy from the incoming photon is used to create an elementary excitation (see Figure 2.13). This results in the energy of the outgoing photon being lower than the incoming. The negative energy difference, called the anti-Stokes line, is the destruction of an excitation. The initial state must be an excited state for anti-Stokes scattering to occur, usually exhibited in systems whose excited states have been thermally populated. The spectroscopic measurement of a Raman scattering event involves illuminating the sample with a monochromatic laser, and measuring the energy shift away from this laser energy of the outgoing photons. From this measured energy shift, the difference in energy between the initial and final states of the particle scattering the light is inferred.

**Electronic Raman Scattering from Isolated Donor States**

Raman scattering experiments on silicon doped with phosphorus and performed at low temperatures, have revealed an electronic transition of energy 13.1 meV between the $1s(A_1) \rightarrow 1s(E)$ states of the bound phosphorus donor electron [50], see Figure 2.14. Electronic Raman scat-

---

Figure 2.13: Schematic of Stokes and anti-Stokes transitions in Raman scattering. The labels are explained in the text.
tering transitions have been observed from most of the shallow donor and acceptor species in silicon [51]. All the donor transitions occur within the split $1s$ electronic states. The diamond type semiconductors silicon carbide [52] and germanium [53] also show electronic Raman scattering from donors and acceptors of a similar form to silicon. The scattering in all these systems has only been observed with below band gap illumination.

The theory behind these transitions follows. The interaction of radiation with $N$ electrons can be described by the Hamiltonian for the motion of a charge in an external electromagnetic field:

$$H = \sum_{i=1}^{N} \frac{1}{2m} \left[ \vec{p}_i - \frac{e}{c} \vec{A}(\vec{r}_i, t) \right]^2 + V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$$

(2.6)

where $\vec{p}_i$ is the momentum operator, $\vec{A}(\vec{r}, t)$ is the vector potential in the Coulomb gauge, $V$ is a potential, $e$ is the charge on an electron, $m$ is the mass of an electron and $c$ is the speed of light. Donor level electrons are included via the effective mass approximation $m^*$, with the effective mass at the conduction band minimum used. Raman scattering is a two photon process (no net change in the number of photons), any term which destroys an electron must be accompanied by one which creates an electron and vice versa. The cross section is calculated by expanding the Hamiltonian up to second order in terms of these interactions and applying Fermi’s golden rule. The differential Stokes-Raman cross section, between the initial and final states, requires the transition to proceed through an intermediate state $n$, and is expressed as:

$$\frac{d\sigma(0 \rightarrow f)}{d\Omega_R} = \left( \frac{e^2}{mc^2} \right)^2 \frac{\omega_R}{\omega_L} \left| \sum_n \frac{\langle f | \vec{r}_L \cdot \vec{r}_R | n \rangle \langle n | \vec{v}_L \cdot \vec{p}_n \rangle}{E_0 - E_n + \hbar\omega_L} + \frac{\langle f | \vec{r}_L \cdot \vec{r}_R | n \rangle \langle n | \vec{v}_R \cdot \vec{p}_0 \rangle}{E_0 - E_n - \hbar\omega_R} \right|^2$$

(2.7)

Equation 2.7 has been used by Jain et al. [51] to calculate the likely transitions for a scattering event off electronic states of donors in silicon. The terms in the summation are the two photon terms, where the donor electron is taken between the initial $|0\rangle$ and final $|f\rangle$ state through the intermediate state $n$. The naive picture of this process looks like that shown in Figure 2.14, where the electron starts and finishes in the phosphorus electronic states, which lie just below the conduction band, with the transition passing through a virtual state somewhere in the conduction band. The theory of Jain et al. does not proceed in this way, but that the transition with any appreciable cross section, that between the two valley-orbit split phosphorus donor $1s$ states [52], proceeds via a virtual transition to the valence band. This view of the electronic Raman scattering process for donors in silicon is confusing, as it involves a transition of the electron (even if virtual) which
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Figure 2.14: Schematic of the electronic Raman scattering process for a phosphorus donor electron in silicon. The electron is scattered via a virtual transition to a virtual state.

proceeds down in energy through the interaction with radiation. We raise here some uncertainty as to the mechanism of a transition proceeding in this way.

Continuing with Jain’s theory, the energy of the initial state is approximated by the conduction band minimum \( E_0 \approx E_c \) and that of the intermediate state as the valence band at the same point in \( k \) space as the conduction band minimum \( E_n = E_v \). The difference between the two states is the direct band gap \( E_G \). The initial and final states are set as the donor electron wavefunctions from the effective mass theory, reducing the cross section equation to the following:

\[
\frac{d\sigma}{d\Omega_R}(0 \rightarrow f) = r_0^2 \frac{\omega_R}{\omega_L} R_{12} (\mu_\parallel - \mu_\perp)^2 \left| \sum_{j=1}^{6} \alpha_j^{(f)} \alpha_j^{(0)} (\hat{n}_L \cdot \hat{n}_j)(\hat{n}_R \cdot \hat{n}_j) \right|^2
\]

with:

\[
R_{12} = \frac{E_G^2}{E_G^2 - (\hbar \omega_L)^2}
\]

\( R_{12} \) is the resonance enhancement factor, \( r_0 = e^2/mc^2 \) is the classical radius of the electron, \( \hat{n}_j \) the unit vector along the direction of the \( j \)-th conduction band valley, and \( \mu_\parallel \) is the parallel component of the effective mass tensor and \( \mu_\perp \) the perpendicular component, which arise due to the anisotropy of the conduction band with \( \mu = m^{*+1} \). The \( \alpha_j \)'s are terms which indicate the symmetries of the states [54], and the products of these with the polarisation and orientation set the selection rules for the scattering.

For light close to the energy of the transition to the intermediate state, the virtual state approaches a real state, and the resonant factor of Equation 2.9 increases the cross section remarkably. The resonance condition of the theory as stated by Jain et al. [51] is a direct transition across the band gap at the conduction band minimum. Ultra violet light is required to meet this condition. No experimental observation of the electronic Raman scattering transition using ultra violet light
(or any other light of frequency above the indirect band gap energy) has been reported, which is usually attributed to the small penetration depth of the UV light leading to a small absolute scattering cross section.

**Measuring Exchange Coupling via Electronic Raman Scattering**

Koiller et al. [28] proposed a method to directly estimate the strength of the exchange coupling between donors in silicon with electronic micro-Raman scattering spectroscopy. The ground state of the donor is sensitive to the environment and is influenced by the strength of the donor pair coupling and pair orientation. These will influence the spectroscopy of the single donor electronic Raman line via changes in its shift and width, which could lead to valuable information on the state of the donor system. Other influences on the line are the photon polarisation and temperature.

The proposal was based on Jain et al.’s theory and relied on the resonance term in the Raman cross section, Equation 2.9, to achieve single donor spectroscopy. As the direct band gap was chosen as the resonance condition, the use of a UV laser at 3.8 eV was suggested.

The Raman spectrum of the donor pair originates from transitions from the $1s(A_1)$ spin singlet and triplet states to the $1s(E_1)$ and $1s(E_2)$ spin singlet and triplet states. The degeneracy of the two $1s(E)$ states is lifted by the axial perturbation of the donor pair. This leads to four possible transitions, shown in the insert of Figure 2.15 (a). The exchange energy $J$ is shown as the energy difference between the singlet to triplet ground states. The figure shows the changes in the energies of these transitions for donor separations along the [100] direction. As the separation between the donors decreases, the difference in the energy of the transition from the isolated donor case increases. At separations above $\sim 15$ nm the spectrum becomes indistinguishable from that of the single donor case $\Delta_0$.

The polarisation and temperature are controllable parameters and both affect the relative intensity of the four lines. The scattering equation, Equation 2.8 contains polarisation terms, which relate to the relative orientation of the exchange coupled donor pairs. A study of the line spectrum with various polarisations could provide information on the orientation of the pair. The equilibrium populations of the initial singlet and triplet states follows a Boltzmann’s distribution with temperature:

$$\frac{n_t}{n_s} = 3 \exp \left( \frac{-J}{k_b T} \right)$$  \hspace{1cm} (2.10)

with $n_t$ and $n_s$ the number of donor pairs in spin singlet and triplet states respectively, and $k_b$ is Boltzmann’s constant. Figure 2.15 (b) shows the polarisation and temperature dependence of the intensity of lines for a donor pair in the [100] direction. As expected from Equation 2.10 the intensity of the triplet lines increase with temperature while that of the singlet lines decrease. The left hand side panels (i) and (iii) indicated a different polarisation to the right hand side panels
2.3. EXPERIMENTAL MEASURES OF PHOSPHORUS INTERACTIONS

(ii) and (iv). This information can be used to estimate $J$, as shown in Figure 2.15 (c). There is a temperature where the intensity of the singlet and triplet lines of the same $1s(E)$ state are equal. This crossover occurs at a temperature $T = J/k_B$, thus providing a value for $J$.

For ensembles of donors, a system easier to observe than single pairs, this technique should be able to distinguish between samples with non-Poissonian axial distributions of donor pairs. This is illustrated in Figure 2.15 (d), where the top panels are from a sample with a ‘dumb-bell’ distribution of donors, where donors were placed along the [100] direction but have moved randomly by up to 1 nm (such as might be expected from a ‘bottom-up’ fabrication discussed in Section 1.1.2). Polarisation of the light along the axis of the pairs (box (i)) yields a different result to polarisation crossed in respect to the axis of the pair (box (ii)). Panels (iii) and (iv) are for a sample with a separation of 10 nm within the pairs, but with spherical symmetry in their distribution such as might be expected from a $P^+_{2}$ implantation (discussed in Chapter 4). In this case the symmetry of the distribution does not lead to different results in measurements with different polarisations. The large central peak is due to the majority of donors which are only weakly coupled. The directional dependence of the exchange coupling leads to only a small number of strongly coupling pairs, which produce tails to either side of the peak. The temperature dependence to the intensity of these tails indicate the presence of coupled donors, and at the temperature where the intensity of both sides are equal an estimate of $J$ for the ensemble can be calculated.

2.3.2 Electron Paramagnetic Resonance

Electron paramagnetic resonance (EPR) observes the hyperfine interaction of the donor electron with the magnetic moment of the donor atom nucleus. The states are observed as absorption of microwave energy at the points where the spin flip transitions occur. The phosphorus atom has nuclear spin-1/2, resulting in two lines in the spectrum whose spacing is proportional to the hyperfine interaction [55]. Systems with two exchange coupled donor electrons give an extra resonance line exactly half way between the two main lines [29], and for exchange coupling between more electrons, more lines are observed [56]. Figure 2.16 shows a schematic of the expected spectrum from an isolated phosphorus atom in panel (a) and two exchange coupled electrons in panel (b). In bulk doped silicon clusters of atoms of various sizes can form and increase in size as the doping concentration increases, a combination of all these lines have been observed [57], which eventually blend into a broad single line. In samples doped above the metal insulator transition the donor electrons behave as free electrons resulting in a single sharp resonance line, approximately half way between the phosphorus hyperfine split lines but distinct from the exchange coupled line.

The onset of exchange coupling in EPR experiments on donors in silicon occurs when the strength of the exchange interaction is larger than the strength of the hyperfine interaction, $J > A$, believed to occur for donors with a separation of approximately $< 20$ nm [58,59]. EPR is not able
Figure 2.15: Figures related to Koiller’s proposal for measuring the exchange coupling of donors in silicon with Raman spectroscopy. (a) The change in energy of the Raman lines (see insert) with interdonor separation for pair of separation 10 nm along the [100] direction. (b) The change in intensity of donor pair Raman lines with polarisation and temperature. (c) The temperature dependence of lines showing the temperature cross over from which \( J \) can be estimated. (d) Line shape changes with polarisation and temperature for ensembles of pairs, top panels have axial symmetry and the bottom panels are without axial symmetry [28].
2.3. EXPERIMENTAL MEASURES OF PHOSPHORUS INTERACTIONS

Figure 2.16: A schematic diagram of the expected electron paramagnetic resonance lines for: (a) Isolated P electrons, (b) two coupled P electron spins, and (c) the \( P_b \) interface defect. The lines are shown as the derivative spectra.

to measure the strength of \( J \) between any particular pair of donors, but can only show whether they are coupled. It is a binary process where for isolated donors only two lines are observed, and for a coupled pair of donors the central line appears. As such, the main use for this technique was to identify samples which contained exchange coupled phosphorus atoms.

Electron paramagnetic resonance is sensitive to other defects in silicon, such as the \( P_b \) defect, a dangling bond at the silicon–silicon dioxide interface [60,61]. Defects such as the \( P_b \) centre can trap electrons, ionising the donors and reducing any signals originating from the donors. Their presence in the spectra is within range of the phosphorus transitions, with a broad peak which can mask the left hand side phosphorus resonant line, see Figure 2.16 (c). As the phosphorus atom qubits will be placed only 20 nm from the interface with the oxide, the identification of any charge trap at this interface is important. The use of thermally grown oxides drastically reduces the number of \( P_b \) defects in a sample, as discussed in Chapter 3.

2.3.3 Photoluminescence

A quick introduction to photoluminescence spectroscopy and how it may be used to measure donor interaction follows, as well as a discussion on the literature regarding the possible optical readout of a qubit nuclear spin state. The details of the photoluminescence process is included in Chapter 7, where the experimental results will also be discussed.

Photoluminescence spectroscopy is the measurement of recombination radiation from optically generated electron hole pairs, known as excitons. These excitons can bind to donors and acceptors forming stable complexes. The electrons and holes recombine sometime later either through an Auger process or by releasing radiation. Spectroscopy of this radiation has been used to identify the presence of impurities in silicon [62], as well as to measure their concentration within the silicon [63]. Spectroscopy of highly doped silicon has shown donor and acceptor lumi-
nescence peaks which shift and broaden due to impurity and exciton interactions as the dopants
get closer together [64]. The exchange coupling interaction between neighbouring donors may
not be solely responsible for these observed changes, as the extra charged particles bound to the
donors would also influence the energy of the phosphorus states. While the strength of the ex-
change coupling may not be directly measurable, modelling of the interactions may produce basic
information such as the separation within pairs of atoms.

As long as the change to the coupled donor pair peak is larger than the resolution of the instru-
ment and the width of the isolated donor peak, then this process should be observable in samples
containing an ensemble of donor pairs. The width of the phosphorus bound exciton line in natural
silicon is $5 \mu$eV, and resolvable with interferometric techniques [41]. So small changes to the peak
width are resolvable. If the changes in the energy of the transition are smaller than the linewidth
in natural silicon, then isotopically enriched $^{28}$Si could be used, where the linewidth of the phos-
phorus bound exciton transition was recently observed to be 150 neV using photoluminescence
excitation spectroscopy [32]. Ultra-low densities of donors have been observed with photolumi-
nescence spectroscopy, down to $1 \times 10^{10}$ cm$^{-3}$ [65], making the observation of an ensemble of
shallow implanted phosphorus ions possible.

Readout of the spin state of a phosphorus qubit using photoluminescence has been discussed
by Fu et al. [31]. The advantages of an optical readout scheme are that electrical probes to mea-
sure the spin state are not required, thus reducing their interference on the system through charge
fluctuations. In a magnetic field, the phosphorus donor has a hyperfine split ground state, and the
bound exciton has Zeeman split hole states. The energy of the transition from the recombination
of the bound exciton differs depending on the spin state of the nucleus due to the hyperfine split-
ting, enabling the detection of the nuclear spin state via the transition energy. By using $^{28}$Si the
transition line widths are smaller than the hyperfine splitting. The inefficiency of the radiative
recombination process makes detection of the spin state of a single phosphorus atom problematic.
This can be overcome by placing the donor atom in a photonic band gap cavity which increases
the collection efficiency of the light, and by using single photon detection.

Yang et al. [32] have demonstrated the optical detection of the spin states of an ensemble of
phosphorus donor in silicon. Using the narrow line width of photoluminescence excitation spec-
troscopy of a $^{28}$Si crystal in a magnetic field, the strength of the Zeeman splitting of the bound
exciton hole, and the hyperfine splitting of the donor electrons were measured. The same transi-
tions were detected electronically by measuring the change in current due to Auger recombination
of the bound excitons. The process works in both cases by directly populating the phosphorus
donors with a particular spin states with bound excitons, with the use of a laser of the exact en-
ergy required for the transition. As the Auger recombination is more efficient than the radiative,
the electronic detection of a single phosphorus spin has been proposed by the authors. The di-
rect pumping of spin states, as well as optical detection allows for the ionisation and selection of specific spin states.

2.4 Summary

This chapter provided the background information for the thesis. The structural properties of the silicon crystal, such as the tetrahedral covalent bonds, the expansion of the lattice with temperature and the vibrational properties were discussed. Silicon electrical properties are related to the band structure of solids, with silicon being an indirect band gap semiconductor. The band gap shrinks with increasing temperature. The optical properties are also influenced by the band gap, with weak absorption for light of energy below the gap and strong above. Electrical conductivity can be changed by doping the silicon with elements which provide either an extra electron or a hole. These donors and acceptors form states close to the conduction and valence bands, which can be modelled by the effective mass approximation. The electronic states of donors are analogous to those of the hydrogen atom, but the influence of the silicon lattice results in interference in the wavefunction.

The concept of exchange coupling of electrons was introduced, as well as the form this interaction takes, for electrons bound to phosphorus donors in silicon. The strength of the interaction $J$ is the difference in energy between the singlet and triplet spin states, which is proportional to the wavefunction overlap between the two electrons and thus the separation between the two donors. The interference in the wavefunctions of electrons in silicon lead to oscillations, and an orientation dependence of the exchange coupling energy. Measurement of $J$ was proposed through the use of electronic Raman scattering, electron paramagnetic resonance and photoluminescence.

The process of Raman scattering was introduced, as well as the theory specific to scattering from electronic states of donors in silicon. Here, the electron in the ground state of the phosphorus donor is scattered to another $1s$ state via a virtual transition. The cross section is dependent on the polarisation of the light and has a resonance enhancement factor when laser light is close to the direct band gap of silicon. Uncertainties regarding the intermediate state involved in this transition remain. This transition is sensitive to perturbations to the electronic levels of the donor due to effects such as the exchange coupling. A proposal to measure the exchange energy using changes in linewidth and shift of the electronic Raman scattering line was described, where the temperature dependence of the coupled singlet and triplet lines providing a value for $J$.

Isolated phosphorus produces two resonance peaks in electron paramagnetic resonance experiments. An exchange coupled pair introduces a third peak, between the other two, as long as the exchange energy is greater than the hyperfine interaction. Larger clusters of donors increased the number of lines in the spectrum. Using this method, experiments would be able to track whether a
sample had exchange coupled pairs, but would not be able to measure the energy of the interaction.

The illumination of silicon by above band gap radiation produces excitons, which can bind to neutral donors and acceptors. The recombination of the electron-hole pair produce light whose spectroscopy can identify the chemical species of the donors and acceptors. The interactions between the donors, with the excitons bound to more than one donor, shifts the energy of the bound exciton transitions and thus providing a means to study such interactions.
Chapter 3

Materials and Methods

3.1 Introduction

The experiments discussed in this thesis require silicon samples containing strongly interacting donors. This chapter covers the production and characterisation of such samples. Also discussed are the experimental techniques and equipment used in the measurements on the samples. These include the optical spectroscopy instruments for Raman scattering and photoluminescence and the cryogenics used to cool the samples.

3.2 Preparation of Samples

Following the discussions in Chapter 2 for the experimental measurement of donor interactions, this section explains the phosphorus implanted silicon sample production methods and technology. For a discussion on the physics and simulations of ion implantation processes see Chapter 4.

3.2.1 Silicon Substrates and Surfaces

Silicon Substrates

Commercially sourced high resistivity single crystal silicon wafers of (100) orientation and 2 inch diameter were used as the base material for the implanted samples. They were purchased from the TopSil corporation where they were grown by the float-zone method [35]. The growth begins by placing a seed of single crystal silicon into contact with a polycrystalline silicon feed rod. Starting from the seed end, a radio-frequency (RF) coil heats and melts a small volume of the crystal. As the RF coil is moved along the length of the feed rod the silicon recrystallises into a single crystal using the crystalline structure of the seed as a template. Multiple float-zone passes are used to
reduce impurities in the rod. The molten section holds impurities and depositing them at the end of the rod, which is removed before the next pass.

Wafers of 300 µm thickness were sliced from the rod, with one side then polished. The main impurities are carbon and oxygen both with a concentration \(< 1 \times 10^{16} \text{ cm}^{-3}\) \cite{66}. The wafers were of high purity undoped p-type and n-type, resistivity \(>8000 \text{ Ohm-cm}\) giving background dopant concentrations of \(< 2 \times 10^{12} \text{ cm}^{-3}\) \cite{67}. On average, the distance between the background dopants was approximately 500 nm. Measurements of the concentration of dopants in the substrates using photoluminescence will be discussed in Chapter 7.

A set of silicon wafers bulk doped with various shallow impurities and with a large concentration range were purchased from Montco Silicon Technologies, Inc. and used in the electronic Raman scattering experiments. No independent measurements of the doping concentration were performed on these wafers. Also available were isotopically enriched silicon epitaxial layers from the Isonics Corporation, where a 10 µm layer of silicon enriched to 99.99 % $^{28}$Si was grown via chemical vapour deposition on a base substrate.

**Silicon Surface Termination**

Silicon oxidises naturally, coating the surface with a 2 nm SiO$_2$ layer. This has a high concentration of defects and charge traps both within the oxide and at the interface with the silicon substrate, such as: sodium, fixed oxide charges, oxygen vacancies, and silicon dangling bonds at the interface \cite{68}. Since the shallow donor electron can easily be trapped, the large trap density within the native oxide of silicon poses a problem to donors in silicon in close vicinity to this surface. To reduce the presence of these defects, the native oxide can be chemically removed and replaced with a thermally grown oxide. The thickness and quality of the thermal oxide can then be controlled \cite{35}. Thermal oxide growth offers a cleaner and more controlled environment, preventing sodium infiltration and the incorporation of fixed charges, resulting in lower levels of oxide and interface defects, and allows for further passivation with H$_2$ gas \cite{69}.

Thermal oxides used in this study were grown at the Semiconductor Nanofabrication Facility at the University of New South Wales in Sydney. Growth was performed in a triple walled furnace in an oxygen atmosphere at 800 °C for 40 minutes. This yields an oxide of 5 nm thickness. Further processing in forming gas (a 5 % mix of hydrogen gas in nitrogen gas) at 400 °C for 15 minutes passivates most of the remaining charge traps in the oxide and at the interface. Deep level transient spectroscopy (DLTS) measurements of these thermally grown oxides reveal a trap density of the order of $2 \times 10^{10} \text{ cm}^{-2}$ \cite{70}, a vast improvement on the native oxides. On average, the separation between the charge traps for this thermally grown oxide is 100 nm, and would thus rarely interact with a donor close the interface.

Another way to treat the silicon surface was to remove the oxide and terminate the dangling
CHAPTER 3. MATERIALS AND METHODS

silicon bonds at the surface with hydrogen. The hydrogenated surface reduced the oxidation rate of the silicon when the sample was exposed to air, thus increasing the available handling time between cleaning and insertion into a vacuum chamber. The following section on sample cleaning contains the processing steps.

Silicon Substrate Cleaning

To reduce the chance of the samples being contaminated by organic and metallic particles, which can lead to defects and charge traps, the samples were thoroughly cleaned before implantation and annealing. The process was as follows:

- Large particular matter was first removed by rinsing the samples in de-ionised water.
- Organic matter was removed with a Piranha clean, immersing the sample in a mix of 4:1 sulphuric acid to hydrogen peroxide at 90 °C.
- Trace metals were removed from the silicon surface with a RCA SC-2 clean, 5:1:1 water, peroxide and hydrochloric acid at 70 °C.
- Finally, if the oxide was to be removed and the surface terminated with hydrogen, the sample was dipped into an alcoholic hydrogen fluorine (HF) solution. A mix of equal proportions of methanol, ethanol and propan-2-ol was mixed with water and 49 % HF in the proportion 10:1:1 resulting in a HF concentration of 4 % by volume.
- The final rinse for the samples was in de-ionised water if the oxide was not removed, and in the alcoholic solution if the oxide was removed.

3.2.2 Ion Implantation

The implantation of phosphorus ions into silicon was performed at both the University of Melbourne and at the Australian National University (ANU). Both of these ion implantation instruments are discussed below.

The Melbourne ion implanter, located at the School of Physics, University of Melbourne, is a modified commercial Colutron ion beam system. Both solid and gas sources can be handled with ions accelerated up to 15 keV for singly charged ions and focused ion currents up to 20 µA. Figure 3.1 is a schematic of the Colutron ion implanter.

To generate $^{31}\text{P}^+$ ions, a solid red phosphorus source was vaporised in an oven creating a gas of phosphorus atoms, an arc between a hot filament anode ionises the gas giving a DC plasma of electrons and positively charged phosphorus ions and molecules. These ions were electrostatically
extracted and accelerated to an energy of 14 keV by an applied potential. The ion beam was focused electrostatically into a well defined beam and travelled down the beam line, which was kept at a very high vacuum to reduce ion scattering and neutral particle formation. The desired ion species was selected by a linear Wien velocity filter \[71\], a magnet, a pair of electrostatic deflection plates, and a mass selection aperture. The ion beam was finally electrostatically steered and raster scanned over the sample to implant uniformly into large areas.

The sample sat behind a 1 cm $\times$ 1 cm aperture within a copper shield held at greater than $-120$ V to suppress secondary electron emission. The implanted fluence was measured from the integrated charge collected off the sample. Molecular $^{31}\text{P}^+$ ions were also implanted using this machine.

The ANU ion implanters, located at the Department of Electronic Materials Engineering at the Australian National University are a high energy 1.7 MV NEC tandem implanter and an NEC low energy implanter, which is similar to the high energy implanter but without the acceleration tank. Figure 3.2 shows a schematic of the 1.7 MV NEC tandem ion implanter.

The 1.7 MV NEC tandem implanter produced a negative ion beam from a source of caesium ions which sputter the material to be implanted (SNICS) from a Cu cathode in which the material to be implanted was pressed. The beam was accelerated by electrostatic potentials and ions of the desired mass are selected by passing them through a 90° analysing magnet. The beam was then passed through an acceleration tank, which can accelerate ions up to multiples of 1.7 MeV depending on their charge state, but was not used for ions less than 100 keV. A further 15° bending magnet was used to select a charge state.

Samples were housed in the target chamber on a Ni block and held down with clamps. Surrounding the samples was a copper shield, held at 77 K to trap organic molecules and biased at $-300$ V, to suppress secondary electron emission and ensure correct charge integration, leading to more accurate dosimetry. The beam was electrostatically scanned over the samples to ensure an even implantation fluence and to provide large area implants.
3.2.3 Rapid Thermal Annealing

Samples were passed through a rapid thermal annealing (RTA) process so as to repair the damage caused by ion implantation and to electrically activate the implanted dopant atoms. The furnace used was a RTP-600xp rapid thermal annealer from the Modular Process Technology Corp., a schematic of which is shown in Figure 3.3. The cleaved silicon samples were placed on a silicon support wafer sitting on a quartz tray in a quartz isolation tube. Tungsten-halogen globes surrounding the isolation tube provided heat via high intensity infra-red and visible illumination. Annealing occurred in a flowing argon atmosphere. Temperature was monitored by a thermocouple touching the support wafer and a pyrometer underneath it.
3.2. PREPARATION OF SAMPLES

The anneal schedule used for the samples in this work is shown in Figure 3.4, where lamp intensity and gas flow were software controlled. Argon gas purged the chamber before the lamps were turned on. The intensity of the lamp was controlled in a way so as to heat the sample rapidly to 1000 °C, and to hold this temperature for 5 seconds. The heat lamps were then turned off and the flow of argon gas cooled the samples to room temperature before they were removed.

The advantages this technique holds over a furnace anneal, were the faster speed of heating the sample, the better temperature control as the wafer temperature was measured and not the furnace...
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walls, and the short processing times. The RTA has the disadvantage that the temperature gradients from the rapid heating of the sample can induce thermal stress leading to slip dislocations [35].

Diffusion of the implanted phosphorus during the rapid thermal anneal was minimal. Intrinsic diffusion of P was calculated from the following equation: \[ D = D_0 \exp\left(-\frac{E_0}{kT}\right) \] with \( D_0 = 3.38 \text{ cm}^2/\text{s} \) and \( E_0 = 3.66 \text{ eV} \) [72]. To calculate the linear diffusion during an anneal of length of time \( t \): \( (Dt)^{1/2} \) was used. The samples were produced by the recipe: \( T = 1000 \degree C \) for \( t = 5 \) s, so \( D = 1.1 \times 10^{-14} \text{ cm}^2/\text{s} \) and linear diffusion of the phosphorus atoms was 2.3 nm.

3.3 Sample Characterisation

Characterisation of implanted samples was performed with electron paramagnetic resonance and electrical measurements. Photoluminescence characterisation will be discussed in Chapter 7.

3.3.1 Electron Paramagnetic Resonance

Electron paramagnetic resonance experiments were performed on samples to identify the presence of exchange coupled donors, to study the activation of implanted phosphorus ions, and to examine any other paramagnetic defects in the sample. Experiments were performed on a Bruker ESP300 spectrometer with a standard x-band cavity coupled to a flow cryostat. Samples were usually held at temperatures between 5 to 15 K with the use of liquid helium. Illumination of the samples with above band gap light helped improve the signal, by photo-neutralising any ionised phosphorus atoms. The samples were bathed in microwave energy. Scans of the resonances were performed by varying the magnetic field surrounding the sample. Spectra were usually averaged over a number of scans.

The results of these experiments will be presented here and will be referenced in later experimental discussions. A summary of the EPR experiments follows:

- The blank silicon did not show any phosphorus resonances, whereas the implanted and annealed samples did show phosphorus signals the intensity of which however did not scale with implanted fluence. This loss of signal may be due to the interactions of the donors with oxide defects, and will be discussed in Chapter 7.

- At lower doses and lower energies (< 15 keV), coupled donors were expected to be observed in the P\(_2^+)\) but not the P\(^+\) implants. This trend was not found, as none of the P\(_2^+)\) samples showed the central resonance line of exchange coupled pairs. These results caused concern that the molecular implants were not producing the distributions of coupled pairs expected from the simulations presented in Chapter 4. The interface traps may have been interacting
with the donor electrons whereby the resulting resonance was not of sufficient intensity to be observed over the noise.

- All the samples measured with a surface oxide showed the $P_b$ defect at varying degrees. The $P_b$ resonance originated from charge traps at the oxide interface. When the samples were measured with no oxide, no $P_b$ defects were observed. In general $P^2_2$ implants produced more $P_b$ centres than the $P^+$ implants as the molecular ions probably caused more damage than the atomic when impacting with the oxide.

- Samples where a central line was observed in their spectra were those implanted with a reasonably high fluence of phosphorus ions. Figure 3.5 shows the derivative EPR spectra for samples implanted with atomic ions at a fluence of $1 \times 10^{13}$ cm$^{-2}$ at 15 (red line), 35 (green line) and 70 keV (blue line). These samples were used in the photoluminescence study (Chapter 7). A hyperfine split P doublet is present in the spectra of all samples, centred at 3380 G with a splitting of 42 G. The left hand side peak is obscured by the large $P_b$ defect centred at 3365 G. The intensity of this doublet resonance scales with implantation energy as the longer range of the ions results in a greater separation between the donors and thus more isolated donor atoms. The central line also scales as expected, with a larger intensity for the shallower implant as the ions are more likely to be closer together. The presence of this central line indicated that coupled electrons were present in these samples, but the size of the coupled atom clusters were not able to be determined, though the signal is unlikely to originate from high dose ‘metallic’ electrons. Simulations performed to determine the size of clusters responsible for the broad central line in bulk doped EPR studies found that clusters of four atoms or more dominate such spectra [73]. Simulations for clusters in implanted samples will be discussed in Chapter 4.

### 3.3.2 Electrical Measurements

The four point probe method of measuring resistivity involves placing four in-line thin metal probes, with a separation $s$, in contact with the surface of the silicon, applying a current $I$ to the outer probes and measuring a voltage $V$ with the inner two probes. This method removes the influence of any contact resistance between the metal and the semiconductor as well as the resistance of the wires. The four point probe measures the resistivity, $\rho$ of a semiconductor and the sheet resistance, $R_{sh}$ of a thin layer of thickness $t$. For implanted layers which are much thinner than the separation of the probes the sheet resistance has the form:

$$R_{sh} = \frac{\rho}{t} = \frac{V}{I}$$

(3.1)
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Figure 3.5: Electron paramagnetic resonance derivative spectra of $P^+$ implanted samples at a fluence of $1 \times 10^{13}$ cm$^{-2}$ and energies of 15 (red), 35 (green) and 70 keV (blue). Peaks labelled $P_{LHS}$, $P_{RHS}$ and $P_{central}$ originate from isolated and coupled phosphorus electrons, and the peak labelled $P_b$ is from dangling bonds at the silicon/silicon dioxide interface.

where $G$ is a geometrical factor governed by the size of the sample in relation to the probe orientation and spacing, and the thickness of the conducting layer [68]. The phosphorus was implanted into a square sample geometry, giving $G \approx 4$ [74]. $R_{sh}$ is an average of the resistivity over a sample thickness. The resistivity $\rho$ can be converted into a carrier concentration measurement by using standard charts [67]. This is a useful method for finding the fraction of implanted ions that have been electrically activated after processing, as it measures the free charge available for conduction. The disadvantage of this method is that errors occur when the silicon is closely compensated: where the number of donors is almost equal to the number of acceptors, and the free charge available is small.

Problems with measuring the thin implanted layers arise when the sheet resistance of the thin implanted layer matches the resistivity of the bulk wafer supporting it. The probe tips are placed with some force onto the sample penetrating the thin layer and contacting the bulk. When the resistance of both layers matches there is difficulty in separating the resistivity due to the implanted layer from that of the bulk, keeping in mind that it is the resistance that is measured.

For example, for a 15 keV $P^+$ implant into silicon the peak of the implanted concentration occurs at about 20 nm below the surface. Assuming $1 \times 10^{13}$ ions cm$^{-2}$ were implanted, the peak
concentration was simulated by SRIM [75] (see Chapter 4) to be $3.5 \times 10^{18} \text{ cm}^{-3}$. Converting this to a sample resistivity gives $\rho = 10^{-2} \text{ Ohm-cm}$, with the implant depth $t = 20 \text{ nm}$, $R_{sh} = 2 \times 10^4 \text{ Ohm/square}$. The value of the resistance of the layer is of the same order of magnitude as that of the bulk material ($8 \times 10^3 \text{ Ohm-cm}$), making the differentiation of the two layers difficult.

Measurements using a lab built four point probe proved difficult for samples implanted with fluences below $1 \times 10^{13} \text{ ions cm}^{-2}$. As most samples were implanted with low energy ions, and with implanted fluences less than this number, the four point probe did not provide reliable measurements of sample resistivity and dopant activation. The problems stated above may be overcome by using the van der Pauw methods or Hall bars [68], with contacts to be engineered onto the sample producing a well isolated layer of doped silicon.

3.4 Raman Scattering Spectroscopy

Raman scattering is the inelastic scattering of light off a particular system. In semiconductors scattering can occur off vibrational states and electronic states. Theoretical aspects of Raman scattering were discussed in Chapter 2. The spectroscopy of Raman scattering necessitates the use of specialised equipment. The small scattering cross section and frequency shifts involved lead to the use of a powerful monochromatic excitation source, e.g. a laser, as well as a high resolution spectrometer, and efficient light collection, stray light rejection and detection. The following is a discussion about a Raman spectrometer configured for visible wavelengths and another for the near infra-red.

3.4.1 Visible Wavelength Raman Spectroscopy

The instrument described in this section was used to investigate electronic Raman scattering of phosphorus in silicon (see Chapter 5) and to measure the low temperature phonon behaviour of silicon for its use as a local probe of temperature (see Chapter 6).

A schematic of the instrument is shown in Figure 3.6 and a photo in Figure 3.7. The laser excitation source was a Coherent Innova 70 argon ion laser with its main lines operating at 514.532 nm and 487.998 nm. Plasma emission lines were removed using a prism monochromator. The laser power was regulated via a neutral density filter wheel. The laser was brought onto the sample through a 50/50 beam splitter and an Olympus 50× ultra long working distance microscope objective lens with a numerical aperture of 0.55. The sample was housed in a cryostat designed for microscopy which is described in Section 3.7. Scattered light is collected in the "backscattering geometry", through the microscope objective and the beam splitter and into the spectrometer.

The model X-Y spectrometer was supplied by Dilor, capable of confocal operation and included three 0.5 m focal length Czerny-Turner monochromators. Collected light was focused
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Figure 3.6: Schematic of visible Raman scattering spectroscopy instrument.

Figure 3.7: Photo of visible Raman scattering spectroscopy instrument.
3.4. RAMAN SCATTERING SPECTROSCOPY

![Czerny-Turner monochromator diagram]

Figure 3.8: The Czerny-Turner monochromator.

through the entrance slit, stray light and the laser line rejected via the first two monochromators with the third dispersing the spectrum of interest onto a multi-channel detector - a liquid nitrogen cooled silicon 1024 × 256 element CCD detector. The spectrum was collected on a digital personal computer. Each monochromator had an 1800 grooves/mm holographic diffraction grating.

A schematic of the Czerny-Turner monochromator is provided in Figure 3.8. The light enters through the entrance slit, at the focus of a mirror which collimates the light onto the diffraction grating. The grating is tuned to diffract the wavelengths of interest through the exit slit, while unwanted wavelengths are blocked. When a multi channel detector is used there is no exit slit and the emergent light is dispersed across the detector plane.

The Dilor spectrometer operates in two distinct modes. One was subtractive mode, where the fore-monochromator was set to reject the maximum stray light. By being able to remove the large intensity of the laser line, the spectrum close to the laser line was able to be analysed. The spectrometer was used in this mode for experiments on the electronic Raman scattering (Chapter 5), as the energy of the transition of interest placed the signal close to the laser line. The other possible mode was additive mode, or high dispersion mode. The three gratings were run in series and very high resolution spectra were achieved. Measurements of small changes in the silicon phonon line with temperature required operation of the spectrometer in this mode (Chapter 6).

The aspirin spectrum in Figure 3.9 shows the Dilor working in subtractive mode, light is cut out for wavenumbers below 70 cm\(^{-1}\) with the first aspirin peak resolved at 81 cm\(^{-1}\). The intensities of the two peaks at lower energies have been slightly reduced by the laser line filtering. Peaks in the area of interest for electronic Raman scattering of phosphorus in silicon, at \(\sim 100\) cm\(^{-1}\) are clearly resolved.
3.4.2 Near Infra-Red Raman Spectroscopy

The following experimental setup was used to investigate the electronic Raman scattering of phosphorus in silicon, as presented in Chapter 5. This instrument was developed so as to perform measurements at wavelengths below the silicon band gap, in the near infra-red, as all previous work on electronic Raman scattering in silicon was in this wavelength range [50, 51], and to take advantage of the low absorption of silicon in this region. The Dilor spectrometer mentioned above was not designed for operation in the near infra-red as the CCD detector was not sensitive in the 1 µm wavelength range of interest.

The near-IR Raman spectroscopy instrument we developed is shown as a schematic in Figure 3.10, and a photo in Figure 3.11. The excitation source was a Coherent Nd:YAG laser which could produce up to 2 W of power at 1064 nm (1.165 eV). As well as the main laser line, weak luminescence lines were also emitted. So as not to confuse these artefacts with signals of interest from the samples, band pass filters designed to only let through 1064 nm light were placed in the path of the laser, see Figure 3.12. (Semrock [76] and Iridian laser plasma line rejection filters for 1064 nm were used). The beam was then expanded via a telescope assembly to fill the microscope objective, an Optics For Research LMH-20×-1064, a 20× objective with a working distance of 6 mm and a numerical aperture of 0.4 providing a laser spot size of ~30 µm². The objective had
Figure 3.10: Schematic of the near infra-red Raman instrument. Note the laser was guided into the microscope objective either by reflection off the laser line rejection filter or a mirror beside it, angle of incident light not to scale.

Figure 3.11: Photo of the near infra-red Raman instrument, with laser light reflected off the laser line rejection filter into the microscope objective.

antireflection coatings for 1064 nm with transmission up to 1600 nm. The laser was reflected into the microscope either off a laser line rejection filter or a mirror placed beside it. The light was focused onto a sample sitting in a cryostat designed for microscopy (see Section 3.7).
Scattered light was collected in the backscattering geometry, back through the microscope objective and towards the spectrometer entrance slit. Any of the reflected or Rayleigh scattered laser light was stopped from entering the spectrometer via laser line rejection filters. Two types of filters were employed interchangeably, a notch filter (U filter) and an edge filter, designed for use with a 1064 nm laser. These filters were angle tuned to block the laser and scattered light out to approximately 80 cm\(^{-1}\). (The notch filter was from Kosi and the edge filter from Semrock). Collected light was analysed with an Acton SpectraPro 2500i, a single Czerny-Turner monochromator with a focal length of 0.5 m and a turret which held three gratings. A single channel InGaAs detector collected the spectrum by turning the grating to let the desired wavelength through the exit slit and sent the data to be stored on a digital personal computer. Spectra were normally collected with a 600 g/mm grating blazed at 1 \(\mu\)m or a 1200 g/mm grating blazed at 750 nm.

The white light response of the spectrometer is shown in Figure 3.13, the laser line rejection filter cut off starts at 60 cm\(^{-1}\) with maximum transmission from 80 cm\(^{-1}\). The sulphur spectrum in Figure 3.14 also shows that lines can be resolved down to 80 cm\(^{-1}\) with the intensity of the line at 60 cm\(^{-1}\) reduced by the filter.

Figure 3.12: The response of the plasma filter for 1064 nm laser. OD > 7 [76].
3.5 Photoluminescence Spectroscopy

The instrumentation used in the photoluminescence experiments in Chapter 7 will be discussed in this section. Photoluminescence spectroscopy was used to investigate the doping density of the silicon substrates, interactions between donors in silicon, and the observations of other impurities and defect centres in silicon. Spectrometry in the near infra-red was required as the luminescence was produced by recombination across the indirect band gap of silicon (\(\sim 1.1 \text{ eV}\)). The signals were sensitive to temperature, thus cryogenic cooling was also necessary.

Described below are two systems used for the PL experiments, a dispersion grating instrument set up at the University of Melbourne, and a Fourier transform system at Simon Fraser University in Canada.

3.5.1 Dispersion Grating System

The photoluminescence experiment using the dispersion grating system was a modification on the near-IR Raman instrument described in Section 3.4. Figure 3.15 shows the instrument schematically. Above band gap illumination was provided by a Coherent Innova 70 argon ion laser operating at 514 nm, which was located on a separate optical table to the near-IR spectrometer. In order to avoid having a free space beam crossing the room, the light was coupled into a multimode optical fibre via a 5\(\times\) microscope objective and expanded onto the other bench via a 20\(\times\) microscope.
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Figure 3.14: Sulphur spectrum taken with 1064 nm at 500 mW, and white light spectrum, showing the response of the laser line rejection filter on the near IR system. Note the roll off of the laser line rejection filter in the white light spectrum is reproduced in the sulphur spectrum. Resolution indicated on graph. (600 g/mm grating, 250 µm slits, 200 ms collection time).

The laser light was then reflected through the 20× OFR microscope objective onto the sample housed in the cryostat designed for microscopy. This lens then collected the luminescence from the sample, guiding it through a band pass filter to remove the Rayleigh scattered light, and into the Acton spectrometer which dispersed the spectrum onto the single channel InGaAs detector, as described in Section 3.4. The band pass filter was designed to cut out the 514 nm laser light and let through light out to 1200 nm, above which the filter efficiency drops.

3.5.2 Fourier Transform Photoluminescence Spectrometer

The following section describes the photoluminescence instrument at Simon Fraser University in Burnaby, Canada. The experimental setup is shown in Figure 3.16. The excitation source for this instrument was either a 532 nm solid state pumped laser, whose power was regulated by way of neutral density filters, or a 1047 nm Nd:YLF laser at 500 mW. The size of the laser spot on the samples was 2 mm. Samples were held strain free in a Janis helium bath cryostat, described in Section 3.7.

Sample photoluminescence was collected in a Bomem DA-8 Fourier transform spectrometer, a commercially available Michelson interferometer which included a quartz beam splitter. The
Figure 3.15: Schematic of the photoluminescence instrument using the grating spectrometer. Not to scale.

Figure 3.16: Schematic of Bomem DA-8 Fourier transform photoluminescence instrument at Simon Fraser University in Canada.
interference pattern produced by the beam splitter and the two optical paths was focused through an aperture and band pass filter before being detected with a liquid nitrogen cooled, germanium detector. Band pass filters were employed to stop laser light entering the detector. A 780 nm glass high-pass filter was used for the 532 nm laser and a 1047 nm edge filter for the 1047 nm laser.

A Michelson interferometer [78] splits the incoming light into two paths using a 50/50 beam splitter. One path leads to a fixed mirror and the other to a movable mirror, both reflecting the light back to the beam splitter. Interference between the beams occurs at the beam splitter. By moving one of the mirrors the path difference of the beams changes, and the conditions for constructive and destructive interference change for each component of the collected light. The intensity collected was the Fourier transform of the frequency spectrum. This instrument moved the mirror at a constant velocity and measured the signal intensity versus time. The finite travel of the mirror meant that the Fourier transform was not able to be taken over infinite space, and side lobes were produced on the peaks in the resulting frequency spectrum. Apodization, or the removal of the side lobes from the collected signal was performed using the Blackman Harris function [79], which provided the highest side lobe suppression with minimal effect on the lineshape. The resulting line width was increased to only $1.14 \times$ the theoretical linewidth.

Typically, the spectrum was averaged over many scans. The aperture was set to its maximum of 3.5 mm, providing a resolution of 0.5 cm$^{-1}$ (0.06 meV) which was enough to resolve the luminescence lines of interest, while passing the maximum light through to the detector.

3.6 Spectroscopy Using an Array Detector

Near the end of my PhD candidature, a new joint Raman-PL spectroscopy system with a near infra-red array detector and a silicon CCD was purchased. The new spectrometer could be configured for Raman spectroscopy as well as photoluminescence in both the visible wavelengths and in the near infra-red regions of the spectrum.

The instrument, housed at the University of Melbourne’s Bio21 Institute, was a Renishaw inVia Reflex micro-Raman which was equipped with a 0.25 m working distance spectrometer, and a Princeton Instruments OMA V InGaAs array detector cooled using liquid nitrogen (see Figure 3.17). This detector had 1024 discrete photodiodes as pixels in a linear array, operating at $-100 \, ^\circ\text{C}$ to reduce dark current and sensitivity to background radiation, and a spectral range of 0.8–1.7 µm. Illumination was provided by a Nd:YAG laser operating at 1064 nm. The instrument optics were optimised for the near infra-red, except for the 20 $\times$ long working distance microscope objective used in this work. The resolution of the instrument was about 3 cm$^{-1}$ with the 830 g/mm grating and 0.8 cm$^{-1}$ with the 1200 g/mm as determined from the full width at half maximum of a neon emission line. The edge filter for the 1064 nm laser blocks scattered laser light out to
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Figure 3.17: Photo of the Renishaw inVia Reflex Raman micro-spectrometer with the InGaAs linear array detector.

Figure 3.18: Laser line cutoff filter response on the Renishaw system running the 1064 nm Raman spectroscopy mode.

55 cm$^{-1}$ (see Figure 3.18), allowing for the collection of the electronic Raman scattering from donors and acceptors in silicon.
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Through the same optical path, a 532 nm laser can illuminate the sample. The luminescence from silicon was detected using the InGaAs array detector. By switching to the silicon CCD detector visible wavelength Raman scattering measurements were also available. The working modes of the system were easily switched using interchangeable optical components requiring minimal user realignment. No photoluminescence measurements using this instrument with 532 nm excitation were reported in this thesis.

3.7 Cryogenics

The cryogenics used in the experiments will be described in this section. Cryogenic equipment was used to reduce the temperature of the samples by either immersing them in a cryogenic liquid or attaching the sample to a cold stage cooled by a cryogen. This equipment was designed to give optical access to the sample for measurement, while minimising heating from atmospheric sources.

3.7.1 Continuous Flow Microscopy Cryostat

The spectroscopy instrument setup at the University of Melbourne, as discussed in the previous sections, involved the use of a Janis ST-500 microscopy cryostat system. This instrument was designed to cool a sample (using liquid helium) to 4.2 K while placing the sample as close as possible to a window, allowing optical access for a microscope (Figure 3.19). The sample sat in vacuum on a gold plated copper cold finger and was cooled by the continuous flow of cryogenic liquid at the base of the cold finger. A vacuum was used to stop convection cooling of the outer jacket which leads to frosting of the window. Temperature was monitored with a silicon diode thermometer at the base of the cold finger and temperatures from 4.2 K up to room temperature were controlled via a feedback system consisting of the sensor, a 25 Ω heating ring and a LakeShore PID temperature controller. The cryostat cold finger design provided a low vibration sample mount, with a footprint small enough to sit within a standard microscopy setup, while still capable of cooling the sample to liquid helium temperatures. Figure 3.20 shows a photo of the cryostat with the window flange removed.

Thermal conductivity between the sample and the cold finger was increased by applying a thermal grease such as Apiezon N, silver paste, or with the use of an indium spacer, which were also required so as to stick the samples onto the cold finger for horizontal mounting of the cryostat. The optical port sat 1 mm above the cold finger and was made of 1.57 mm thick quartz, which is transparent to visible and near infrared wavelengths and gave safe access to the surface of the silicon samples using microscopes with a working distance longer than 3 mm. Physical access to the sample was provided by removing the window flange. The cold finger was protected from
environmental radiation heating by the radiation shield cooled to 4.2 K by the liquid helium flow. The whole assembly was surrounded by a vacuum jacket which was evacuated to less than $1 \times 10^{-4}$ Torr using a turbo molecular pump. Liquid helium was transferred from a storage Dewar to the cryostat via a flexible, evacuated transfer tube and when in use the waste helium gas was vented to the atmosphere.

The use of lasers as an excitation source can lead to localised heating of samples, adversely affecting the measurement. To avoid such heating care was taken with the amount of laser power used. A simple one dimensional heat conduction model gives an estimate of sample heating for the above case of a sample sitting in vacuum, on a cold finger, and illuminated by a laser through
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a microscope. With a steady state heat source the heat conduction through the sample is expressed as:

$$\frac{dQ}{dt} = \kappa A \frac{dT}{dx}$$  \hspace{1cm} (3.2)

where $dQ/dt$ is the absorbed power, $\kappa$ the thermal conductivity, $A$ the illuminated area, and $dT/dx$ the temperature difference over a given distance [37]. The following is an example of typical conditions for the photoluminescence experiment. A laser of $\lambda = 514.5 \text{ nm}$ is used to excite a silicon wafer of $l = 300 \mu\text{m}$ thickness sitting on a cold finger at $T_{cf} = 4.2 \text{ K}$, using a lens with an N.A. = 0.4, and a laser power of 8 mW. The silicon will reflect 35% of the incident light, and below 10 K thermal conductivity $\kappa = 0.08 T^3 \text{ W/cmK}$. The diffraction limited area illuminated by the microscope can be estimated using the following expression [80]:

$$A = \pi V^2 \text{ with } V = 1.22 \frac{\lambda}{\text{N.A.}}$$  \hspace{1cm} (3.3)

Solving Equation 3.2 for the temperature differential and assuming a $T^3$ thermal conductivity (good for low temperatures):

$$T_s^4 - T_{cf}^4 = \frac{4Ql}{0.08\pi V^2}$$  \hspace{1cm} (3.4)

gives the surface temperature at the laser spot, $T_s = 30 \text{ K}$, a significant increase in the local sample temperature. The area calculated is the minimum possible the laser will focus to, thus the temperature calculated is an upper limit to the true temperature. Other factors affecting the final temperature are the actual thermal conductivity of the sample and the thermal contact between the sample and the cold finger.

3.7.2 Helium Bath Cryostat

Photoluminescence experiments performed at SFU in Canada, as described in Section 3.5, had the samples immersed in liquid helium in a Janis helium bath cryostat, see Figure 3.21. The inner reservoir of the cryostat was filled with 10 litres of helium liquid, surrounded by a vacuum chamber and a liquid nitrogen bath radiation shield. The liquid nitrogen shield reduced the environmental radiational heat load on the liquid helium chamber, as this load is proportional to the temperature difference to the power of 4:

$$Q = S(T_2^4 - T_1^4)$$  \hspace{1cm} (3.5)

where $S$ is the Stefan-Boltzman constant ($5.57 \times 10^{-8} \text{ W/m}^2\text{-K}^4$) [81]. With the liquid nitrogen shield $T_1 = 4.2 \text{ K}$ and $T_2 = 77 \text{ K}$, so $Q = 2 \text{ W/m}^2$, and without the shield $T_2 = 295 \text{ K}$, and $Q = 429 \text{ W/m}^2$. The relatively inexpensive nitrogen shield saves a large amount of helium from unnecessary evaporation.
Optical access to the samples was through a port consisting of a quartz window in the helium reservoir, a hole in the liquid nitrogen shield and a quartz window in the vacuum jacket, see Figure 3.21. The sample holder was attached to the end of a long metal rod which could be moved vertically and rotated to select the sample to be measured.

Samples were mounted strain free by placing them into cavities in an aluminium sample holder and covered with a quartz microscope slide. With this sample holder, twenty samples could be loaded at once. No pressure or strain was placed on the samples using this mounting. A photo of the stage is shown in Figure 3.22. For samples immersed in liquid helium, excitation powers of less than $250 \text{ mW/mm}^2$ do not lead to significant heating [37].

The temperature of the helium was reduced below 4.2 K by pumping on the reservoir using a Stokes pump, which reduced the vapour pressure, supercooling the liquid. Typically the system was run by reducing the pressure to $\sim 2 \text{ mm Hg}$ which gave a temperature of $\sim 1.5 \text{ K}$ [82].
Figure 3.22: Photo of the sample holder for the helium bath cryostat. Silicon samples are held strain free under a quartz microscope slide.
Chapter 4

Modelling of Implantation Distributions

4.1 Introduction

Implantation of phosphorus ions into silicon was chosen as the sample production method. It provided a controllable means of producing ensembles of both isolated and interacting donors. The interactions of ions with matter during implantation involve statistical processes. The simulation of these processes help in understanding the final distributions of the implanted ions. Software packages have been developed to simulate the process, most notably the computer program Stopping and Range of Ions in Matter (SRIM) [75].

This chapter will discuss the novel technique of implanting molecular dimer ions to produce samples with an ensemble of pairs of interacting atoms. In traditional doping of semiconductors with ion implantation, atomic ions are implanted at a particular energy, which determines the depth of the ions, and a fluence, which determines the density of the doping. So the separation between the ions $D$ is governed by the fluence, (see Figure 4.1 (a)). As the implantation is a random process there is a distribution to the values of $D$. At low fluences, most donors are isolated but a few may be in a position to interact. The only way to increase the number of donors close enough to couple is to increase the fluence, but as the process is statistical, control of the actual separation is difficult and clusters of more than two atoms also form. Eventually, as the fluence is increased these many body interactions dominate producing a metallic band. The implantation of molecular dimer ions, e.g. $P_2^+$, provides a way of producing isolated pairs of atoms in solids controllably. The implantation energy of the ion governs the separation within the pair $d$, while the fluence can be kept low to keep the distance between pairs $D$ large (see Figure 4.1 (b)). In this way, many pairs of interacting donors can be placed in a sample while keeping the fluence low and avoiding the metal insulator transition.

This chapter begins by considering how well the ion implantation simulation code SRIM mod-
4.2 Ion Solid Interactions

4.2.1 Ion Stopping and Range

The distance travelled by an ion implanted into a material, called the range \((R)\), is governed by the rate at which an ion loses energy as it passes through the material. This is known as the stopping power \((S)\) and is made up of both nuclear and electronic contributions. The nuclear stopping term arises from the transfer of energy during collisions from the implanted ion to the...
target nuclei, which deflects the ion and dislodges the target atom from its lattice position. The electronic stopping term is the coulombic interaction between the ion and the target electron cloud resulting in the excitation of electrons to higher states, as well as ionisation of atoms resulting in the formation of electron hole pairs. Energy transferred by these processes can be dispersed through the crystal as phonons. The total stopping power of an ion with energy $E$ along its path $x$ is expressed as:

$$ S = \frac{dE}{dx} = \left| \frac{dE}{dx} \right|_N + \left| \frac{dE}{dx} \right|_e $$

(4.1)

with the subscript $N$ denoting nuclear and $e$ electronic terms. Integrating this expression over the path of the ion provides the range as:

$$ R = \int_0^R dx = \int_{E_0}^0 \frac{1}{dE/dx} dE $$

(4.2)

with $E_0$ the initial energy of the ion. This range can be calculated analytically [35], but a greater degree of accuracy can be obtained using computational simulations informed by experiment such as with the computer program SRIM-2006 [75].

Of greater interest than the range of the ion is the distance an ion stops along the implanted axis of incidence, which is called the projected range ($R_P$). The stochastic nature of the ion-solid interaction leads to statistical fluctuations in the projected range and the projected straggle ($\sigma_P$), as well as statistical fluctuations perpendicular to the axis of incidence, the lateral straggle ($\sigma_\perp$). The implantation profile can be approximated by a Gaussian centred at $R_P$ with the straggle as the variance.

The relative magnitude of the nuclear and electronic contributions to the stopping for a particular material depends on the atomic number of the ion and the implantation energy. Figure 4.2 shows the electronic and nuclear contributions to the stopping for As$^+$, P$^+$ and B$^+$ implanted into silicon at various energies. The nuclear stopping term increases linearly at low implantation energies then drops off at higher energies, and increases with increasing atomic mass. The electronic stopping term is proportional to the ion velocity and has approximately the same trend and magnitude across ion species. For P$^+$ the nuclear stopping dominates for energies below approximately 130 keV and has a maximum at approximately 15 keV.

4.2.2 Ion Channelling

An ion incident along a major crystallographic direction can be guided between rows of atoms. Subsequent energy loss is mainly due to electronic stopping as nuclear interactions are avoided, which increases the range of the ions travelling along the channel. This phenomenon is called ion channelling. Simulations which ignore channelling effects can lead to inaccuracies in the sim-
Figure 4.2: Nuclear and electronic contributions to ion stopping for the dopants arsenic, phosphorus and boron in $^{28}$silicon [35].

Channelling during ion implantation can be minimised by tilting the sample away from a channelling axis or with the use of a thin capping amorphous layer such as silicon dioxide, which randomises the direction of the ion as it enters the crystalline substrate. The effectiveness of de-channelling by a thin amorphous layer increases with decreasing ion implantation energy. For a 15 keV P$^+$ implant into silicon with a 5 nm capping oxide, simulations performed by Wilson et al. [83] on the deflection of an ion on exiting the oxide found that only 20% of the implanted ions will enter the [100] channel. For 15 keV P$^+$ ions implanted along the silicon [100] channel, simulations performed with the Crystal-TRIM software package [84], which simulates the effect of the crystal structure on implantation, showed that using a 5° tilt avoided axial channelling. The critical angle to stop ions channelling has a $1/\sqrt{E}$ dependence, where $E$ is the ion energy [85]. At low ion energies (few keV) it becomes increasingly difficult to stop ions travelling through the channel. This would effect the distributions of ions in the sample.

For the samples implanted without a capping oxide, the silicon crystals were tilted by 7° to avoid axial channelling, and rotated by 10° to avoid planar channelling. These angles were chosen to stop ions from entering the channel with the higher energy implants and reduce the number in the channel at lower energies. With such an orientation the implanted ions face a random atomic configuration in the crystal.
4.2.3 Implantation Damage

The process of electronic energy loss transfers energy by exciting electrons to higher states or by generating electron hole pairs and does not displace any host lattice atoms. On the other hand, nuclear stopping involves collisions between atoms. Energy is transferred both through phonons, when the energy provided by the ion is less than that required to displace host atoms from their lattice positions, and through the displacement of atoms. These displaced atoms then knock out subsequent atoms in their path, dissipating the kinetic energy in knock-on collisions. This causes a tree of disorder in lattice damage. Figure 4.3, a SRIM simulation of implantation induced damage shows the path of the ion and the displaced silicon atoms. The dislodged atoms take up positions in the crystal at or near interstitial positions forming stable complexes such as interstitial clusters, leaving vacancies in the lattice.

To knock a silicon atom out from its lattice site, 15 eV of energy is required. A low energy P⁺ ion has enough energy to knock silicon atoms out of their positions throughout its whole path. For example, a 15 keV P⁺ ion has a nuclear stopping of ~ 500 eV/nm (see Figure 4.2), and a projected range of approximately 23 nm. SRIM simulated a total of 385 atoms displaced from their lattice position for each ion implanted. Phonons dissipate the remainder of the energy lost through nuclear stopping.
4.3 Ion Implantation Simulations

Discussed within this section is the simulation of phosphorus ion implantation into silicon and the resulting distributions of final ion positions. Two approaches were taken to simulate the ion implantation, molecular dynamics and SRIM.

Molecular dynamics (MD) simulations of the ion implantation process provide more accurate results than the binary collision simulations of SRIM, but are very computationally intensive. SRIM is a Monte Carlo simulation program using the binary collision approximation [86]. It describes the motion of the ion by simulating sets of binary collisions between the implanted particle and target atoms along its trajectory, calculating the nuclear stopping. For the electronic stopping, the binary collisions are screened Coulombic interactions using the Zeigler-Biersack-Littmark (ZBL) universal repulsive potential [86], a semi-empirical electronic stopping potential. These approximations make SRIM simulations very fast and thus more desirable than MD simulations. Unlike SRIM studies in molecular dynamics were limited to energies of only a couple of keV per atom. Molecular dynamics also had the advantage of being able to set up the exact lattice structure of silicon.

If both methods return similar results then SRIM can be used with some confidence. The MD simulation could only be performed for ions of a couple of keV in energy, as the simulation were too computationally expensive for energies greater than this, while the SRIM simulations were performed over a larger range of implantation energies. We would expect the comparison at 1–2 keV to continue to the higher energies for the following reasons. Most of the damage to the crystal caused by the implanted ions occur when the ion has only a few keV in energy, at the end of range when most nuclear stopping and subsequent crystal damage occurs. For higher implantation energies this end of range gets pushed further into the substrate but the interactions between the ions and the solid in this region are similar to those for the low energy ions. The low energy MD simulations are applicable to the end of range of the higher energy implants. Experimental studies have been reported also showing the accuracy of SRIM simulations of ion implantation into silicon down to sub 100 nm projected range, for example, using secondary ion mass spectroscopy [87].

As SRIM can only simulate atomic ions we needed to know whether P_{2}^+ can be implanted as two independent P^+ ions of half the total energy each, hitting the surface at the same point. Molecular implants can behave differently to atomic implants in the following ways. At higher energies, where electronic stopping dominates, an electronic wake from one ion increases the stopping for the other [88], also coulomb repulsion may push the ions apart. The above processes were not considered of importance since our samples were implanted at low energies, where the nuclear stopping dominates. For molecular implants the nuclear stopping could be affected by a lattice-mediated vicinage or “clearing the way” effect. This process has been found to be important
for larger ions, e.g. gold in silicon [89]. The binding of the atoms within the ionic molecule are weak compared to the implantation energy, thus the molecule will easily break on impact with the surface of the substrate. We turn to molecular dynamics to answer the above queries.

4.3.1 Molecular Dynamics Simulations of Implantation

Full molecular dynamics (MD) calculations on the implantation of \( P^+ \) and \( P^+_2 \) ions into silicon at energies of 1 and 2 keV/atom were performed by H.F. Wilson [90] in collaboration with us. I performed the SRIM simulations as part of this work. An environment dependent interaction potential was used in combination with the ZBL universal repulsive potential. The goal of the work was to compare the differences between the atomic and molecular implants, and to judge the accuracy of SRIM simulations.

Molecular dynamics calculations were performed using 100 ions per run, and with both atomic and dimer molecular ions of 1 and 2 keV/atom. Ions were implanted at an angle of 7\(^\circ\) off the [100] axis to reduce channelling, the 10\(^\circ\) planar rotation was not included in these simulations. Results showed that there was no significant difference in simulating the implantation of a molecular ion as a single molecule or as multiple atomic implants. The results were also consistent with those from SRIM. The 2 keV/atom implantation simulation is shown in Figure 4.4, where the depth distribution is compared in panel (a) for the dimer, and panel (b) for the atomic implants. The histogram shows the MD simulations, and the broken line is from SRIM. The atomic ions gave 8.2 nm and 5.0 nm for the average depth and standard deviation respectively, matching the values of 8.4 nm and 5.2 nm from the dimer implant. The distributions of the separations between ions \((d)\) were similar in the dimer (Figure 4.4 panel (c)) and the atomic (Figure 4.4 panel (d)) simulations. The average spacing and standard deviation for the atomic case was 8.3 nm and 5.9 nm, and for the dimer was 8.2 nm and 5.7 nm. The above molecular dynamics simulations indicate that the implantation into silicon of the dimer molecular ion can be modelled as two separate atomic ions impacting on the surface of the substrate at the same point.

The broken lines on the plots of Figure 4.4 are the results of SRIM simulations of \(10^4\) ions, which are consistent with the results of the MD simulations. Thus SRIM can be used to estimate the range and straggle of low energy phosphorus ion implants into silicon. The main difference between the simulations of atomic and molecular implants was the number of lattice distortions produced in each, see Figure 4.5. For SRIM an atom was either at a lattice site or not, whereas MD had a much greater accuracy to the position of the atoms in the crystal throughout the length of the simulation. The displacement of an atom from its original lattice position by more than 0.235 nm after 10 ps of the simulation was defined as a lattice distortion (the implanted ion had come to rest in 1 ps). The dimer implant produced on average more lattice damage per ion than the atomic implant. This was consistent with the results of the EPR characterisation, where more
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interface traps were detected in P$_2^+$ implants into silicon capped with an oxide than in the equivalent energy and fluence P$^+$ implants. Not enough damage would be produced for a channelling measurement to pick the difference between the two cases, but electrical measurements such as deep level transient spectroscopy could potentially measure the defects produced [68]. As the subsequent thermal treatment would have repaired the damage to the bulk silicon and oxide, these differences in damage should not affect the measurements.

4.3.2 Ion Range and Straggle

As the results from simulations of low energy phosphorus ion implantation into silicon using SRIM were consistent with those obtained using MD, all subsequent simulations were performed using SRIM.

Averaging over a large number of SRIM simulated implanted ions provided estimates of the projected range and straggle for the conditions of sample fabrication. Figure 4.6 shows histograms

![Histograms of implanted ions depth and spacing](image)

Figure 4.4: Comparison of atomic and molecular implants from molecular dynamics and SRIM simulations for 2 keV/atom. (a) The depth of the dimer implanted ions, (b) the depth of the atomic ion, (c) the spacing in the dimer implants, and (d) the spacing in the atomic implants. Broken line is the results from $10^4$ SRIM ions. Y axis units are number of ions for the molecular dynamics data, and the SRIM data is scaled for comparison [90].
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Figure 4.5: Number of lattice distortions per atom comparison of atomic and molecular implants from molecular dynamics simulations with 1 keV/atom. Y axis unit is number of ions [90].

of the projected range of implanted P$^+$ ions into silicon with a 5 nm thick silicon dioxide capping layer, and Figure 4.7 gives the projected range and straggle of P$^+$ into silicon for various implantation energies, both were produced using $10^5$ simulated ions. The peak concentration gives a measure of the local implanted ion density when multiplied by the implanted ion fluence. The projected ion range is almost linear with energy and the straggle (width of distribution) increases with increasing energy.

The effect of the thin capping oxide on projected range is minimal, as the density of crystalline silicon and its amorphous oxide are similar. The projected range for a 14 keV P$^+$ ion implanted into a substrate with a 5 nm capping oxide is 1 % less than if the ion was implanted into a substrate without a capping oxide. For a 3 keV P$^+$ implant the difference is only 3 % less with the oxide than without. The results of the simulations presented here can be applied to samples either possessing or not possessing a thin capping oxide without the loss of accuracy. For implantation into silicon capped by a 5 nm oxide, the range of the ions into the crystalline silicon is 5 nm less than without. This places the remainder of the the ions closer to the oxide layer and its associated charge traps.

The main issue with the capping oxide was the loss of the implanted ions which end up within the oxide. At implant energies below 15 keV a significant percentage of the ions have a projected range within the thickness of the capping oxide. Figure 4.8 has a comparison of the ions left in the oxide for implants into silicon with capping oxides of thickness 2 nm and 5 nm. For example, for a 10 keV P$^+$ implant through a 5 nm oxide 5 % of the ions are left in the oxide, while at 5 keV this increases to 14 %. More ions stopping within the oxide could lead to an increase in the level of oxide and interface defect states (charge traps), and lower dopant activation levels as ions in the oxide do not contribute to the electrical properties of the material.

The lower energy implants were performed into silicon stripped of its oxide so as to reduce
Figure 4.6: Histogram of projected ion ranges into silicon with 5 nm capping SiO$_2$. Simulations were for P$^+$ ions of 15 keV, 35 keV and 70 keV with $10^5$ SRIM simulated ions.

Figure 4.7: The mean total projected range and the projected straggle for P$^+$ ions implanted into Si with 5 nm capping SiO$_2$. From $10^5$ SRIM simulated ions.
the number of ions lost. The subsequent re-growth of the native oxide consumed a lower number of implanted ions than those which would be lost in a 5 nm thermal oxide, but the native oxide has higher oxide charge trap density. The proximity of implanted phosphorus to a poor quality oxide increases the chance that the phosphorus electron will be ionised by a trap, and stripping the oxide again before the measurement of a sample would be preferable. To complicate matters, implanting at the lower energies without an oxide makes the ions more susceptible to channelling given the \(1/\sqrt{E}\) dependence of the critical angle. Such a loss of ions from the expected distribution due to ions entering the channels was not considered. The effect of the oxide traps on the experiments on donors in silicon will be discussed in Chapter 7.

Studies on the interface trap density in silicon with a thermally grown oxide after implantation and annealing have been encouraging. DLTS experiments performed by McCallum et al. [70] of 15 keV P\(^{+}\) ions implanted at fluences up to \(1 \times 10^{12} \text{ cm}^{-2}\) through a 5 nm thermally grown oxide and rapid thermal annealed, have observed no net increase in oxide and interface defects compared to unimplanted and annealed samples. They also note that in some cases of larger trap densities to begin with, the implantation improved the oxide quality. It is still unknown how the lower energy P\(_2\)\(^{+}\) implants will affect the charge trap density.

![Graph showing percentage of P\(^{+}\) ions whose projected range is within the oxide thickness of 2 nm and 5 nm for various implantation energies.](image)
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4.3.3 Molecular Dimer Implantation

Molecular dimer ion implants were used to produce samples with isolated pairs of phosphorus atoms. Without a method to experimentally measure the positions of ions implanted into silicon, simulations inform the expected distribution of separations within the pairs. Taking a cue from the molecular dynamics results mentioned earlier, the dimer implantation process was modelled as two SRIM ions of equal energy, (each having half the total kinetic energy of the dimer ion) entering the crystal at the same position, as shown in Figure 4.9. This figure shows the path of the ions during a SRIM simulation which implanted a 20 keV $P^+_{2}$ ion as two $P^+$ ions of 10 keV each. Statistics for the distributions of intra-pair separations were computed using a FORTRAN code by calculating the separation between all possible pairs of ions in $10^5$ SRIM simulated final ion positions (SRIM implanted all the ions into the simulated silicon crystal at the same point). The average, standard deviation, and distribution of separations for various implant energies were calculated.

Figure 4.10 shows the mean separation of atoms within an isolated pair as a function of implantation energy, with the error bars indicating the standard deviation of the distribution. The separation is an almost linear function of energy. For an implantation energy of 14 keV $P^+_{2}$ the
mean separation is 12.8 nm with a standard deviation of 5.7 nm. Samples produced by implantation of 10 keV P$_2^+$ ions led to about 50% of the implanted pairs with intra-pair separations below 10 nm, suitable for investigating strong coupling. As mentioned earlier, care must be taken when implanting low energy ions, as a larger proportion of the ions end up in the capping oxide. For the 10 keV P$_2^+$ ion implants into silicon with a 5 nm oxide, 15% of the implanted ions were expected to remain in the oxide.

### 4.3.4 Simulations of Large Area Implants

The previous section of the thesis presented results for the separation of atoms within a pair ($d$) resulting from a dimer molecular ion implant. The simulations relied on the SRIM method of implanting all ions at the same point. These results were only able to be applied to low fluences where the separation between pairs $D$ was very much larger than that within pairs $d$. In this case pairs can be considered isolated, but as the fluence is increased the chance of neighbouring pairs interacting also increases. This leads to a point where two atoms from the same molecular implant are not necessarily nearest neighbours, and where clusters containing more than two atoms form. A more accurate picture of implanted samples produced at a fluence where all the pairs could not be considered isolated, was achieved by moving away from the single implant point of the SRIM.
simulated ions, and by spreading the implantation over a large area resembling the surface of a sample.

The method described here was used to produce simulated areas of both atomic and molecular implants so as to calculate mean nearest neighbour separations and distributions, and for use in the clustering calculations described in the next section. These simulations were used to study the effect fluence had on distributions of implanted donor separations. The simulations were performed with FORTRAN code by firstly setting up an area \( A \) where the ions were to be implanted. To keep the computation time between simulations similar and manageable, the total number of atoms \( N \) in each run was kept constant, and the simulated area was changed according to the desired fluence \( F \):

\[
A = \frac{N}{F}. \tag{4.3}
\]

The area was considered square with side length \( \sqrt{A} \). The atoms were implanted into this area by firstly choosing ion impact points \((x_i, y_i, 0)\) at random within this area. There were \( N \) ion impact points for atomic implants, with one ion per point, and \( N/2 \) impact points for dimer molecular implants, with two ions per point. The next step was to simulate the implantation process by adding to the ion impact points the final ion positions of individual SRIM simulated ions, resulting in the atoms placed at points:

\[
(x_i + x_{srim}, y_i + y_{srim}, z_{srim}) \tag{4.4}
\]

Nearest neighbour separations were calculated by computing a matrix of separations between all the atoms in the simulation with the smallest separation for each atom chosen as the nearest neighbour. From this matrix the statistics of the distribution were calculated: the mean and standard deviation, as well as the individual nearest neighbour separations binned as a histogram.

Figure 4.11 shows the final X-Y positions for 50 simulated implants of phosphorus atoms into an area of \( 220 \times 220 \text{ nm}^2 \). Figure 4.11 (a) shows 50, 5 keV \( \text{P}^+ \) implants and (b) shows 25, 10 keV \( \text{P}^+ \) implants, noting that both cases contain the same number of implanted atoms. The fluence as calculated from Equation 4.3 was \( 1 \times 10^{11} \text{ cm}^{-2} \). The dimer implants are more likely to be in pairs than the atomic implants.

Figure 4.12 shows the trend in the mean nearest neighbour separation for various \( \text{P}^+_2 \) implantation energies as the ion fluence was varied, from \( 10^9 \) to \( 10^{12} \text{ cm}^{-2} \). At low fluence the values plateau to those of the isolated pair simulations, \( d \), shown in Figure 4.10, and reproduce the results of an increase in implant energy leading to an increases in \( d \). With an increase in the fluence, and as \( d \) being a constant for each implantation energy, the separation between pairs \( (D) \) decreases and eventually dominates the nearest neighbour statistics. This can also be observed in Figure 4.13, where a comparison is made between 5 keV \( \text{P}^+ \) and 10 keV \( \text{P}^+_2 \) at various fluences. The fluence
Figure 4.11: Projections of the simulation of the implantation of (a) 5 keV P\(^+\) (the (+) points) and (b) 10 keV P\(_2^+\) ions (the (◦) points) into a large area. Note that the atoms implanted as P\(_2^+\) ions are generally in close pairs while the P\(^+\) ions are not. The simulated fluence for both is \(1 \times 10^{11}\) atoms-cm\(^{-2}\) in this plot is measured as the total number of atoms/cm\(^2\). At low fluences the difference in the nearest neighbour separations between the two cases was large. For the dimer the implant energy governs separation, but for the atomic ion it is the fluence. At the higher fluences the values of the mean nearest neighbour separations match, as \(D < d\). An estimate of \(D\) for the dimer implant can be produced by taking the value of nearest neighbour separation in the atomic case for half the implant energy, at half the dimer fluence (there are half the number of pairs as atoms).

The measurements of coupling were to be conducted in the molecular implanted samples, which would sample an ensemble of donors. Evidence of coupling was to be provided by comparing the differences in the signals between the dimer implanted sample and its complimentary atomic implant. The implanted ion fluence is an important parameter in such comparisons, as a very low fluence will not provide many donors to measure, and too high a fluence will result in a similar distribution of separations within the atomic and molecular implants. Figure 4.14 compares the nearest neighbour separations of a dimer-atomic complimentary pair of samples, 5 keV P\(^+\) and 10 keV P\(_2^+\) ions at fluences of (a) \(1 \times 10^{11}\) cm\(^{-2}\) and (b) \(1 \times 10^{12}\) cm\(^{-2}\). Again, note that there are the same amount of atoms implanted in the atomic and the dimer case. At the lower fluence the molecular implant had a distribution of nearest neighbours considerably closer together than the atomic ion implant, and measurements should distinguish this. At the higher fluence the two distributions are almost indistinguishable.
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Figure 4.12: Mean nearest neighbour separations of $P_{2}^{+}$ ions implanted into silicon at various doses and various energies. At low doses the separation between pairs ($D$) is greater than within ($d$) so the fluence does not influence mean nearest neighbour separations. At the higher fluences, $\approx 5 \times 10^{10} \text{cm}^{-2}$, the pairs get close enough so that $D < d$ dominates the mean separation.

Determining the usefulness of samples for measuring the coupling between atoms was aided by considering the percentage of the atoms within the sample likely to be strongly coupling so as to cause a measurable shift in the spectrum. Since the exchange coupling strength is a function of inter-donor separation (ignoring the directional dependence), calculating the percentage of donors with a separation less than a critical value provided such information. For example, in regard to the electronic Raman scattering experiment and Figure 2.15 (a), at a separation of about 10 nm there would be a peak shift of about 1% in 105 cm$^{-1}$ (an easily measurable 1 cm$^{-1}$ shift) on either side of the main peak. Closer separations result in larger shifts. The greater the number of pairs with such separations, the greater the differences between the coupled donor spectra and the isolated donor spectra. Figure 4.15 shows the percentage of donors with a nearest neighbour separation of less than 10 nm for implantations of various fluences and energies. At the lower fluences the $P^{+}$ implants had very few atoms with separations of less than 10 nm, whereas the donor pairs produced by the $P_{2}^{+}$ implants resulted in about half the number having such separations. As the implantation energy of the molecular ions was reduced, the percentage of closely spaced pairs increased, but at the expense of sitting closer to a surface. At the higher implantation fluences the separation between donors was reduced and most would have separations less than 10 nm, on the
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Figure 4.13: Comparison of simulated nearest neighbour separations for a 5 keV $P^+$ and a 10 keV $P_{2}^+$ implant at various fluences using $10^5$ SRIM ions. Note that the fluence in this plot is in units of (atoms/cm$^2$) resulting in the same total number of atoms at each fluence.

Figure 4.14: Histograms of the nearest neighbour separation for a 5 keV $P^+$ and a 10 keV $P_{2}^+$ implant. At (a) $1 \times 10^{11}$ cm$^{-2}$ and (b) $1 \times 10^{12}$ cm$^{-2}$. From $10^5$ SRIM ions.
way to producing an impurity band. This plot again highlights the advantages of molecular dimer implants at low fluence for producing samples containing closely spaced and strongly coupled pairs.

The main source of error in these simulations was an error in the fluence due to the lateral straggle of the implanted ions, placing them outside of the area set as the simulated crystal surface. Even though the impact point was within the set area the straggle placed the ion outside it, effectively increasing the top surface area of the crystal, thus affecting the calculated fluence through Equation 4.3. The main concern with errors was in the simulations of implanted ions with high lateral straggle (larger implant energies), those with high fluences (small areas), and those using a low number of simulated ions (small areas). Due to these errors there was a discrepancy in the fluence when comparing the simulated samples to the samples produced. The differences were not significant, as shown below.

As an example of this type of error, a simulation of 14 keV P⁺ at \(1 \times 10^{12} \text{ cm}^{-2}\) is provided. The implant surface area of the crystal was set using this fluence and \(10^4\) simulated ions, giving a surface area of \(10^6 \text{ nm}^2\) with a side length of 1000 nm. The lateral straggle of these ions was 10 nm. Adding this straggle to each end of the side length (1020 nm) and recalculating the area gave a fluence of \(f = 9.6 \times 10^{11} \text{ cm}^{-2}\). This fluence is 4% smaller than the fluence originally set. So the distributions calculated from the simulations using these parameters matched those for

Figure 4.15: Plot of percentage of ions with nearest neighbour separations of less than 10 nm at various fluences and various energies.
a sample with a fluence 4\% smaller than that quoted.

The 70 keV, $1 \times 10^{13}$ cm$^{-2}$ P$^+$ implant was the highest energy and highest fluence implant performed. Simulations on the nearest neighbour separations included $10^5$ ions. The lateral straggles for these ions was 38 nm which gave a change in area that lead to a fluence of $8.6 \times 10^{12}$ cm$^{-2}$, a 14\% error to the simulated fluence. This figure of 14\% was the largest error within these simulations. Such errors can be eliminated in future simulations through the use of periodic boundary conditions.

The above simulations considered the effect of the implanted fluence on the nearest neighbour separations for both P$^+$ and P$_2^+$ ions, which gave distributions of separations which could be directly compared to samples produced, and thus informed the selection and analysis of samples for the various experiments.

4.3.5 Interacting Clusters of Atoms in Ion Implanted Samples

The simulations reported in the previous sections calculated the distributions of nearest neighbour separations for implanted ions, but ignored whether the next nearest neighbours were also in a position to interact with the pair. Clusters of more than two interacting ions can form. A cluster is here defined as a group of atoms close enough to each other to be interacting. As the concentration of phosphorus atoms in a sample increases, clusters of interacting atoms of larger size form, until all the atoms in the sample become part of one large cluster, the metallic impurity band [91].

Simulations to calculate the distributions of cluster sizes in ion implanted samples were performed. They involved setting up a random implant into a “large area” simulated crystal, as described in the previous section, and calculating the separation matrix between all of the ions. An atom was chosen and atoms with separations less than $r_{\text{MAX}}$ (from it) were grouped with this atom as a cluster. $r_{\text{MAX}}$ was defined as an interaction distance where atoms with a separation less than this value were considered to be interaction and those with separations larger than this value as not interacting. Atoms within $r_{\text{MAX}}$ of the newly added atoms were then added to the cluster, and so on until there were no more atoms close enough to add. A new cluster was then started and the process repeated. Once an atom was included into a cluster it was no longer available to be grouped into another cluster. Finally, the number of clusters of each size was calculated.

The various experiments were sensitive to the donor interactions in different ways. Values from the literature for the radius in which interactions between donors begin, are consistent such that $r_{\text{MAX}} = 4a_0$ where $a_0$ is the Bohr radius of the particle of interest [92]. For example, the phosphorus donor electron has $a_0 = 2.5$ nm, and electronic Raman scattering spectroscopy has been predicted to be sensitive to strong coupling donors less than 10 nm apart. Electronic paramagnetic resonance is said to be sensitive to interactions for donors less than 20 nm apart, and in regards to photoluminescence the exciton has an $a_0 \approx 5$ nm [92]. A range of $r_{\text{MAX}}$ (10, 15,
Figure 4.16: The percentage of clusters of size $n$ in the 5 keV $P^+$ simulations for a variety of fluences. $r_{MAX} = 20$ nm. Simulations of 3000 SRIM ions.

Figure 4.17: The percentage of clusters of size $n$ in the 10 keV $P_2^+$ simulations for a variety of fluences. $r_{MAX} = 20$ nm. Simulations of 3000 SRIM ions.
and 20 nm) values were chosen for simulations performed with 3000 SRIM ions, to calculate the distributions of cluster sizes in phosphorus ion implanted samples.

A comparison of the atomic and dimer implantations, Figures 4.16 for 5 keV P\(^{+}\) ions, and 4.17 for 10 keV P\(_2^{+}\) ions, show the percentage of clusters of a certain size calculated for various fluences. In general, at low fluence there are many small clusters and as the fluence increases the size of the clusters increase, and from \(1 \times 10^{12}\) cm\(^{-2}\) and above the atoms form one big cluster. In the dimer case, at low fluence there are more 2 and 4 atom clusters than single atom cluster, whereas for the atomic ion implant there are more single atom clusters, as expected. The atomic implants follow similar trends to clustering calculations performed for bulk doped silicon by New [73], where clusters of greater than four atoms dominate the distribution once the number of isolated atoms becomes negligible. It is not only the distributions of nearest neighbour separations which are distinguishable between the atomic and the dimer implants at \(1 \times 10^{11}\) cm\(^{-2}\), as was mentioned earlier, but also their distribution of clusters. About 35\% of the atoms in the 5 keV P\(^{+}\) ion implant at this fluence can be considered isolated, and \(\sim\)20\% are in pairs, with the number of large clusters diminishing. For the 10 keV P\(_2^{+}\) ions, \(\sim\)40\% are in pairs and \(\sim\)20\% in clusters of four. Whereas at \(1 \times 10^{12}\) cm\(^{-2}\) the distribution of clusters is indistinguishable.

The calculation of the size of clusters of interacting phosphorus atoms in silicon compliments the calculation of the nearest neighbour separations, as the influence of any possible multi-particle interactions in a sample can be identified and characterised.

### 4.3.6 Nitrogen Dimer Implants in Diamond

The work on nitrogen in diamond presented here was performed in collaboration with T. Gaebel et al. [34], with the SRIM simulations my contribution to the work. The measurement of the state of a small number of phosphorus donors in silicon, as will be discussed in Chapters 5 and 7, is difficult whereas that of the nitrogen vacancy (NV) centre in diamond is relatively easy, to the point where single centres can be individually addressed. The diamond system provided a way of showing the effects of coupling between the pair of spins introduced via the implantation of molecular ions.

The measurement of the coupling of the spin of a single NV centre in diamond with a single neighbouring spin has been performed [34]. Colour centres in diamond provided a system where the simulations of molecular ion implantation could be tested against experimental results. The controllable introduction of coupled spins into diamond was achieved by the implantation of N\(_2^{+}\) ions, with the proportion visibly coupling matching that predicted by SRIM simulation [34]. The simulations and experiments relating to this work will be discussed in this section.

The projected range of the nitrogen ions into diamond and the mean nearest neighbour separations are shown in Figure 4.18 and were calculated as per phosphorus in silicon. The range
increased with increasing implantation energy and so did the nearest neighbour separation. Figure 4.19 shows the percentage of pairs which have separations of less than 3, 2 and 1.5 nm for various implant energies. By decreasing the implantation energy, the percentage of pairs with a separation within these bands increased, placing more atoms within the range of strong and measurable coupling.

The nitrogen-vacancy centre in diamond is made up of a substitutional nitrogen joined to a vacancy. It has a large oscillator strength between the transition from its ground state to its first excited state, this allows for single centre detection (see Figure 4.20). The NV centre has a spin of 1 with long spin coherence times at room temperature, $T_2 = 0.35$ ms.

Implantation of nitrogen into diamond produced vacancies in the crystal lattice. During high temperature annealing, these vacancies migrated and became trapped to a nitrogen atom creating the NV centre. Samples were produced with 14 keV $N_2^+$ ions implanted at a fluence of $\approx 1 \times 10^9$ cm$^{-2}$ into high purity, low background nitrogen diamond and annealed for 1 hour in an argon atmosphere. The conversion of the molecular ion to a NV-N pair was much more likely than to NV-NV, and it was coupling within the NV-N system which was observed. Figure 4.21 shows a picture of the implantation of $N_2^+$ forming a NV-N coupled pair and the energy level diagram of such a pair.

The spin-1 NV and spin-1/2 N in diamond couple via dipolar coupling, with the split in ener-

![Figure 4.18: Simulated range and nearest neighbour (NN) separation ($d$) for $N_2^+$ implantation in diamond. From 10^5 SRIM ions.](image)
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Figure 4.19: Percentage of pairs with separations less than the stated value for $^{14}N_2$ implantation into diamond, from $10^5$ SRIM ion simulations.

Figure 4.20: Pictorial representation of the nitrogen vacancy (NV) centre in diamond, (a) structure and (b) transitions [34].
4.3. ION IMPLANTATION SIMULATIONS

Figure 4.21: Pictorial representation of (a) $N_2^+$ ion implantation and resulting NV-N couples pair and (c) available ESR transitions for the coupled NV-N pair [34].

Figure 4.22: Experimental results of optically detected ESR for (top) a single NV centre and (bottom) a coupled NV-N pair. Transitions labels as per Figure 4.21 (c) [34].
gies expected to be $\Delta = 14$ MHz for a separation of 1.5 nm. For spins with a separation greater than about 2 nm the energy splitting due to dipolar coupling could not be observed with the experimental setup, placing an upper limit to the separations within a pair for coupling to be observed. Evidence of NV-N coupling was seen in optically detected electron spin resonance experiments, with the samples held in weak (40 G) B fields. Figure 4.22 shows the results of the experiment for an isolated NV and a coupled NV-N system. Lines associated with transitions are listed in Figure 4.19. The coupled spectrum shows a splitting of 14 MHz, consistent with theory for a separation of 1.5 nm. Calculations of nearest neighbour distributions for 14 keV $N_2^+$ found that only 1 to 2 % of pairs were expected to have separations of less than 2 nm. Measurements on many single centres found only 1 % of the centres were coupling, consistent with the simulations.

4.4 Conclusion

To produce samples with strongly coupled atoms the strategy of implanting $P_2^+$ ions was followed. This enabled the production of an ensemble of pairs whose separation was dependent on the energy of the implantation, while avoiding metallic doping levels. Implanted ions interact with the atoms in the substrate material and lose energy through nuclear and electronic contributions. These processes transfer energy, knocking atoms out from the host crystal structure producing vacancies. The implanted ions have a range and straggle determined by the implantation energy.

Simulations of the ion implantation process were performed with both molecular dynamics and SRIM. A comparison of the two techniques revealed that a $P_2^+$ ion can be simulated by two independent atomic ions implanted at the same spot, each of half the energy of the molecular ion. The results obtained by SRIM simulations of phosphorus implanted at a couple of keV were consistent with those from full molecular dynamics simulations. This meant that SRIM could be used with some confidence to simulate low energy phosphorus ion implantation.

Simulations provided information on the range and straggle of ions in silicon, as well as the amount of ions left in the capping oxide layer. Loss of ions to the oxide reduce the number of donors available for measurement, and damage to the oxide could increase the charge traps present. Increasing the distance of the ions from the oxide reduces the chance of interactions with the charge traps.

The separation between pairs of atoms from implanted dimer molecular ions was calculated, with lower energies leading to smaller mean intra-pair separations. The distributions of phosphorus ions implanted into realistic large areas of silicon were also calculated, as were the size and distributions of interacting clusters of atoms in the samples. These simulations enabled the direct comparisons of nearest neighbour distributions within samples physically produced, both atomic and dimer ions, and in terms of both energy and fluence. Such simulations informed the selection
of samples to be measured, and helped with the analysis of the results obtained. For example, mean intra-pair separations within a 10 keV P$^+_2$ implanted sample, was found to be $\sim$10 nm, and with about half of all pairs strongly coupled with a separations of $<$10 nm. The implanted fluence also plays a role in the distribution of the ions, with molecular implanted ion distributions resembling atomic at higher fluences. Results on the measurement of a 10 keV P$^+_2$ implanted sample should be distinguishable from a 5 keV P$^+$ sample for the implanted fluence of $1 \times 10^{11}$ cm$^{-2}$ but not of $1 \times 10^{12}$ cm$^{-2}$. Such analysis provided the implantation parameters for atomic and molecular implants used in the study of interacting pairs of phosphorus donors in silicon.

Finally, calculations of the simulated intra-pair separation from SRIM simulations were tested against experimental results for N$^+_2$ implants into diamond. Individual coupled NV-N centres were measured, with the results of the percentage of observed coupled pairs matching the percentage expected to show coupling obtained by simulations. These results confirmed experimentally the use of the methods described in this chapter.
Chapter 5

Electronic Raman Spectroscopy of Phosphorus in Silicon

5.1 Introduction

Koiller et al. [28] proposed a method for measuring wavefunction overlap of neighbouring phosphorus donors in silicon via observing changes to the electronic Raman scattering (ERS) spectrum from the coupled phosphorus donor states with temperature. The question this chapter will address is, to what extent we can implement Koiller et al.’s proposal to measure coupling, in ion implanted samples (atomic and molecular implants) using state of the art Raman spectrometers, and what difficulties may be encountered. The exchange coupling was to be measured in the molecular implant samples as they should have an increased number of coupled pairs available for this study, as described in Chapter 4.

This chapter begins with a review of the literature on electronic Raman scattering in semiconductors. A summary of the theory has been covered in Chapter 2. It is followed by the experiments, results and analysis of the visible and near infra-red Raman spectroscopy measurements, a discussion of these results, and finally the conclusion and prospects for further work.

5.2 Literature Review

Raman scattering spectroscopy of crystals traditionally considers scattering from collective modes of vibrational states, where the interaction of the light with the crystal creates or destroys a phonon [93]. Information on the vibrational frequencies of the crystal lattice has been collected in this way. Raman scattering from electronic transitions in crystals was first proposed by Elliot and Loudon [94] for paramagnetic rare earth ions within crystals. Their proposal provided a way
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To use visible radiation (of order eV) to observe low energy electronic transitions (of order a few meV) between states of the same parity (i.e. one photon forbidden transitions). They also predicted enhancement of the scattering cross section as the incident radiation approached a strong absorption.

5.2.1 Electronic Raman Scattering in Silicon

Observations of electronic Raman scattering from donor and acceptor levels in silicon was first reported by Wright and Mooradian [50]. Experimentally, a 1 W Nd:YAG laser operating at 1064 nm was used to illuminate samples cooled by immersion in liquid helium, with scattered light collected at 90° so as to reduce the scattered excitation entering the spectrometer. In phosphorus doped silicon, a peak was observed at an energy of 13.1 meV and was identified as a transition between the 1s(\text{A}_1) and 1s(E) levels of the donor atom in the valley-orbit split ground state of the phosphorus donor. These states had been inferred from far infra-red absorption measurements [44], (see Figure 2.10). Wright and Mooradian modelled this process using the transitions of an electron to an interband intermediate state within a two band model, one band lying above the conduction band and another below it. Electronic Raman scattering from boron doped silicon was also observed at 23.4 meV, though the authors could not identify the acceptor levels involved. A theory for acceptor transitions was developed by Klein [95] involving transitions between valence band 1s like states in the acceptor but is still to be fully developed.

The majority of work on electronic Raman scattering of phosphorus in silicon reported in the literature was performed by Jain et al. [51]. The spectrum in Figure 5.1, which was reproduced from Jain’s work, shows the electronic Raman transition of phosphorus in silicon with a peak at 13.6 K.

![Figure 5.1: Spectrum of the 1s(A1) to 1s(E) electronic Raman scattering transition from 2.5 \times 10^{17} \text{ cm}^{-3} \text{phosphorus donors in silicon. Spectrum taken from the PhD thesis of K. Jain [96]. (5 W laser power at 1064 nm excitation. Sample temperature quoted as “T” = 21.6 K as sample sitting in liquid helium was heated by the laser) [96].}](image-url)
105 cm$^{-1}$ (13.1 meV). Note that this peak is about half the size of the silicon TO phonon peak at 520 cm$^{-1}$ indicating that the cross section for the transition is large. This work investigated the impact the metal insulator transition has on the electronic Raman scattering of phosphorus electronic states as more and more donors interact forming a metallic band. Experimentally, this was achieved by measuring samples with a range of donor concentrations both semiconducting and metallic. Like Wright and Mooradian, Jain also used a high power Nd:YAG laser at 1064 nm with large samples held in liquid helium. Light was collected at 90° and analysed using a 3/4 m double monochromator with two 1200 lines/mm gratings and a photomultiplier tube detector. They measured the absorption of silicon and found that this laser energy matched the minimum in absorption at low temperatures. With up to 6 W of laser power, sample heating was a problem but the signal could still be detected at temperatures estimated to be up to 60 K. As the doping level approached the metal insulator transition, the line at 105 cm$^{-1}$ first broadened and shifted to lower energies. The line broadening was modelled via neighbouring donor wavefunction overlap using Heitler-London theory with the peak shift towards lower energies due to electrons spending less time close to the ionic core of the donor atom. At high concentrations, a low energy continuum was observed originating from inter valley electron density fluctuations in the now metallic impurity band and conduction band. The authors cover the theory of scattering from isolated donors which was introduced in Chapter 2. Unlike Moodarian, the donor transition from the $1s(A_1)$ to the $1s(E)$ level was modelled as a virtual transition to the valence band. This paper also identified the electronic Raman transitions from many different species of donors and acceptors in silicon.

Electronic Raman scattering has been used to observe the stress and magnetic field responses of the electronic ground states of acceptors in silicon. Cherlow et al. [97] studied the stress response and the Zeeman splitting of the electronic Raman scattering of boron acceptors in silicon providing the deformation potential and g values. Samples of the order of millimetres in all dimensions and with $5 \times 10^{15}$ B cm$^{-3}$ were measured either immersed in liquid helium, or attached to a cold finger cryostat. To reduce sample heating the Nd:YAG laser was pulsed with an energy of 0.1 J per 100 $\mu$s at a range of 1 - 2 pulses per second. They did not quote any sample temperatures during measurements. Light was collected at 90° and spectrally dispersed with a double monochromator. Using the same instrument configuration, they were also able to collect photoluminescence from arsenic doped silicon samples as there was enough absorption of the 1064 nm laser to produce luminescence.

5.2.2 Other Semiconductors

Electronic Raman scattering transitions have been observed in many semiconductors. The multi-conduction band valley, tetrahedral semiconductors such as: silicon carbide, gallium phosphide, and germanium have donor states similar to silicon where the $1s$ states are valley-orbit split. Ra-
man transitions have been observed within the split 1s states.

Colwell and Klein [52] performed electronic Raman scattering measurements on n-type silicon carbide. They found transitions from the 1s($A_1$) to the 1s($E$) levels of nitrogen donors, which have different energies depending on which of the inequivalent lattice sites the atom resides. The theory used to model this was the same as that used by Jain et al. [51] with an interband transition between the conduction band minimum and valance band maximum, at the indirect gap with an energy of 3 eV. This paper stated that the only possible Raman transition for donors within these multivalley semiconductors was between the split 1s states. Peaks from the mixing of the donor transition with phonon states and a continuum from overlapping nitrogen states and free carriers were also present in the spectra. Measurements were performed using a sub band gap argon ion laser operating at 514 nm with 1 W illumination on the samples, which were cooled directly in cold helium gas, with the scattered light collected in back scattering geometry.

Measurements in germanium showed electronic Raman scattering transitions from acceptors and donors. In the works of Doehler et al. [53,98,99], an ABC-YAG laser working at 2.1 $\mu$m was employed to measure arsenic and gallium doped germanium. Samples of millimetre size were cooled directly with cold helium gas and light was collected at 90°. As in the case of donors in silicon, the arsenic bound electrons in germanium underwent a scattering transition between valley-orbit split ground states, in this case 1s($A_1$) to 1s($T_2$). Germanium has an indirect band gap at 0 K of 0.74 eV and the laser used, with an energy of 0.59 eV, was sub-band gap. Previous Raman scattering studies on germanium performed with above band gap radiation only observed phonon scattering processes. As 2.1 $\mu$m was also at the absorption minimum for germanium, the authors believed that the biggest difference with their study was the increase in scattering volume compared to the micron or so penetration depth of the above band gap light.

### 5.2.3 Resonances

Raman scattering from bound electronic states has also been observed in direct gap semiconductors. Studies of resonance enhancement of the Raman scattering signal have been widely performed in direct gap semiconductors, where the laser energy was tuned to a real transition in the crystal. Resonant enhancement of Raman scattering from impurity electronic levels was discussed in a review article by Weisbuch and Ulbrich [100]. Enhancements of up to 12 orders of magnitude had been observed from the scattering of donor states in GaAs and CdTe [101]. The enhancement occurs when the laser energy matched that of the fundamental excitonic levels. The theory used to describe this enhancement was scattering of exciton-polaritons by the donor electrons [102], since this is the propagation state of light in semiconductors near absorption. This is a third order process, where a photon converted to an exciton-polariton at the surface, is scattered to another exciton-polariton state by the donor electron and then converted back into a photon as it leaves the
crystal. Such processes have been shown to produce a larger cross section than the band gap resonance of Equation 2.9, though this has been disputed by Feigenblatt [103]. Resonant enhancement of Raman scattering has also been observed in quantum dot states [104] with an increase in the measured scattering intensity when the laser energy matched a real state of the system.

Scattering from phonon states can also be resonantly enhanced (see the comprehensive review article by Cardona [105]). The main features of resonant enhancement were that they primarily occur when excitation laser frequencies approach the energy between critical points in the Broullin zone. For indirect gap semiconductors such as silicon, the absorption at the indirect gap is weak and only affects phonon Raman scattering if the phonons are aiding the absorption process of the light. Phonon scattering enhancement has been observed in silicon in scattering by two phonons when the laser energy was near the indirect $X$ point in the band [106]. Prevot and Wagner [107], using classical scattering arguments, have also demonstrated that the scattering intensity peaks at critical points in the band structure of crystals.

5.2.4 Other Types of Electronic Scattering

Bound electron Raman scattering is not the only electronic scattering process in semiconductors. The other electronic scattering processes will not be covered in detail here, however Klein [95] has a comprehensive review article on the topic. Mobile electron scattering, spin-flip scattering and coupling between electronic and phonon states are all possible processes.

5.2.5 Conclusion

Electronic Raman scattering has been observed from donors and acceptors in silicon. It has been used to measure magnetic field and strain effects in silicon, showing sensitivity to external perturbations to the donor state. Changes to the line shape have also been observed due to interactions between many donors as the doping concentration was increased. All the previous studies reported issues with laser heating of the sample at the powers required to observe a signal. Scattering from donor and acceptor states has been studied in many semiconductors. In those with direct band gaps, resonance enhancements have been observed at laser frequencies approaching real transitions in the samples. Whereas for indirect band gap semiconductors, electronic Raman scattering has only been observed with laser frequencies below the indirect band gap.

There has been a 30 or so year gap between the work of Jain et al., the last report in the literature of a study on the electronic Raman scattering from donors in silicon, and Koiller et al.’s paper, where they proposed the use of this technique to measure donor electron exchange coupling. In this time there have been no other reports on the observation of this transition. What has changed during this time so that no other Raman study performed on silicon observed this ERS transition?
Many studies have been performed in the intervening years on the TO phonon of silicon (see Chapter 6), but all these have used above band gap radiation. These studies were also performed in the backscattering geometry. The frequency dependence of the electronic Raman scattering transitions in the theory (Equation 2.9) does not discriminate against visible excitation even though it lies above the indirect band gap of silicon. In fact, the cross section should increase as the frequency approaches the energy of the direct band gap of silicon. The reason stated in the literature for not observing the ERS transition with laser energies above the indirect band gap was that the orders of magnitude increase in the absorption of the light at these frequencies led to a smaller scattering volume (the light did not penetrate far into the silicon). The problem with this statement is that modern spectrometers have developed, through the use of microscopy and sensitive multichannel CCD detectors, into very sensitive instruments where the reduction in the scattering volume may not necessarily be such a detrimental issue. Studies using above band gap illumination to observe the silicon TO phonon may have just not bothered to resolve the ERS signal as it lies so close to the laser line. The possibility that measurements with above band gap excitation using contemporary spectrometers may show the ERS transition is still open.

A curiosity in the electronic Raman scattering spectrum observed by Jain [96] and shown in Figure 5.1, was that the size of the ERS peak was about half the size of the silicon TO phonon peak, even with the many orders of magnitude difference in the number of phosphorus atoms compared to silicon. As the spectrum was illuminated with 1064 nm light, the $\omega^4$ (light frequency to the power of four increase in the scattering cross section) dependence of the classical scattering term was working against the silicon TO peak intensity, whereas the ERS transition does not possess such a term in its cross section (see Equation 2.8). A resonance process may have also increased the ERS cross section. The Nd:YAG laser frequency was not close to the direct band gap energy required for resonance, but it was still close to a critical point, the indirect band gap, and also close to the excitonic transitions of silicon. No study has looked into the possibility of a resonance at these wavelengths.

The theoretical discussion of electronic Raman scattering from isolated and coupled donors in silicon was covered in Chapter 2. The main points to note were that the transition occurs between the $1s(A_1) \rightarrow 1s(E)$ states of the phosphorus donor electron through a virtual transition to an intermediate state, though there is an uncertainty with the choice of the valence band as this virtual intermediate state. The strength of the transition is determined by the orientation of the crystal axis with respect to the polarisation of the laser.

Koiller’s proposal to measure the exchange coupling between neighbouring phosphorus electrons involved a study of the temperature dependence of the intensity of the ERS peaks. For measurements on ensembles, a broadening of the peak was expected. The states associated with the edges of the broadened peak would be those which show the strongest intensity changes with
temperature. By observing this change in peak shape, the presence of exchange coupled pairs would be revealed.

### 5.3 Electronic Raman Scattering Spectroscopy Experiments

As this was the first time in approximately 30 years that there has been a report on electronic Raman scattering from donor states in silicon, we will start with an examination of bulk doped crystals with near infra-red spectroscopy. Experiments were performed to check the suitability and sensitivity of the spectrometers to the desired signal, and to check the previously reported trends. The issue of laser heating of the samples was also investigated. Attempts were then made to measure an ERS signal from ion implanted samples. Finally, experiments with visible wavelength excitation were performed to study the resonance enhancement of the electronic Raman scattering equation.

#### 5.3.1 Samples

Experiments were performed on commercially sourced silicon wafers, bulk doped with phosphorus, boron, antimony, and arsenic. A selection of samples with resistivities between $1 \times 10^{-3}$ to $1 \times 10^4$ Ohm-cm, which correspond to a doping density of $1 \times 10^{12}$ to $1 \times 10^{20}$ cm$^{-3}$ [67], were measured. Wafer thicknesses ranged from approximately 200 to 700 µm. The doping density range in the samples contained isolated impurities, weakly and strongly interacting impurities, and metallic samples. Table 5.1 lists the bulk doped samples and their relevant properties.

A set of phosphorus implanted silicon samples were also measured, including P$^+$ and P$_2^+$ implanted ions at energies from 5 to 15 keV, and P$^+$ up to 70 keV, with fluences from $1 \times 10^{10}$ to $1 \times 10^{13}$ cm$^{-2}$. The implanted silicon contained ensemble distributions of isolated atoms, closely spaced pairs and metallic samples.

#### 5.3.2 Near Infra-Red Raman Spectroscopy

Spectra obtained using the in-house developed near infra-red Raman system with a single channel detector did not show any evidence of electronic Raman scattering from donors or acceptors in silicon. The reasons were numerous and included: instrument instabilities exacerbated by the long scanning times required of the single point detector, laser heating of the samples and the associated luminescence this produced, and spectral artefacts from the laser emission. These initial experiments are reported in Appendix A.

Many of the above mentioned problems were overcome in the Renishaw system (described in Chapter 3). The main advantage of this system was the near infra-red multi-channel array detec-
### 5.3. ELECTRONIC RAMAN SCATTERING SPECTROSCOPY EXPERIMENTS

<table>
<thead>
<tr>
<th>Name</th>
<th>Dopant</th>
<th>Resistivity $\text{Ohm-cm}$</th>
<th>Doping Conc. $\text{cm}^{-3}$</th>
<th>Mean Nearest Neighbour Sep. $\text{nm}$</th>
</tr>
</thead>
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<tr>
<td>P-A</td>
<td>P</td>
<td>$&gt;1000$</td>
<td>$&lt;4 \times 10^{12}$</td>
<td>$&gt;350$</td>
</tr>
<tr>
<td>P-B</td>
<td>P</td>
<td>$10 – 20$</td>
<td>$2 \times 10^{14} – 4 \times 10^{14}$</td>
<td>$95 – 75$</td>
</tr>
<tr>
<td>P-C</td>
<td>P</td>
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<td>$3 \times 10^{14} – 8 \times 10^{14}$</td>
<td>$83 – 60$</td>
</tr>
<tr>
<td>P-D</td>
<td>P</td>
<td>$2.5 – 4$</td>
<td>$1 \times 10^{15} – 2 \times 10^{15}$</td>
<td>$55 – 44$</td>
</tr>
<tr>
<td>P-E</td>
<td>P</td>
<td>$1 – 2$</td>
<td>$2 \times 10^{15} – 5 \times 10^{15}$</td>
<td>$44 – 32$</td>
</tr>
<tr>
<td>P-F</td>
<td>P</td>
<td>$0.5 – 0.9$</td>
<td>$6 \times 10^{15} – 1 \times 10^{16}$</td>
<td>$30 – 26$</td>
</tr>
<tr>
<td>P-G</td>
<td>P</td>
<td>$0.3 – 0.4$</td>
<td>$1 \times 10^{16} – 2 \times 10^{16}$</td>
<td>$26 – 20$</td>
</tr>
<tr>
<td>P-H</td>
<td>P</td>
<td>$0.1 – 1$</td>
<td>$5 \times 10^{15} – 8 \times 10^{16}$</td>
<td>$32 – 13$</td>
</tr>
<tr>
<td>P-I</td>
<td>P</td>
<td>$0.05 – 0.1$</td>
<td>$8 \times 10^{16} – 2 \times 10^{17}$</td>
<td>$13 – 9.5$</td>
</tr>
<tr>
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<td>$0.02 – 0.05$</td>
<td>$2 \times 10^{17} – 1 \times 10^{18}$</td>
<td>$9.5 – 5.5$</td>
</tr>
<tr>
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<td>$1 \times 10^{18} – 4 \times 10^{18}$</td>
<td>$5.5 – 3.4$</td>
</tr>
<tr>
<td>Sb-C</td>
<td>Sb</td>
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<td>$6.6 – 2.8$</td>
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<td>$2.6 – 1.2$</td>
</tr>
<tr>
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<td>$&lt;2 \times 10^{12}$</td>
<td>$&gt;440$</td>
</tr>
<tr>
<td>B-A</td>
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<td>$550 – 305$</td>
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<tr>
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<td>$75 – 62$</td>
</tr>
<tr>
<td>B-C</td>
<td>B</td>
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<td>$60 – 57$</td>
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<tr>
<td>B-D</td>
<td>B</td>
<td>$8 – 12$</td>
<td>$1 \times 10^{15} – 2 \times 10^{15}$</td>
<td>$55 – 44$</td>
</tr>
<tr>
<td>B-E</td>
<td>B</td>
<td>$4 – 8$</td>
<td>$2 \times 10^{15} – 4 \times 10^{15}$</td>
<td>$44 – 35$</td>
</tr>
<tr>
<td>B-F</td>
<td>B</td>
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<td>$1 \times 10^{16} – 1.5 \times 10^{16}$</td>
<td>$26 – 22$</td>
</tr>
<tr>
<td>B-G</td>
<td>B</td>
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<td>$1.5 \times 10^{16} – 2 \times 10^{16}$</td>
<td>$22 – 20$</td>
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<tr>
<td>B-H</td>
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<td>$12 – 9.5$</td>
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<td>B-J</td>
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<td>$3 \times 10^{18} – 8 \times 10^{18}$</td>
<td>$3.8 – 2.8$</td>
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</table>

Table 5.1: The bulk doped Silicon samples studied in this work. Resistivity as quoted by manufacturer, doping density via Reference [67], and mean nearest neighbour separation as per Reference [108].
tor, which increased the sensitivity of the detection while drastically reducing the total collection time for each scan, as 1024 spectral points were collected at the same time. Also for these experiments, silver paste was used as the thermal contact between the sample and the cryostat cold finger providing better heat transfer than the thermal grease used in the initial experiments.

Figure 5.2 shows the Raman spectrum from a 0.3–0.4 Ohm-cm \((1-2 \times 10^{16} \text{ cm}^{-3})\) phosphorus doped silicon sample measured with the Renishaw system. The sample was bonded with silver paste to the cryostat cold finger cooled to 4.2 K. The main features of the spectrum are labelled, including the electronic Raman scattering transition between the phosphorus donor \(1s(A_{1}) \rightarrow 1s(E)\) levels at 105 cm\(^{-1}\). The rest of the features were a combination of Raman scattering from the phonon states of the silicon crystal and photoluminescence from bound and free excitons. The silicon luminescence lines are fixed in energy and would be observed in different spectral positions in Raman spectra of different excitation sources. (A decrease in the PL energy would show up as an increase in wavenumbers in these plots, whereas for a Raman process an increase in energy would show up as an increase in wavenumbers). The expected positions of the silicon luminescence lines in the 1064 nm Raman spectra are included in Table 5.2. A more detailed discussion of the photoluminescence (PL) process in silicon is included in Chapter 7, only a minimal explanation of the PL required to understand the data will be provided in this chapter. The position of the main Raman features observed are also included in the table.

The peak observed at 120 cm\(^{-1}\) arises from the P\(_{\text{NP}}\), while that at 269 cm\(^{-1}\) is from the P\(_{\text{TA}}\), and that at 587 cm\(^{-1}\) is from the P\(_{\text{TO}}\) bound exciton photoluminescence. The large peak at 524 cm\(^{-1}\) is the zone centre TO phonon Raman line of the silicon crystal. The shoulder to this peak at \(\sim540 \text{ cm}^{-1}\) is a combination of the TO and LO replica of the silicon free exciton (FE) luminescence. Raman scattering from the second order phonon spectrum was also present just above the background, with the \(2\times\) TA phonon line at 305 cm\(^{-1}\) the most prevalent feature. The discrepancy between some of the observed and expected bound exciton peak positions was greater than the resolution of the instrument (3 cm\(^{-1}\)) which could not be adequately explained, but as they were observed in the expected series we had confidence in the identification of these lines.

The measured spectrum from silicon doped with \(1-1.5 \times 10^{16} \text{ cm}^{-3}\) boron is shown in Figure 5.3, with the main peaks labelled. The B\(_{\text{ERS}}\) peak can clearly be observed at 184 cm\(^{-1}\), the B\(_{\text{TA}}\) at 265 cm\(^{-1}\), and the B\(_{\text{TO}}\) at 581 cm\(^{-1}\), but unlike with phosphorus the B\(_{\text{NP}}\) transition is very weak [37] and was not observed. Again, the bound exciton peaks did not show up in the expected positions, but were in the correct series.

The appearance of photoluminescence was not unexpected, as the spectra collected were in the right energy range, and while the absorption of the laser light was minimal at these wavelengths, it was not zero (aided by the energy of the phonons assisting the process). For example, the small peak at 122 cm\(^{-1}\) next to the phosphorus ERS peak in Figure 5.1 collected by Jain, is likely to
5.3. ELECTRONIC RAMAN SCATTERING SPECTROSCOPY EXPERIMENTS

Figure 5.2: The Raman spectrum of 0.3-0.4 Ohm-cm phosphorus doped silicon showing the ERS peak at 105 cm$^{-1}$. The peaks are labelled with description in text. (100 mW laser at 1064 nm, 10 s integration time, $T_{cryo} = 4.2$ K).

be the P$_{NP}$ photoluminescence peak. Also they report on a line at 130 cm$^{-1}$ in an arsenic doped sample which they could not identify [51], this is the As$_{NP}$ photoluminescence transition. Cherlow et al. had previously used the Nd:YAG laser to study the As$_{NP}$ transition. The absorption of this light by silicon increases with an increase in the doping which results in more luminescence.

The bulk doped silicon samples listed in Table 5.1 were measured in a cryostat held at 4.2 K (see Figure 5.4 for the P doped samples and Figure 5.6 for B), and also at 81 K (Figures 5.5 for P and Figure 5.7 for B). The figures show the trends in the spectra with doping density.

**Donor Doped Samples**

Figure 5.4 shows the samples doped with donors with the spectra stacked from lowest doping at the bottom of the figure to highest at the top. The intensity of the ERS peak increased with increasing doping density. Various phosphorus doped samples with doping levels up to $1 \times 10^{17} \text{ cm}^{-3}$ were measured. We observed an increase in the intensity of the ERS peak, at 105 cm$^{-1}$, with an increase in doping density except for the sample P-H. The loss of expected ERS signal from the sample P-H could be linked to defects and impurities in the silicon interacting or ionising the donors, as indicated by a series of luminescence lines from 600 - 800 cm$^{-1}$ which could be related to carbon and oxygen in the silicon [37]. The lowest doping level from which ERS was observed was from
Table 5.2: Expected positions of the main free exciton and shallow impurity bound exciton luminescence, the phonon Raman lines, and the electronic Raman scattering lines from silicon in the 1064 nm and 532 nm Stokes Raman spectra. Peak position for samples measured at 4.2 K and doped in the isolated donor regime [51, 109].

<table>
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<tr>
<th>Peak</th>
<th>PL position</th>
<th>PL position</th>
<th>1064 nm Raman</th>
<th>532 nm Raman</th>
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<td></td>
<td>meV</td>
<td>Abs cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
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<tr>
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<tr>
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<td>9130.1</td>
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<td>129.4</td>
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</tr>
<tr>
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<td>597.5</td>
<td>9996</td>
</tr>
<tr>
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<td>9949.5</td>
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</table>

\[2 \times T\text{A}_{\text{phonon}}\]
\[T\text{O}_{\text{phonon}}\]

<table>
<thead>
<tr>
<th></th>
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Sample P-D at \(1 \times 10^{15} \text{ cm}^{-3}\). The highest doped phosphorus sample (P-I) does not contain a significant proportion of interacting donors and the linewidth has not been noticeably broadened. In general the relative intensity of the bound exciton (at 120 cm⁻¹ and at 269 cm⁻¹) to the free exciton luminescence increased with an increase in the doping level. The broadened free exciton luminescence may indicate an elevated temperature in sample P-I at the laser focus.

The two antimony doped samples which were measured, were doped at a higher level than the phosphorus doped samples, in a range where interaction between the donors would be expected. For isolated donors the position of the ERS peak from Sb is at 98 cm⁻¹. Sample Sb-A has the ERS peak at this position with a tail broadened towards lower energies and sample Sb-B shows a shift in the centre of the peak to lower energies as well as greater broadening. This trend is in line with that observed from phosphorus in this concentration range in Jain work, and indicated that all the
donors had similar behaviour due to nearest neighbour interactions. The bound exciton luminescence was concentration broadened and shifted to lower absolute energies (higher wavenumbers in this plot) in the higher concentration samples. As the Bohr radius of the exciton is larger than for the donor electron, concentration effects are greater in the PL than the ERS features.

The arsenic doped sample had the highest doping level of all the donor samples at about $5 \times 10^{19} \text{ cm}^{-3}$. The arrow in the figure indicates the expected position of the ERS peak from isolated As atoms, at 180 cm$^{-1}$. The ERS peak in this sample has been broadened and shifted significantly. The bound exciton luminescence has also been broadened and shifted, with the As$_{NP}$ peak at 370 cm$^{-1}$ and the As$_{TO}$ peak above 800 cm$^{-1}$.

The effects of nearest neighbour interactions on the ERS peak, and thus on the donor levels themselves, are consistent across the various shallow donor species in silicon with the peak broadening and shifting towards lower energies. The effects of the interactions were noticeable from samples doped to a mean nearest neighbour separation of less than 10 nm.

The $2 \times $TA phonon was very similar across the samples. Note that while the samples were silver pasted onto a cryostat cold finger held at 4.2 K, the samples did undergo some laser heating with the temperature at the laser focus estimated from the PL spectrum to be at 15–20 K (as discussed shortly).
Figure 5.4: Raman scattering spectra of silicon bulk doped with donors taken using the Renishaw system in near IR Raman mode. (100 mW laser at 1064 nm, 10 s integration time, $T_{\text{cryo}} = 4.2$ K). Spectra displaced vertically for clarity. The sample containing the highest concentration is at the top of the page. The samples are labelled as per Table 5.1.
Figure 5.5: Raman scattering spectra of silicon bulk doped with donors taken using the Renishaw system in near IR Raman mode. (100 mW laser at 1064 nm, 10 s integration time, $T_{\text{cryo}} = 81$ K). Spectra displaced vertically for clarity. The sample containing the highest concentration is at the top of the page. The samples are labelled as per Table 5.1.
The spectra measured at a temperature of 81 K (see Figure 5.5) show a shorter and broader ERS peak than those measured at 4.2 K, while at the same spectral position. The ERS peak was observed in samples doped down to $1 \times 10^{16}$ cm$^{-3}$. For example, for sample P-I, the peak half width (from a Lorentzian fit) increased from 3.3 cm$^{-1}$ at 4.2 K to 6.3 cm$^{-1}$ at 81 K. The integrated intensity of the peak (scaled by laser power and integration time) dropped from 340 au to 150 au. More on the temperature dependence will be mentioned shortly. The sharp bound exciton peaks did not show up at these temperatures, with the luminescence spectrum dominated by a thermally broadened TO & LO replica peak seen at the base of the TO phonon peak. At the higher doping densities, the concentration broadened bound exciton lines also contribute to this broad peak, shifting the peak energy. The TA replica free exciton luminescence also increased in intensity at the higher temperatures.

**Acceptor Doped Samples**

Acceptor states in silicon do not have the same electronic structure as donor states in silicon [95], but still produce an electronic Raman scattering transition. The energy levels of the acceptors are made up of valence band maximum like states and are shown in Figure 5.8 with the relevant ERS transition labelled B. The ERS transition from boron in silicon appears at 184 cm$^{-1}$ and is shown in Figure 5.6 from silicon samples doped with various concentrations of boron. Again, the lowest doped sample is at the bottom of the figure. The lowest doping from which the ERS transition was observed was from a sample with $1 \times 10^{15}$ cm$^{-3}$ boron acceptors. The ERS intensity increased with doping density, and up to a doping density of $2 \times 10^{17}$ cm$^{-3}$ (Sample B-I) the peak position was constant within the 3 cm$^{-1}$ error. At this concentration the peak started to broaden due to wavefunction overlap of nearest neighbours, with what looks like a tail to higher energies. The mean nearest neighbour separation in this sample, less than 10 nm, matched that for which nearest neighbour interactions were first observed in the donor case.

The highest boron doped sample, at $\approx 8 \times 10^{18}$ cm$^{-3}$ (B-J), had an ERS peak shifted to higher energies and broadened, with the centre of the peak at 210 cm$^{-1}$. This was the first study on the concentration dependence of ERS from acceptors in silicon and the first report of the ERS peak shifting to higher energies due to the increase in acceptor concentration. The shift in the position of the ERS peak with concentration for the boron acceptors was the opposite to that of the donors.

The explanation provided by Jain et al. for the shift to lower energies with the donors follows. The $1s$ donor states are split due to valley-orbit coupling, with the $1s(A_1)$ state pulled down from the other $1s$ states due to what is termed the central cell corrections (see Figure 2.10 for the donor levels). Basically, the wavefunction of the $1s(A_1)$ state is non-zero at the donor site and feels the attractive impurity potential more than the other states, and thus the energy of this state is more tightly bound than the others. The ERS transition energy is dependent on the energy difference
Figure 5.6: Raman scattering spectra of silicon bulk doped with acceptors using the Renishaw system in near IR Raman mode. The electronic Raman scattering from the boron acceptors (at 180 cm$^{-1}$) as well as the phonon Raman spectra and some luminescence lines are visible. (100 mW laser at 1064 nm, 10 s integration time, $T_{\text{cryo}} = 4.2$ K). Spectra displaced vertically for clarity. The sample containing the highest concentration is at the top of the page. The samples are labelled as per Table 5.1.
Figure 5.7: Raman scattering spectra of silicon bulk doped with acceptors using the Renishaw system in near IR Raman mode. The electronic Raman scattering from the boron acceptors (at 180 cm$^{-1}$) as well as the phonon Raman spectra and some luminescence lines are visible. (100 mW laser at 1064 nm, 10 s integration time, $T_{\text{cryo}} = 81$ K). Spectra displaced vertically for clarity. The sample containing the highest concentration is at the top of the page. The samples are labelled as per Table 5.1.
between the $1s(A_1)$ and the $1s(E)$ states and thus on the amplitude of the electron wavefunction at the donor site. For exchange coupled and interaction donors, the system can be thought of as a hydrogen like molecule, the electrons are shared around the donors spending less time at the donor sites. The donor ground state in this interacting system does not feel the impurity potential as strongly and is closer in energy to the other states, thus the ERS transition energy is smaller. Jain et al. have calculated the expected ERS line shape, using the wavefunctions of the donors states, for pairs of donors at various separations which follow the expected probability distribution of the donors for bulk doped samples and find the ERS peak broadening to lower energy.

A possible explanation for the boron data follows. The boron acceptor states are made up of valence band like states and the ground state is not dominated by the central cell corrections. The electrons which make up the valence band are those which bond the silicon atoms together to form the crystal. Electrons in these valence states are more tightly bound to two atoms than to an isolated atom. Considering the hole as a particle with a wavefunction this would hold true for the acceptor states as well, where the hole interacting with more than one acceptor is bound more tightly, and thus the energy of the ERS transition (transition B in Figure 5.8) would increase with an increase in the concentration of the acceptors.

The trends in the luminescence from the acceptors was similar to those from the donors, with the bound exciton luminescence increasing relative to the free excitons and then concentration broadened. Sample B-I shows both luminescence from isolated acceptors as well as the broadening from clusters of acceptors.

In Figure 5.7 the spectra were collected with the samples held at 81 K. Here the ERS peak is broader and shorter, and in the same spectral position. The luminescence in the spectra is dominated by the thermally broadened free exciton recombination.

We also note the observation of a Fano type resonance observed in sample B-J, silicon doped with boron acceptors to $8 \times 10^{18}$ cm$^{-3}$. A Fano resonance is an interaction between a continuum electronic state and a discrete state. In this case the continuum was the electronic scattering from the boron acceptor states, broadened to a continuum due to wavefunction overlap, and the silicon TO phonon scattering to the discrete state. Figure 5.9 showed the spectrum from this sample with the Fano resonance being the asymmetry in the silicon TO phonon peak consisting of the anti-resonance on the left hand side of the peak at 515 cm$^{-1}$. Cedeira et al. [110] have studied this effect and found that the strength of the resonance is dependent on the excitation wavelength, the doping concentration and the dopant used. The TO phonon peak we measured was non-linear least squared fitted to the equation reported in the Cedeira et al. paper and is also shown in the figure, confirming the observed effect as a Fano resonance.
Figure 5.8: Schematic of the acceptor states and possible electronic Raman transitions. The observed transition is labelled B. [51]

Figure 5.9: The Fano resonance observed in Si:B sample B-J, doped from $3 \times 10^{18}$ to $8 \times 10^{18}$ cm$^{-3}$. The crosses (x) plot the experimental data and the solid line is the non-linear least squares fit using the Fano-type equation from Cedeira et al. [110]. (100 mW laser at 1064 nm, 10 s integration time, $T_{\text{cryo}} = 4.2$ K).
Sample Temperature

Concerns with laser heating in our measurements led to the collection of spectra at various laser powers. The temperature could not be estimated by performing a Stokes to anti-Stokes intensity ratio for the ERS peaks (which was how Jain et al. estimated their sample temperature), as the use of an edge filter blocked the anti-Stokes region of the spectrum. Changes to the phononic structure in the spectrum with temperature could also aid in estimating the temperature, but such changes would be small below 80 K [111] and were not expected to be resolved using the 830 g/mm grating used in this work. Instead, the presence of the photoluminescence lines in the spectra were used to give an estimate of the temperature. Estimates were provided by comparing the peak shape and intensity of the photoluminescence lines at various laser powers and cryostat temperatures to previous studies of the temperature dependence of photoluminescence. The photoluminescence was more sensitive to temperature changes because of the relatively small binding energy of the excitons to the shallow impurities compared to the electrons and holes of the shallow impurities.

Figure 5.10 shows spectra from a highly B doped sample (B-H at $\sim 1 \times 10^{17}$ cm$^{-3}$) at various laser powers and Figure 5.12 a moderately doped P sample (P-F at $\sim 5 \times 10^{15}$ cm$^{-3}$). All of the spectra were scaled by the laser power used. The ERS peak scaled linearly with the laser illumination intensity in both samples, indicating the scattering intensity was proportional to the applied excitation density and was not significantly affected by any sample heating. While the various replicas of the bound exciton luminescence have relative differences in intensities between dopant species, their behaviour with temperature was expected to be consistent across species as the exciton binding energies are similar [62].

In Figure 5.10 the TO replica of the bound exciton luminescence from the $1 \times 10^{17}$ cm$^{-3}$ Si:B sample has two components, a peak at 585 cm$^{-1}$ (1092.6 meV in PL) corresponding to the isolated acceptor B$_{TO}$ peak, and a broader peak centred at 620 cm$^{-1}$ (1088 meV in PL) from excitons bound to clusters of acceptors. At lower laser powers, the cluster peak dominates. As the laser intensity was increased, the population in the cluster component decreased while that in the isolated acceptor component increased. This behaviour was a thermal effect where the higher energy isolated donor transition was thermally populated by the heating of the sample due to the higher laser powers.

Estimates of the temperature in each of the spectra was achieved by comparison to the study of the temperature behaviour of the P$_{TO}$ peak in phosphorus doped silicon by Nishino et al. [112]. Figure 5.11 shows their spectra for a $1 \times 10^{17}$ cm$^{-3}$ Si:P sample at various temperatures. At 8 K the P$_{TO}$ peak was broad and made up of two components (not to be confused with the peak labelled P$_{1}$TO in the figure), with the lower energy component (cluster) dominating over the higher energy component (isolated). As the temperature was increased, the peak from the donor clusters decreased in intensity relative to the isolated donor peak, which with further increase in tempera-
Figure 5.10: Laser power study of highly doped Si:B sample B-H at $1 \times 10^{17}$ cm$^{-3}$. (Laser at 1064 nm, 10 s integration time, $T_{\text{cryo}} = 4.2$ K). Spectra displaced vertically for clarity and scaled by the measured laser excitation power.

Figure 5.11: Temperature dependence of photoluminescence from a $1.2 \times 10^{17}$ cm$^{-3}$ Si:P from Nishino et al. [112].
ture then decreased in intensity relative to the free exciton peak (labelled as I\textsuperscript{TO}). By comparing the individual spectra, the temperature was estimated: our 4 mW and 7 mW spectra compared well to the 8 K spectra of Nishino et al., and our 35 mW spectrum was most similar to their 13 K spectrum, where the cluster peak can still be seen. For the 100 mW spectrum the closest match were the 16 K and 22 K spectra as the P\textsubscript{TO} peak was present, unlike for 30 K where the bound exciton luminescence disappeared.

Figure 5.12 shows the spectrum from silicon doped with $1 \times 10^{15}$ cm\textsuperscript{-3} P donors, as the laser power was increased the bound exciton peak decreased in intensity relative to the free exciton peak. The ratio in intensity between the P\textsubscript{TO} and FE\textsubscript{TO} peaks at 4.2 K has been well established in photoluminescence studies and used to measure the doping level of crystals, see Figure 7.4 (b) which plots the ratio as a function of doping density. For this sample at 4.2 K the P\textsubscript{TO}/FE\textsubscript{TO} intensity ratio was expected to be 100, and a comparison to the measured ratios helped identify which spectra suffered from laser heating. The 100 mW spectrum had an intensity ratio of \textasciitilde0.3, and the 35 mW spectrum had a ratio of \textasciitilde2, indicating the sample was heated at the laser focus in both spectra. In both the 4 mW and the 7 mW spectra, the free exciton peak can not be resolved above the noise, and while the exact ratio was not established, both were much closer to 4.2 K than with the higher power measurements.

![Figure 5.12](image_url)

**Figure 5.12:** Laser power study of moderately doped Si:P sample P-F at $5 \times 10^{15}$ cm\textsuperscript{-3}. (Laser at 1064 nm, 10 s integration time, $T_{\text{cryo}} = 4.2$ K). Spectra displaced vertically for clarity and scaled by the measured laser excitation power.
The estimation of the temperature reported so far has relied on a comparison to previous photoluminescence studies, and also assumed all effects were temperature related. To discount any pure laser power effects on the observed changes to the luminescence [113], and to compare measurements across different temperatures, the cryostat temperature was varied and the samples were measured with low laser powers. Figure 5.13 (b) plots the spectra from sample B-I \(\left(2.5 \times 10^{17} \text{ cm}^{-3}\right)\) at various cryostat temperatures, and at 7 mW of laser power. The spectra were scaled to aid in the comparison of the peak shapes. The analysis focused on the concentration broadened \(B_{\text{TO}}\) peak at 580–620 cm\(^{-1}\), which as in Figure 5.10 comprised of two components relating to isolated acceptors and clusters of acceptors. Again the relative intensity of the components changed with an increase in temperature, the isolated (higher energy in PL) component increased, and the cluster (lower energy) component decreased, which is consistent with a thermal process. The luminescence disappeared by 25 K. An estimate of the temperature of sample B-I at the laser focus when held to the cryostat at 4.2 K and measured with 100 mW excitation (the spectrum at the bottom of Figure 5.13 (b)) was performed by comparing the shape of the luminescence spectrum to those measured at various temperatures with low laser powers (where we don’t expect significant heating or power effects). The shape of the luminescence most closely matched those taken at 15 K and 20 K.

The analysis of the sample temperature at the laser focus by observing changes to the photoluminescence spectra indicated that heating of the samples at higher laser powers was occurring. The following temperature ranges were estimated for the various laser powers: for 4 and 7 mW, the temperature was between 4.2–10 K, for 35 mW 10–15 K, and for 100 mW 15–20 K. Thus, the spectra in Figures 5.4 and 5.6, while obtained from samples attached to a cryostat at 4.2 K were heated locally to 15–20 K. The measurement of ERS at 4.2 K is achievable with the use of low laser powers. While estimates of the temperature were possible using the luminescence present in some spectra, the major limitation of this technique is that it was not independent of sample doping.

**Temperature Dependence of the ERS Peak**

The proposal by Koiller et al. to measure the strength of the exchange coupling between pairs of phosphorus donors in silicon relied on resolving changes in the ERS peak shape with temperature (see Figure 2.15 (d)). In bulk doped samples, where only a few of the donors or acceptors would be in exchange coupled pairs with no preferred orientation, the only changes to the tails of the ERS peak would be expected with temperature. We were not able to resolve any such small changes in our spectra. The observed temperature effects on the ERS peak were due to thermal broadening of the peak, and thermal depopulation of the donor and acceptor states.

With an increase in temperature, from the estimated 15–20 K to 81 K, the ERS peak width
5.3. ELECTRONIC RAMAN SCATTERING SPECTROSCOPY EXPERIMENTS

Figure 5.13: (a) The ERS peak from sample B-I at various cryostat temperatures. (1064 nm laser at 7 mW, 100 s integration time except for T=4.2 K and 81 K with 10 s integration time). (b) The luminescence from sample B-I at various cryostat temperatures. Spectra obtained at 7 mW scaled for comparison to 100 mW spectrum as an estimate of sample laser heating (1064 nm laser). Spectra displaced vertically for clarity and scaled by integration time and laser power.

broadened and the height decreased, as seen when comparing Figures 5.4 & 5.5, and Figures 5.6 & 5.7. For example, for sample P-I the ERS peak width, as measured by a fit to a Lorentzian function, increased from 5.5 cm$^{-1}$ to 11.7 cm$^{-1}$ while the peak height dropped to 20 % of the lower temperature value. For sample B-I, the width increased from 6.4 cm$^{-1}$ to 12.6 cm$^{-1}$ while the height dropped to 33 % of the lower temperature value. On the other hand the integrated intensity of the scattering dropped to only 40 % for the P and 65 % for the B. For temperatures between 4.2 K and 25 K, as shown in Figure 5.13 (a), the ERS peak does not change significantly with temperature.

The electronic Raman scattering intensity is expected to be directly related to the ground state population of the donors and acceptors. As occupation of these states is temperature dependent but also independent of the state of the other donors and acceptors in the crystal (focusing here on non-interacting dopants), the scattering intensity is expected to follow a Maxwell-Boltzmann distribution. This distribution relates the thermal occupation of two states (the initial and final states of the ERS transition), to the energy separation between the states relative to the sample
temperature, and to their degeneracy. For an increase in temperature, the occupation in the initial state of the Stokes ERS decreased and thus the intensity of the peak decreased, but at the same time the occupation in the final state increased which increased the intensity of the anti-Stokes ERS. Note that we did not observe any anti-Stokes scattering due to the use of an edge filter to reduce the laser intensity entering the spectrometer, for P this peak would appear at \(-105 \text{ cm}^{-1}\).

The energy separation in the B ERS is 23.4 meV compared with 13.1 meV for the P ERS, thus the thermal occupation of the B ground state is expected to be greater than that of the P at 81 K. This would lead to the intensity of the B Stokes ERS peak at 81 K relative to the intensity at 4.2 K to be greater than that measured for the P. This trend was observed, but further work is required to establish how well the scattering intensities follow the Maxwell-Boltzmann distribution.

A potential application of ERS spectroscopy of donors and acceptors in silicon would be the identification of donor and acceptor elements in silicon using liquid nitrogen cooling, which is much simpler and cheaper than the liquid helium required in PL. Dopant identification would be limited to samples with a narrow doping density range, in the region of only weak interactions at approximately \(1 \times 10^{16}\) to \(1 \times 10^{18} \text{ cm}^{-3}\). The major disadvantage of this technique is that, unlike in photoluminescence using above band gap excitation, any donors or acceptors ionised by defects or compensation doping, would not be photo-neutralised by the 1064 nm laser and would not contribute to the scattering, so an accurate measurement of the doping concentration could not be provided.

ERS Peak Intensity

Table 5.3 compares the scattering intensity we measured to that measured by Jain, and Wright and Mooradian for samples of similar doping density. Such comparisons can give details on the differences between the measurements. The ratio between the intensity of the ERS peak to the silicon TO peak was used as a way to normalise the data to facilitate comparison. The intensity ratio from both the P and B measurements we performed was approximately an order of magnitude larger than that of Wright and Mooradian, for samples of comparable doping density. Whereas the intensity ratio from Jain's work was an order of magnitude larger than ours.

Both of the previous studies were conducted by collecting the light 90 degrees to the excitation, whereas we collected the scattered light using the backscattering configuration. Also, both previous studies mention alignment of the samples to the polarisation of the laser and analysis of the polarisation at the collection to optimise the strength of the ERS peak, whereas we did not take any care in orienting samples. It is of interest that the two previous studies used similar experimental geometries with one study finding a larger ratio than ours and the other a smaller one.

The orientation of the crystal, the polarisation of the excitation source and the collection
5.3. ELECTRONIC RAMAN SCATTERING SPECTROSCOPY EXPERIMENTS

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<td>P-I</td>
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<td>Jain</td>
<td>$2.5 \times 10^{17}$ P cm&lt;sup&gt;-3&lt;/sup&gt;</td>
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<tr>
<td>Sb&lt;sub&gt;ERS&lt;/sub&gt;</td>
<td>Sb-A</td>
<td>$2 \times 10^{17} - 1 \times 10^{18}$ P cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>$3 \times 10^{-1}$</td>
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<tr>
<td>P&lt;sub&gt;ERS&lt;/sub&gt;</td>
<td>P-G</td>
<td>$1 - 2 \times 10^{16}$ P cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>$1.8 \times 10^{-2}$</td>
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<tr>
<td>W &amp; M</td>
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</tr>
<tr>
<td>B&lt;sub&gt;ERS&lt;/sub&gt;</td>
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<td>$1.4 \times 10^{-3}$</td>
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Table 5.3: ERS peak to silicon TO phonon peak intensity ratios, a comparison to the literature. Scattering intensity data collected by integrating the area under the peaks. Data from previous literature: Jain [96], an estimate we made from Figure 5.1, and Wright and Mooradian (W & M) [50].

and the geometry of the experiment, can greatly affect the intensity of a Raman scattering process [114]. For example, the TO phonon can be eliminated from a spectrum with the correct parameters. As we did not control for any of these parameters comparison with the previous literature is difficult. For example the ERS to TO phonon ratio observed by Jain may have been due to the choice of such parameters which led to a reduction in the intensity of the TO phonon peak as much as an increase in the ERS peak intensity. Greater control of the crystal orientation and the polarisation should be considered in the future.

As well as the geometrical considerations, the signal strength can also be affected by the sample temperature and any other ionisation of dopants, such as compensation doping. The temperature of the samples were consistent across studies, with Jain estimating this measurement to be at 21 K, and ours was estimated to be 15-20 K. Note also that Jain mentions that care was not taken to keep a constant cathode temperature on their photomultiplier detector, which could change the sensitivity of the ERS peak measurement and the TO peak measurement. The large possible doping range of our sample P-I increased the errors in the comparison to Jain’s sample, and a more accurate measure of the sample doping should be performed.

**Ion Implanted Samples**

Our proposal to measure the exchange coupling strength between pairs of donors in an ensemble was to use implanted samples, where the separation within the pair can be controlled via the molecular ion implantation energy and the separation between pairs by the implanted fluence. The donor distribution in atomic ion implants should be similar to that of the bulk doped samples. The near infra-red experiments performed on our implanted samples did not result in the observation
CHAPTER 5. ELECTRONIC RAMAN SPECTROSCOPY OF P IN SI

Figure 5.14 shows the spectra from two 70 keV P⁺ implanted and annealed samples, which provided our best chance of observing electronic Raman scattering from implanted samples as the projected range of the ions gave a substantial volume of donors, from a silicon blank and from the reflection off of the gold cryostat stage. The as-supplied silicon was TopSil which showed no ERS from donors or acceptors. No ERS was observed in the spectra from either implants, nor was any photoluminescence present. Note that in the later photoluminescence experiments discussed in Chapter 7, these two samples showed luminescence associated with the implanted donors (see Figure 7.13), a concentration broadened bound exciton peak from the centre of the implanted depth and an increase in the isolated donor peak originating from the tails. Photoluminescence is a much stronger process with above band gap illumination, where luminescence from even $1 \times 10^{12} \text{ cm}^{-3}$ impurities have been observed, see Figure 7.8 showing the PL spectrum from the blank TopSil silicon, than with 1064 nm excitation which did not have the sensitivity to such low doses.

The spectrum of the blank silicon below 300 cm⁻¹ follows that of the gold cryostat stage, whereas the implanted samples did not show these features. As the gold stage was partly coated with the silver paste, the signal observed probably originated from the ingredients in the paste, with the small peak at around 520 cm⁻¹ indicating some silicon was involved. The surface of the blank silicon may have been accidentally coated with silver paste while it was mounted onto the stage. All the silicon samples showed a very clear phonon Raman scattering spectrum.

An ERS signal from these two implanted samples was expected for the following reason. The confocality of the microscope was at best 2 µm, and in the bulk we observed ERS from samples doped down to $1 \times 10^{15} \text{ cm}^{-3}$. The thin layer of doping in the 70 keV P⁺ implants was $\approx 100$ nm and the implanted fluence produced a doping density of approximately $1 \times 10^{18} \text{ cm}^{-3}$. The samples were doped three orders of magnitude greater than the minimum sensitivity we found in the bulk, and the doped volume samples by the microscope was two orders of magnitude less than in the bulk, so an ERS signal was expected to be observed. One reason for the lack of an observed peak was that all the donors may not have been activated by the anneal, but the PL experiments suggested that most were activated (as the peak observed corresponded to that from the expected implanted distribution). Another possibility could have been the proximity of the implants to the oxide, with the associated traps at the interface ionising the donors. Without an electron at the donor ground state there is no ERS, and unlike photoluminescence with above band gap excitation, the 1064 nm laser would not photo-neutralise the donor.

The experiments on the implanted samples may have been on the cusp of observing an ERS peak, and it could be possible with a few relatively easy steps. Firstly employing better optics, in the form of a long working distance 50× objective with a 0.55 N.A as is available for visible wavelength spectroscopy, but with transmission optimised for the near infra-red. Also, using
5.3. ELECTRONIC RAMAN SCATTERING SPECTROSCOPY EXPERIMENTS

Figure 5.14: Near infra-red Raman spectra of 70 keV P$^+$ implants at: $1 \times 10^{13}$ cm$^{-2}$ and $5 \times 10^{12}$ cm$^{-2}$ (both at 30s integration time, the TopSil blank (at 20s integration time), and the silver paste coated cryostat stage (10s integration time). (100 mW laser at 1064 nm, $T_{\text{cryo}} = 4.2$ K). Spectra displaced vertically for clarity and scaled by integration time.

implanted samples at a larger depth (avoiding the interface traps) and with thicker layers, so as to study the sensitivity of the spectroscopy equipment to the thickness of the implanted layer, before re-trying the near surface implants.

5.3.3 Visible Wavelength Raman Spectroscopy

An increase in the ERS signal could be gained by using excitation radiation with an energy closer to the direct band gap of silicon so as to take advantage of the resonance enhancement (Equation 2.9) in the scattering cross section of Equation 2.8. The proposal by Koiller et al. to measure the exchange coupling between donors in silicon relied on using an ultra-violet laser to gain this resonance enhancement and achieve the few donor sensitivity required. We did not have access to a suitable UV Raman spectrometer, so we performed measurements using visible wavelength Raman spectrometers to study any effects from approaching such a resonance. Raman spectroscopy was performed on the doped silicon samples with both a Dilor system at 488 nm and 514 nm, and a Renishaw system at 532 nm. No ERS peak was observed with either system.

The measurements with the Dilor system involved long integration times (up to 30 minutes), high laser powers and the use of both 488 nm and 514 nm excitation. The Dilor system allowed
for the observation of both the P ERS or the B ERS peak in the measured spectrum as the laser line reduction was tuneable. The results of the Dilor system experiments have been included in Appendix A.

Experiments performed with the Renishaw system were only possible on the boron doped substrates as the laser line edge filter prevented measurement below 120 cm\(^{-1}\) thereby cutting off any P or Sb ERS signals. Figure 5.15 shows the spectra from three silicon samples doped with various concentration of boron. No B ERS was observed at 184 cm\(^{-1}\). The Raman scattering spectrum from phonons in silicon was observed in each of the samples. Photoluminescence was not present in these spectra as the process is fixed in energy, and were outside of the available spectral window (see Table 5.2 for expected line positions).

There is a difference in the absorption coefficient of light in silicon, from 4 cm\(^{-1}\) at 1064 nm to \(10^4\) cm\(^{-1}\) at 532 nm, but this was not responsible for the differences observed. The penetration depth of the light changes from approximately a centimetre at 1064 nm to approximately a micrometer at 532 nm. Without the use of microscopy this would have resulted in a huge difference to the scattering volume, but the confocality of the microscopy system at approximately 2 \(\mu m\) meant that the two measurement volumes were not significantly different.

The larger absorption coefficient of the 532 nm excitation source would have made the sample
more susceptible to heating at the laser focus, but this was not the reason for the non-existence of the ERS peak. As noted earlier, the ERS peak was clearly observed in the near infra-red up to temperatures of 81 K. With 6 mW of laser power at 532 nm, using the 20× objective, and with the sample held at 4.2 K, the temperature at the laser focus was estimated using Equation 3.2 to be approximately 30 K. Thermal depopulation of the acceptor ground state could not account for the lack of an ERS peak when using a visible wavelength excitation source.

5.4 Discussion

The lack of an observed electronic Raman scattering transition when using visible excitation was consistent with the fact that no previous literature had reported observing an isolated donor ERS transition from silicon illuminated with above band gap light. The absence of said signal was usually accounted for by the smaller scattering volume of visible illumination due to its small penetration depth into the silicon (≈1 µm at ≈500 nm). The Raman scattering experiments in the visible wavelengths reported here were performed on a micro-Raman spectrometer optimised for collecting light from systems with a small penetration depth by using a high N.A. lens, and a multichannel detector capable of long collection times. Such experimental considerations led us to believe there may have been another physical reason for why the ERS transition was not observed when illuminated with above band gap radiation, as detailed below.

The electronic Raman scattering transition can be thought of as an electron in the ground state of the system scattered to a final state via a transition to a virtual state. Focusing only on the donor states for simplicity, these are considered to lie below the conduction band minimum. Wright and Mooradian [50] proposed the intermediate state to lie within the conduction band, whereas Jain et al. [51] presented the transition to occur via the valence band as the intermediate state (shown as the line (ii) in Figure 5.16). The cross section of the transition was said to increase as the energy of the laser approached the energy of this virtual transition, but to approach the energy of this transition requires the energy of the excitation to be greater than the indirect band gap.

The use of an excitation source which has an energy above the indirect band gap of silicon results in the formation of an overwhelming number of excitons, with the aid of phonons to conserve momentum. Excitons originate when an electron from the top of the valence band is excited into the conduction band leaving a hole in the valence band (see Chapter 7 for a more detailed description of the process). These two particles are correlated and the electron, through multiple phonon processes reaches the bottom of the conduction band from where it can recombine with the hole, or bind to a neutral donor forming a bound exciton complex. The electronic structure of the bound exciton complex differs from that of the neutral donor, thus reducing the number of donors available at any given time to undergo an electronic scattering event. The lack of an
observed ERS transition in the visible wavelengths is precisely this point, that all the donors and acceptors would host bound excitons.

While free and bound excitons were observed in the near infra-red Raman experiments, the small absorption of the excitation light meant that excitons were rare in comparison to the case of above band gap excitation. The production of bound excitons in the above band gap measurements makes the search for a resonance enhancement with the energy of the direct band gap at the conduction band minimum (in the UV) a useless goal, as any enhancement to the cross section would be insignificant compared to the loss of neutral donors required of the ERS transition.

Even though ERS would not work with above band gap excitation, the theory of Jain et al. as described in Chapter 2 may still be adequate, but the energy required to exploit the resonance term in the scattering equation would not be reached without forming bound excitons. The intermediate states of the Raman process, as they are virtual states, could still be valence band like states. Experimentally, the resonance enhancement as stated by the theory would not be achievable.

There could also be other resonance processes available to the transition, such as with the indirect gap, and with the donor excitonic levels. The energy of the light emitted by the Nd:YAG excitation laser, at 1.1654 eV is just below the energy of the indirect band gap of silicon for

![Figure 5.16: The electron band diagram of silicon showing the possible positions of the P electronic states. Transition (i) is between a P state which sits at the Γ point and the top of the valence band. The no-phonon bound exciton line in photoluminescence is related to this transition. Transition (ii) is between a P state below the conduction band minimum and the valence band at the same point.](image-url)
temperatures below 100 K, e.g. $E_G(T = 4K) = 1.17$ eV. A resonance with the indirect gap is possible here, and was considered by Colwell and Klein [52] in the case of silicon carbide. Their theory for ERS from donors in SiC was similar to Jain et al.’s for Si except that the energy gap in the resonance enhancement factor was at the indirect band gap. No sufficient explanation was found as to why the indirect gap was used in SiC and the energy of the direct gap in Si. The conduction band minimum was used in both cases as an approximation for the donor states, and so the resonance would be between the donor states and the valence band maximum. Processes between these states have been observed previously as discussed below.

If we again consider the bound excitons, we note the existence of the no-phonon (NP) luminescence. Here the exciton (electron-hole pair) bound to the neutral donor recombines without the aid of a phonon, whereas usually the indirect band gap of the crystal requires a phonon to conserve the momentum. This is possible due the presence of the donor atom, which breaks the crystal symmetry [109]. In a sense, the P states while lying below the conduction band minimum also exist at the same point in $k$ space as the valence band maximum, $k = \Gamma$, and direct transition between the top of the valence band and the P states can occur. This is visualised as the line labelled (i) in Figure 5.16, and the energy of the $P_{NP}$ transition is 1.15 eV.

As well as the no-phonon recombination of excitons bound to the neutral donor, the bound exciton can be formed directly onto the neutral donor without the aid of a phonon or the capture of a free exciton, as in the case of photoluminescence excitation spectroscopy [32]. Here a laser exciting the sample with light of the exact energy as the no-phonon luminescence produces these bound excitons directly on to neutral donors or acceptors. This process opens up the possibility of an excitonic resonance, where an exciton-polariton produced by the below band gap laser excitation scatters off a donor ground state electron resulting in the ERS transition. As noted by Koiller et al. in an end note to their paper [28], “Excitonic effects in the intermediate state of the Raman process may sharpen the resonance, as the resonance enhancement factor would then be limited only by the inverse lifetime width of the exciton bound to the neutral donor.”

Studies with variable wavelength lasers in CdSe have observed the changing of the same spectral line from a resonant Raman scattering event to a photoluminescence transition [115], indicating the similarity of the processes. Klein [116] considers some cases of resonant Raman scattering in solids to be equivalent to absorption into a resonant state followed by luminescence. In this case, the inelastic ERS transition could proceed via the absorption of light promoting a valence band electron onto a phosphorus atom with a donor electron already in a $1s(A_1)$ state forming an exciton-like state, with the luminescence transition occurring through one of the electrons and the hole at the top of the valence band, and the other electron filling the $1s(E)$ state. Further studies with variable wavelength lasers are required to better understand the nature of the observed ERS transition, and to investigate the presence of any resonances in the near infra-red.
5.5 Conclusion and Future Work

This chapter covered experiments on the electronic Raman scattering spectroscopy of donor electron states and acceptor hole states in silicon. Previous studies had identified a Raman transition at 105 cm$^{-1}$ between the $1s(A_1) \rightarrow 1s(E)$ states of the phosphorus electron, and it was hoped to use the spectroscopy of this transition to measure the exchange coupling strength between phosphorus donors in silicon.

A new near infra-red spectroscopy instrument with an array detector provided observations of the ERS transition from both donors and acceptors in silicon for the first time in approximately 30 years. Electronic Raman scattering was observed from samples doped with P, Sb, As and B. The ERS peak was observed in samples with doping densities down to $1 \times 10^{15}$ cm$^{-3}$, lower than that previously reported. The observed shift in the ERS peak towards lower energies with increasing doping density and wavefunction overlap followed previous literature for scattering from donors. For the acceptors, the trend was for an increase in the ERS peak energy as the doping density increased. This was the first report of this observation. Speculatively, this shift to higher energies was proposed to be due to the acceptor hole states, made up of valence band like states, bonding stronger to larger numbers of acceptors.

Photoluminescence lines were observed in the measured spectra which led to the estimation of the laser heating of our samples. Laser heating was observed in samples illuminated with high laser powers, and with 100 mW of the 1064 nm laser through the 20× objective the sample temperature at the laser focus was estimated to be between 15–20 K. At low laser powers the temperature at the laser focus was believed to be close to 4.2 K but at least below 10 K. Laser heating did not adversely affect the ERS peak. The peak broadened and reduced in height with increasing temperature, but was still observable up to temperatures of 81 K.

The P ERS peak was not observed in any of the implanted samples due to the reduction in the scattering volume from the thin implanted layer and probably from the ionisation of the donors close to the surface. No measurement of the strength of exchange coupling from donor pairs in silicon was possible with this experimental system.

The ERS transition was not observed in our experiments performed using visible excitation. The lack of an observable signal from illumination with above band gap light was proposed to be due to the presence of an overwhelming number of bound exciton complexes which change the electronic structure of the neutral donor. This was in contrast to Jain et al.’s theory which stated that the transition could occur with above gap illumination. This negated any supposed benefit from a resonance enhancement in the UV as proposed by Koiller et al.. We proposed the presence of a resonance in the near infra-red, with the possibility of a direct transition between the P states and the top of the valence band, or through an excitonic resonance.
Future work could attempt to increase the instrument sensitivity with a higher NA lens optimised for the near infra-red and the use of longer integration times. Such studies may observe ERS from implanted donors, especially with the ions implanted further away from a surface. The sensitivity could be further enhanced with the use of surface enhanced Raman scattering techniques. A study of the nature of the resonance term in the scattering equation using a variable wavelength laser near the indirect band gap (≈1 eV) should also be attempted.
Chapter 6

Temperature Dependence of the Silicon TO Phonon

6.1 Introduction

The measurement of the strength of the exchange coupling between donors in silicon as proposed by Koiller et al. [28] is based on the accurate knowledge of the local crystal temperature when the intensity of the singlet and triplet components of the ERS peaks are equal. Laser based measurements are prone to heating samples at the laser focus above the temperature of the substrate, as was observed in Chapter 5 while performing ERS measurements on bulk doped silicon crystals. A non-contact temperature sensing method capable of measuring the temperature at the laser focus, utilising the properties of the crystal itself, and which can be used concurrently with other laser based measurements would be highly desirable. The temperature at the laser focus was estimated in Chapter 5 by observing changes to the observed luminescence spectra. The luminescence spectrum is not independent of doping, limiting the use of this technique to samples with significant bound exciton luminescence, unlike the high purity silicon required for use with the implantation. The phonic features of the silicon spectrum offer the greatest prospects for a laser based probe of the crystal temperature, especially the use of the intense Raman active TO phonon line, as will be discussed in this chapter.

Raman spectroscopy has been used [111], and is well suited to the non-contact measurement of temperature in the solid-state because the Raman active phonon frequency, intensity and linewidth are strongly dependent on the lattice temperature [117]. One of three methodologies are adopted to perform this type of analysis. They are: (i) the measurement of the Stokes to anti-Stokes peak intensity ratio, (ii) the determination of the linewidth \( (2\Gamma) \) or (iii) the determination of the peak position \( \omega^T_{TO} \). The choice of methodology at low temperatures \((< 150 \text{ K})\) is further constrained
by the Boltzmann distribution of states which results in a vanishingly small anti-stokes peak intensity. As changes to the linewidth and position with temperature are small, a high resolution spectrometer was required.

Discussed in this chapter is the use of Raman micro-spectroscopy as a tool for measuring the temperature of silicon below 150 K while concurrently performing scattering measurements upon the same localised volume. We begin by examining the theory of anharmonicity and how it applies to the temperature dependence of the phonon, continuing with a review of the literature, followed by the experimental results and a discussion on the fit to the trend of peak shift versus temperature, and finishing with a conclusion and prospects for the use of this technique.

6.2 Theory

The phonon of interest in this study was the silicon transverse optic (TO) mode phonon, (see Figure 2.3 for the phonon dispersion diagram of silicon). As Raman scattering is a momentum conserving process the phonon probed with this technique is at the centre of the Brillouin zone ($k = 0$). At room temperature, the TO phonon has an energy of 520 cm$^{-1}$ and a width of 3.17 cm$^{-1}$.

The changes to the phonon mode with temperature were due to the anharmonicity of the interatomic bonds in the crystal [117]. This anharmonicity allows for thermal expansion of the crystal lattice (the change in volume with temperature), and for phonons to interact. Both these processes affect the frequency of the phonon mode and will be discussed.

Phonons are the modes of vibration of atoms in the crystal lattice around their equilibrium position. An increase in the temperature increases the populations of modes of higher energy. If these are approximated by classical harmonic oscillations, they feel a quadratic potential, and the equilibrium separation of the atoms do not change as the energy within the lattice increases. Figure 6.1 shows both an harmonic and an anharmonic interatomic potential. An increase in energy from $E_1$ to $E_n$ does not change the equilibrium separation, $x_1$ of the harmonic oscillator which is halfway between the position of the potential for a given energy. Anharmonicity is expressed by adding higher orders to the interatomic potential:

$$V = V_0 + Ax^2 - Bx^3 - Cx^4,$$

with $B$ representing asymmetry in the mutual repulsion, and $C$ the softening of vibrations at large amplitudes. From the shape of the anharmonic potential in Figure 6.1, the increase in the equilibrium separation from $x_1$ to $x_n$ at higher energies can clearly be seen. This concept of anharmonic thermal expansion can also be shown mathematically by calculating the average displacement by
CHAPTER 6. TEMPERATURE DEPENDENCE OF THE SILICON TO PHONON ENERGY

Anharmonic
Harmonic

\[ x_1 \ x_n \]

\[ E_n \]

\[ E_1 \]

Figure 6.1: Comparison of the harmonic potential and anharmonic potential between two atoms in a crystal. The equilibrium separation is indicated by the \( x \) labels for different energies \( E \).

using the Boltzmann distribution to weight the possible values of \( x \) according to their thermodynamic probability [118]:

\[
\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx \ x \ \exp[-V(x)/k_B T]}{\int_{-\infty}^{\infty} dx \ \exp[-V(x)/k_B T]}. \tag{6.2}
\]

Expanding the integrals for \( U(x) \ll k_B T \) give the mean separation:

\[
\langle x \rangle = \left( \frac{3B}{4A^2} \right) k_B T. \tag{6.3}
\]

The average displacement of the atoms in the crystal from their equilibrium positions is thus temperature dependent and mediated by the anharmonic terms in the potential.

For anharmonic processes relating to the change in frequency and width of the phonon the contributions will be split into those from the volume thermal expansion, and those from phonon interactions. The temperature dependent shift to the phonon frequency \( (\omega_{TO}^T) \) is a combination of both the thermal expansion \( (\Delta_1 \omega) \), and the phonon interactions \( (\Delta_2 \omega) \) with the position of the phonon line described by:

\[
\omega_{TO}^T = \omega_{TO}^0 + \Delta_1 \omega + \Delta_2 \omega \tag{6.4}
\]

The line width is only affected by the phonon interactions [119].

The change in frequency of the mode \( (\omega) \) through the change in volume \( (V) \) can be represented
by the Grüneisen parameter:

\[- \frac{\Delta \omega}{\Delta V} = - \frac{\delta \ln \omega}{\delta \ln V} = \gamma \]  \hspace{1cm} (6.5)

The effect of the temperature on the frequency shift of the phonon from the change in volume at constant pressure was introduced via the volume thermal expansion coefficient (\(\beta\)):

\[\left( \frac{\delta \ln \omega}{\delta T} \right)_P = - \beta \gamma = \frac{\delta \ln V}{\delta T} \frac{\delta \ln \omega}{\delta \ln V} \]  \hspace{1cm} (6.6)

By integrating the above equation, changing the volume expansivity to the linear expansivity (\(\alpha = \beta/3\)), and taking into account the temperature dependence, the thermal expansion contribution to the phonon frequency shift becomes:

\[\Delta_1 \omega(T) = \omega_0 \exp \left( -3\gamma \int_0^T \alpha(T') \, dT' \right) \]  \hspace{1cm} (6.7)

From measured values of the thermal expansion coefficient and \(\gamma\), the expected frequency shift can be calculated. Except in the region of negative thermal expansion, the increase in volume of the crystal lattice contributes a negative shift to the frequency of the mode. Using thermodynamic arguments and the equation of state for an anharmonic crystal (see Kittel [118]), the Grüneisen parameter can be expressed in terms of bulk measurable parameters as:

\[\gamma = \frac{\beta V}{\chi T C_v} \]  \hspace{1cm} (6.8)

with \(\chi\), the volume compressibility, and \(C_v\), the heat capacity of the crystal. This equation highlights the strong relationship between the thermal expansion and the heat capacity of a crystal.

Phonon interactions contribute to changes in both the shift and the width of the phonon line. Phonons can interact with phonons of the same and other modes, creating phonons of higher energy as well as decaying into phonons of lower energy. The physics of phonon scattering can be thought of as the presence of one phonon causing a periodic elastic strain which modulates the elastic constants of the crystal. Other phonons “perceive” these modulations and are scattered. The strength of the phonon interactions are mediated by the coupling coefficients also known as the anharmonic potentials. These coupling coefficients are related to the derivatives of the total energy of the oscillator at equilibrium atom positions, with the atomic displacements due to the phonons. The Hamiltonian for the interaction can be written in terms of phonon creation and annihilation operators and coupling coefficients [120].

The lifetime of a phonon is affected by the likelihood of its interaction with another phonon and the strength of these interactions. The rate of interactions depends on the concentration of the
phonons in the relevant modes. The population of a phonon mode with energy $\omega$ is temperature dependent and follows the Bose-Einstein distribution:

$$n(T) = \frac{1}{\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1} \quad (6.9)$$

The interaction of light with matter introduces a non-equilibrium population of phonons as light scatters off the phonon states. The Stokes scattering creates the TO mode phonons and the anti-Stokes destroys them. The thermal population of phonons in the silicon crystal interact with the non-equilibrium TO mode population which decay to phonons of lower energy. The lower energy phonons can also combine to produce TO mode phonons. These interactions govern the lifetime of a phonon.

The temperature of the crystal affects the populations of the phonon modes, which affect the rates of their interaction. These rates of interaction affect the lifetime of the phonon, and thus the line width of the Raman active phonon mode, as width is the inverse of the phonon lifetime [121]. The temperature dependence of the width of the TO phonon line is related to the thermal population of the phonons in the decay channels. For three phonon interactions, the TO mode phonon decays into two phonons of lower energy, and conservation of energy states that $\omega_a + \omega_b = \omega_{TO}$. The three phonon interaction term follows:

$$2\Gamma(T) = A[1 + n_a(T) + n_b(T)] \quad (6.10)$$

with $A$, the width at zero Kelvin, positive and depending on the coupling constants. The factor $n_a(T)$ is the Bose-Einstein population distribution (see Equation 6.9) for the phonons with frequency $\omega_a$, and $n_b(T)$ for the phonon with $\omega_b$. At $T = 0$ K this interaction term contributes a width $A$ to the phonon. The phonon width is proportional to $n_a(T)$ and $n_b(T)$ and an increase in the temperature populates the phonon modes with $\omega_a$ and $\omega_b$, resulting in an increase to the width of the TO phonon line.

The width and frequency shift of the phonon line are Kramers-Kronig related and so the frequency shift also follows the same form as Equation 6.10, but with opposite sign. For three phonon interactions, the shift to the phonon line has the following form:

$$\Delta_2\omega(T) = C[1 + n_a(T) + n_b(T)] \quad (6.11)$$

with $C$, the anharmonic contribution to the frequency shift, negative and depending on the coupling coefficients of the phonons. The population factors $n_a(T)$ and $n_b(T)$ are as for Equation 6.10. The anharmonic contribution to the frequency shift from three phonon interactions.
has a value of $C$ at $T = 0$ K with the frequency of the TO mode decreasing as temperature is increased. The coefficients $A$ and $C$ can be calculated theoretically or used as the fitting parameters to experimental data, as will be discussed in the literature review.

The anharmonicity of the crystal potential leads to a temperature dependence of the frequency and lifetime of the phonon in the crystal. The two processes associated with the anharmonic effects, are the thermally induced change in volume of the crystal, and the phonon interactions within the thermal population and the non-equilibrium populations of the phonon modes.

6.3 Literature Review

The review of the literature on changes to the silicon TO Raman active phonon with temperature will focus on experiments performed on silicon and other diamond type semiconductors, the anharmonic theories applied to fit the experimental data, and the use of Raman spectroscopy as a probe of temperature.

6.3.1 Experimental Work on Phonon Temperature Dependence

From the early measurement of the Raman effect in diamond by Krishna [122], the behaviour of the phonon mode under the influence of temperature has been studied. The phonon line was seen to decrease in energy and increase in width with an increase in temperature, and was related to the increase in volume of the crystal with the increase in temperature. The first observation of Raman scattering from silicon was by Russell [123] for the optic phonon, which was observed at 523 ± 1 cm$^{-1}$ at room temperature.

The first study of the temperature dependence of the silicon TO phonon was performed by Hart et al. [120] over the temperature range from 20 K to 800 K. The frequency shift was reported as decreasing with increasing temperature, while the width of the line increased with increasing temperature. They noted a lower frequency shift at 20 K than at 77 K, which was consistently observed even within the large error bars (see Figure 6.2).

Tsu and Hernandez [124] measured the TO and the two-phonon Raman spectrum shift of silicon with temperature from room temperature up to 900 °C and observed all the phonon modes decreasing in frequency with increasing temperature. Their data overlapped with Hart et al.’s and linewidths were not reported.

Measurements of the Raman shift and width at higher resolution were performed by Balkanski et al. [125] on silicon in the temperature regime 5 K to 1400 K. Below 100 K, in contrast to Hart et al.’s data, they saw no noticeable shift in the frequency (see Figure 6.3). Their value of the full width at half maximum extracted to $T = 0$ K was $2\Gamma = 1.4$ cm$^{-1}$ and $\omega_{TO}^0 = 525$ cm$^{-1}$ for the phonon frequency.
Menéndez and Cardona [126] measured the Raman shift and width of the optic phonon of silicon with temperature, as well as for germanium and α-tin (see Figure 6.4), with all three following similar trends. The experimentally extrapolated zero temperature values for width and shift were, $2\Gamma = 1.28 \, \text{cm}^{-1}$ and $\omega_{TO}^0 = 524 \, \text{cm}^{-1}$. The instrument broadening of the lines was deconvoluted from their spectra.

### 6.3.2 Theoretical Work on the Temperature Dependence of the Silicon Phonon

Calculations of the position and lifetime (width) of the Raman active phonon of silicon and its variation with temperature began with Cowley [127], who used a shell model for the harmonic interaction with the anharmonic term modelled as the optic phonon mode splitting into modes of lower energy. He estimated the phonon dispersion curves by fitting to inelastic neutron data and the anharmonic potential by fitting to thermal expansion data, and then summed over all the possible interactions numerically. His theory led a width of $\Gamma = 11.34 \, \text{cm}^{-1}$, much larger than those observed.

Klements [121] took a similar approach but only considered one decay channel, where the phonon decays into two acoustic phonons of equal energy, half that of the original and with opposite momenta (where $\omega_a = \omega_b = \omega_{TO}/2$ in Equation 6.10). He assumed the temperature dependence to be related to the thermal occupation number of the acoustic phonons through a rate
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Figure 6.3: The shift in the TO frequency with temperature as measured by Balkanski et al. [125]. The solid line in the plot shows a prediction of the shift which includes both the three and four phonon contributions, and the broken line includes only the three phonon terms [125].

Figure 6.4: The shift in the TO frequency shift with temperature as measured by Menéndez and Cardona [126] (circles). The solid line is the calculated thermal expansion contribution to the shift. The square points are from Cowley’s calculation and the thermal expansion contribution [126].
equation. The calculations led to very small peak widths, $\Gamma = 0.048 \text{ cm}^{-1}$.

The above works were used as the basis for fits to the experimental data in subsequent literature. Hart et al. [120] modelled the frequency shift by considering the interatomic bonds as following a Morse potential expanded up to quartic terms, and noting a negative cubic term dominated over a positive quartic term. Cowley’s theory fitted the frequency shift data well except for the 20 K point. Klements theory fitted the data for peak widths over the whole temperature range better than Cowley. Both models required the use of the experimental 0 K values to fit the data.

The data from Balkanski et al. [125] was analysed with Klement’s model. By including up to fourth order anharmonicity, the optic phonon decaying to three phonons, the high temperature line shift and width were more accurately modelled. They assumed the TO phonon decayed into phonons of equal energy and opposite momenta. As the shift and width are Kramers-Kronig related, phonon-interaction contribution was used to model both. They showed that by adding the higher order contributions the thermal expansion contributions were not required in their fit.

Menéndez and Cardona [126] analysed their experimental data by including the thermal expansion contribution to the shift as well as the cubic anharmonicity. They analysed the peak width using Klements’ model, but found a decay into $\omega_a = 0.35 \omega_{TO}$ and $\omega_b = 0.65 \omega_{TO}$ provided a better fit. Thus, the quartic anharmonic terms were not included. From the phonon density of states and dispersion for silicon they found the decay modes to be (LA-LO) phonon pairs, which are more numerous in silicon than phonons of energy $\omega_{TO}/2$. Recalculating Cowley’s model with a more accurate phonon density of states also fit the data well. This work showed the importance of an accurate portrayal of phonon energies in the temperature dependence equation, as the frequencies chosen corresponded to peaks in the phonon density of states for silicon, unlike the simple Klements model.

Theoretical models have been applied to calculate the harmonic and anharmonic shifts to the phonon frequency at zero Kelvin with improved accuracy, as well as the temperature and pressure behaviour of the mode. Examples of these works follow. Haro et al. [128] performed numerical calculations on an harmonic model and the anharmonic changes to this. Debernardi et al. [129] used density functional theory to look for the possible decay channels and found the third order interaction to be sufficient with decay into two non-equal energy phonons (matching the analysis of Menéndez and Cardona). The value for the peak width calculated, $2\Gamma = 1.45 \text{ cm}^{-1}$, was in agreement with Menéndez and Cardona’s experimental value of $2\Gamma = 1.24 \text{ cm}^{-1}$. Lang et al. [130] used density functional theory and frozen phonon models to calculate the harmonic and the anharmonic shift and widths at 0 K and their temperature dependence. Their calculated $T = 0 \text{ K}$ width was 1.48 cm$^{-1}$, and their shift was 517 cm$^{-1}$. 

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6.3.3 The Use of the Raman Phonon as a Temperature Probe

There are a few instances in the literature of studies into the use of the Raman phonons as a temperature probe. Balkanski et al. [125] in their work on the temperature changes to the silicon TO phonon used the stokes to anti-stokes ratio to verify pyrometer readings on their samples at very high temperatures.

A systematic study on the use of the Raman line to measure the temperature of diamond and silicon was performed by Cui et al. [111]. They noted that the Stokes to anti-Stokes ratio was difficult to use because of differences in experimental arrangement, such as the transmission and cross section at the two frequencies. More accurate temperature estimates, especially at high temperatures, were found using the line shift. A function of the form:

$$\Omega(T) = \Omega_0 - \frac{C}{\exp \left[ D (hc\Omega_0/k_BT) \right] - 1} \quad (6.12)$$

was found to fit the data with $\Omega_0$, $C$ and $D$ as the fitting parameters. This equation has a similar form to Equation 6.11, the phonon-decay model, as its temperature dependence follows the Bose-Einstein distribution (see Equation 6.9). Equation 6.12 does not assume anything about the phonon decay channels and coupling strengths, which are included via the fitting parameters. The values used for silicon were $\Omega_0 = 524 \text{ cm}^{-1}$, $C = 10.53 \text{ cm}^{-1}$ and $D = 0.587$. They did not include a thermal expansion contribution to the shift.

Issues arising from the use of Raman scattering as a temperature probe of semiconductors have been discussed by Menéndez [131] in a review article. The Stokes to anti-Stokes ratio is problematic because of cross section dependence (from material properties and laser frequencies), instrument sensitivity changes in the two regions, and any resonance effects. He mentioned that care should be taken to avoid any stresses on the sample when using the Raman shift as a temperature probe, as stress can shift the peak. Stresses can be caused by thermal gradients due to localised laser heating of the sample. Probing sample temperature through changes in the peak width has the advantage that the width is insensitive to any stresses on the sample. The disadvantage of using the width is that comparisons between samples are made difficult because of sample specific line broadening due to differences in defects and doping levels. A high resolution spectrometer with an instrument broadening less than the linewidth of the phonon is also required for accurate peak width measurements.

Recently, the use of micro-Raman scattering as a temperature probe has been applied to measurements at room temperature and above for silicon in the form of thin films [132], micro-devices [133, 134] and strained samples [135]. Of interest is the study by Beechem et al. [134] where Raman measurements were performed on devices made of silicon which were both strained and heated. The two contributions were separated by measuring the heating through the peak
width and removing the expected shift for this temperature, leaving the strain contribution.

The effects of laser heating on silicon at room temperature and above has been studied by Kouteva-Arguirova et al. [136], who noted smaller than expected shifts to the phonon peak, up to temperatures where the silicon was melted by the focused laser. This was explained by the fact that the Raman intensity drops exponentially with temperature, and that the signal collected was originating from the edges of the Gaussian profile of the laser intensity distribution which have a lower temperature. A secondary effect was from the stress due to the thermal gradients increasing the phonon frequency at the same time as the increase in temperature was decreasing the frequency.

6.3.4 Conclusion

Much experimental and theoretical study has been performed on the Raman active silicon TO phonon over a large temperature range. None of the studies have focused on the low temperature region (below 100 K) as the variations in the phonon properties in this region are small. It is in this temperature range that we are most interested in knowing the local sample temperature. All of the theories and most of the observations have reported little if no shift in this region. Hart et al.’s observation of the 20 K peak shift sitting below the 77 K shift, if reproducible, provided hope for this technique as a temperature probe.

Cubic anharmonic theories had been found to be sufficient to fit both the temperature dependent shift and width data, with decay into modes of unequal energy dominating. Care must also be taken when performing measurements so as not to excessively heat or strain the samples as this can also affect the measured phonon peak shift and width.

6.4 Experimental Methodology

Raman measurements were performed on high resistivity ($\rho > 10^3$ Ohm-cm), $< 100 >$ oriented silicon in the usual backscattering configuration. The 514.5 nm line from an argon ion laser was used with a power of 5 mW as the excitation source, and spectra were collected using the Dilor XY micro-Raman spectrometer operating in triple-additive mode, where the three gratings were operated in series. This resulted in an oversampling of the spectral peak, with each pixel on the detector corresponding to a spacing of 0.02 cm$^{-1}$, providing for a high accuracy in determining the peak positions and widths. The resolution of the instrument was 0.8 cm$^{-1}$ with a slit width of 100 $\mu$m as determined from a neon emission line. The samples were housed in the Janis ST-500 liquid helium microscopy cryostat and anchored to the cold finger with thermal grease. Temperatures were left for 15 minutes to stabilise before measurements were taken. High temperature measurements were performed using a Linkam THMS600 hot/cold microscopy stage. Data were fitted using the
6.5. RESULTS AND ANALYSIS

Thermo Galactic Grams spectroscopy software [137] to a Lorentzian lineshape to determine the peak width and position with errors reported as the standard error to the fit. Correction to the peak position was made at room temperature where the fitted silicon TO line was assumed to have a frequency of 520.0 cm\(^{-1}\). Measurements were repeated to verify the reproducibility of the observed trends, and fitted linewidths were not corrected for instrument broadening.

6.5 Results and Analysis

Raman spectra of the silicon TO phonon at 4.2 K and 295 K are shown in Figure 6.5. The reduction in temperature shifted the line to higher energies, from 520 cm\(^{-1}\) to 523.5 cm\(^{-1}\), and narrowed the width from 3.17 cm\(^{-1}\) to 1.62 cm\(^{-1}\). The 4.2 K value for the shift was lower than that previously reported at 524 cm\(^{-1}\) [126]. The width was larger than that reported by Menendez, 1.24 cm\(^{-1}\) [126] as we did not remove the instrument broadening. The temperature dependence of the shift in the low temperature region is shown in Figure 6.6 and the associated half width at half maximum in Figure 6.7. The peak shift over the full range of measured temperatures is shown in Figure 6.8.

The experimental data which recorded the change in the frequency of the mode with temperature, shows the trend of an increase in the frequency with a decrease in the temperature down to 60 K, (see Figure 6.6). From there, the frequency shift decreases towards the 4 K value. This behaviour had not been observed previously, except for the anomalous 20 K measurement in the study by Hart et al. [120]. The phonon interaction contribution to the shift was modelled using a fit to the equation of Cui et al., Equation 6.12, showing the shift flattening at lower temperatures, as the phonon modes thermally depopulate. This term is responsible for the good fit to the data out to the highest temperature measured, (see Figure 6.8). The thermal expansion contribution has been calculated using Equation 6.7 with data for the linear thermal expansion coefficient taken from Reference [138]. The shape and intensity of the thermal expansion contribution cannot account for the observed shift in the low temperature region.

An empirical fit to the peak shift data across the whole temperature range measured is presented with the following equation:

\[
\omega_{TO}^T = \omega_{TO}^0 - \frac{C}{e^x - 1} + \frac{F y^2 e^y}{(e^y - 1)^2}
\]  

with \(x = \frac{D h \omega_{TO}^0}{k_B T}\) and \(y = \frac{G}{T}\). C, D, F and G are constants, \(\omega_{TO}^0\) is the optic phonon frequency at \(T = 0\) K and the other terms have their usual meanings. The above equation is plotted as the green line in Figure 6.6, and appears to fit the anharmonic shift at low temperatures well. Values for the parameters used to fit the data were \(\omega_{TO}^0 = 523.4\) cm\(^{-1}\), \(C = 10.7\) cm\(^{-1}\), \(D = 0.59\)},
$F = 0.32 \text{ cm}^{-1}$ and $G = 50 \text{ K}$.

The first term in Equation 6.13 is the frequency of the phonon at $T = 0$, whose value was inferred from the fit to the data. The second term is the same as that of Equation 6.12, with the fitted parameters relating to this term match those reported by Cui et al.. The phonon interaction term is responsible for the shift at higher temperatures. The third term in Equation 6.13 was an empirical fit to the data. It has the same form as the specific heat of a phonon mode, which is the derivative of the second term (the thermal occupation of a mode) with respect to temperature. This last term in the equation could also have been included as a Morse type function, which does not have as severe flattening out at the zero Kelvin value. Equation 6.13 can be used when applying the Raman spectroscopy of the TO mode phonon as a local probe of temperature. A possible physical interpretation will be presented in Section 6.6.

The trend to the line width with temperature follows those observed in previous studies, with the linewidth increasing with increasing temperature. A fit to the peak width data was performed using the cubic anharmonic decay model (Equation 6.10). Both the Klements channel, of a decay to two phonons of equal energy, and the Menendez idea, of a decay to two phonons of unequal

![Raman spectra of the silicon TO phonon mode at $T = 4 \text{ K}$ (upper) and $T = 295 \text{ K}$ (lower). Spectra scaled and offset vertically for clarity.](image)

Figure 6.5: Raman spectra of the silicon TO phonon mode at $T = 4 \text{ K}$ (upper) and $T = 295 \text{ K}$ (lower). Spectra scaled and offset vertically for clarity.
energies, were plotted. The expression for the first of these (the 1:1 energy split) was:

$$
\Gamma_{\text{cubic}}^{1:1}(T) = \Gamma_0 \left[ 1 + \left( \frac{2}{e^x - 1} \right) \right]
$$

(6.14)

with $x = \frac{h\omega_0}{k_B T}$, the constants $k_B$, $h$ and $c$ have their standard meanings and $T$ is the temperature. $\Gamma_0$ is the half width at half maximum of the Raman line extended to 0 K. Non-linear least squares fitting gave a value of $\Gamma_0 = 0.82 \pm 0.25$ cm$^{-1}$. The expression for the 2:1 phonon energy split has the following form:

$$
\Gamma_{\text{cubic}}^{2:1}(T) = \Gamma_0 \left[ 1 + \left( \frac{1}{e^y - 1} \right) + \left( \frac{1}{e^z - 1} \right) \right]
$$

(6.15)

with $y = \frac{hc\omega_0}{k_BT}$, and $z = \frac{hc\omega_0}{k_BT}$. $\Gamma_0$ was the same value as in the Equation 6.14. Both these fits were structureless below 100 K and either could be used to fit the data in the measured temperature range.

Raman spectra of the silicon TO phonon at 4.2 K were collected at various laser powers to study the effect of sample heating by the laser. There was no noticeable trend to the shift or width...
Figure 6.7: The variation with temperature of the half width at half maximum of the silicon TO phonon. The experimental data points are the triangles, the green line is the cubic fit with 1:1 phonon energies (Equation 6.14), and the blue line is the cubic fit with 1:2 phonon energies (Equation 6.15).

Figure 6.8: The TO phonon shift with temperature over the full temperature range measured. The line is a fit using Equation 6.13.
6.6 Discussion

The use of the phonon frequency shift as a probe of local temperature was aided by the maximum in the observed frequency shift. The magnitude of the shift at temperatures below 150 K was large enough to estimate the temperature to within about 10 K, which would be enough to identify major laser heating issues. For practical sample temperature measurements, data at two different sample temperatures would have to be taken so as to ascertain on which side of 60 K the sample temperature was. The base temperature of the sample could be either raised or lowered by 10 K and the shift in the peak observed. For example, raising the base temperature by 10 K from a

Figure 6.9: The peak shift (triangles) and width (squares) at various laser powers. All points are within the errors indicating no trend with sample heating from laser power. Measurements taken at $T = 4.2\, \text{K}$. as laser power was increased (see Figure 6.9). Using the one dimensional heat flow analysis of Equation 3.2 with the cold finger at 4.2 K, the temperature at the laser spot is expected to be 22 K for 1 mW of laser and 33 K for 5 mW. The one dimensional heat flow equation does not account for all the heat transfer, and the area used to model the laser spot was smaller than the physical spot, so these values overestimate the heating. Of some concern was that with 30 mW of laser power, no noticeable heating was observed. This could have been due to the fact that as the measurements were taken at $T = 4.2\, \text{K}$, with a large helium flow resulting in a larger cooling power.
measurement at 20 K would increase the frequency of the phonon, whereas at 80 K raising the
temperature by 10 K would decrease the frequency. Measurement of the peak width would also
differentiate between the two temperatures, but as there is more variability between the peak width
in different samples, the measurement would have to be calibrated to the 4.2 K peak width.

The oversampling of the peak resulting from the use of the triple grating spectrometer, and
the subsequent fitting with a Lorentzian function, provided a higher degree of precision to the
measurement of the peak position than to the peak width. The error in the fitting of the Lorentzian
to the peak position was 0.02 % of the value of the centre of the peak. The change in the peak
shift from 4 K to 60 K was about 0.1 % of the peak frequency, larger than the fitting error. By
contrast, the error in the fit to the line width as a percentage of the total half width was 14 %, and
any relatively small change to the trend in the peak width would have been unobservable.

Our observations were possible because of the use of a triple grating spectrometer and our
focus on the low temperature region. The trend in the frequency shift with temperature has never
been observed before, except for the one data point in Hart et al.’s data. No other study of the
temperature dependence of the TO phonon had been performed using such an instrument.

The anomalous shift could have been caused by the way the experiment was conducted but this
was unlikely for the following reasons. As discussed, care was taken to minimise sample heating
by the laser, but it would have been difficult to eliminate it completely in our experimental setup.
A cold finger cryostat with the sample in vacuum and held onto the stage with thermal grease is
prone to laser heating issues. A local temperature of ~ 120 K is required to provide the frequency
shift we observed at 4.2 K. At 120 K the line width was noticeably larger than that at 4.2 K. As the
line width did not change along with the shift below 60 K then heating of the sample is not likely
to have caused the shift, as was also seen in the laser power study.

Stresses on the sample can shift the frequency of a phonon peak without changing the peak
width. Stresses on our samples could have originated from the mismatch of thermal expansivity
between the silicon and the gold plated copper cold finger mediated via the thermal transfer grease,
but as the thermal expansion of the lattice is vanishingly small at these temperatures this was
unlikely. Stress gradients caused by thermal gradients from laser heating could also shift the peak.
Shifts due to such stresses on the sample are difficult to quantify and expected to be small as the
parameter for the shift associated with a stress is only 0.52 cm$^{-1}$ kbar$^{-1}$ [139].

Two possibilities to explain the low temperature frequency shift are left, the anharmonic con-
tribution from the phonon-phonon interactions and from thermal expansion volume change. The
phonon interaction models do not have the appropriate form to explain the observed peak fre-
quency shift below 60 K. The interaction models all follow the trend of Equation 6.11, relating
the frequency to the thermal population of phonon modes involved in the interaction. The rele-
vant phonon populations are thermally depopulated at liquid helium temperatures, and so would

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not exert an influence on the frequency shift. Adding contributions from interactions with larger numbers of phonons would only change the slope of the trend. A corresponding change in the peak width with temperature below 60 K would mean the trend was due to phonon interactions as they are both Kramers-Kronig related, but the accuracy in the width was not sufficient to make this claim.

The volume expansion contribution to anharmonicity would seem to be the most likely candidate to have contributed the observed dip in the phonon frequency shift data at low temperatures. The contribution of the thermal expansion (Equation 6.7) to the frequency shift did show the right behaviour, of an increase in the frequency before a decrease as temperature is increased, but the maximum occurs at too high a temperature, $\approx 130$ K, and the magnitude is too small to reproduce the observed data. The term included into Equation 6.13, the empirical fit to the frequency shift data, to account for the behaviour below 60 K has the same form as the specific heat of a phonon mode. Grouping this term in with the thermal volume expansion contribution to anharmonicity is not unreasonable given the close connection between the thermal expansion, specific heat and bulk Grüneisen parameter (see Equation 6.8). The bulk Grüneisen parameter can also be defined as: $\gamma = (\sum \gamma_r C_r)/C_V$, the weighting of the mode Grüneisen parameters by their specific heat contributions. The Grüneisen parameters of each phonon mode are independent of temperature and the bulk parameter indicates the modes which dominate at each temperature. The bulk Grüneisen parameter calculated using measured parameters, is plotted in Figure 6.10, and exhibits a minimum close to 50 K [140]. This minimum is indicative of the soft TA phonon modes dominating in this temperature regime, which are also responsible for the negative thermal expansion of silicon. The trends in the phonon dynamics were connected to trends in other such physical thermodynamic properties of silicon.

Further work to better understand the observed anomalous TO phonon shift of silicon at low temperatures should be performed with the sample held strain free in helium exchange gas so as to completely eliminate any strain effects on the lattice, and to further reduce the chance of any thermal gradients influencing the measurement. Also, high resolution Raman spectroscopy experiments at low temperatures should be performed on other diamond type semiconductors such as diamond and germanium to search for an analogous shift.

6.7 Conclusion

The accurate knowledge of the local temperature at the laser spot is required for the measurement of exchange coupling as proposed by Koiller et al., as temperature affects the occupation of the coupled donor states. Also, the risk of local laser heating is significant in such measurements.

Experiments performed on the use of the silicon TO phonon as a local probe of temperature
Figure 6.10: The bulk Grüneisen parameter of silicon [140]. The plot was calculated using Equation 6.8.

were reported in this chapter. Observation of the frequency shift of the phonon with temperature matched those of the previous literature for temperatures above 60 K, with the trend that the frequency drops with an increase in temperature. Observations below 60 K had the frequency of the phonon mode increasing with an increase in temperature. The peak width did not change in this region.

Models of phonon anharmonicity, in terms of both direct volume expansion and phonon interaction contributions to the shift, could not account for the observed trend below 60 K. An empirical fit to the data contained a term similar to the specific heat of a phonon mode to fit the low temperatures, and a term similar to the phonon interaction model for the trend at higher temperatures.

A physical interpretation to the low temperature fit was proposed in terms of the close relationship between the thermal expansion and the specific heat as part of the bulk Grüneisen parameter. The influence on the frequency shift of the TO mode may not have been directly in terms of the bulk thermal volume expansion, but may still have been influenced by the thermodynamic properties of the crystal.

The shift in the Raman active TO mode phonon of silicon with temperature can be used to estimate the local temperature of the sample, even down to liquid helium temperatures. This technique could be implemented as a local temperature probe of the measurement volume in other laser based measurements such as the electronic Raman scattering experiment of the previous chapter, as long as a spectrometer with sufficient resolution to the position of the peak is employed.
Chapter 7

Photoluminescence of Phosphorus Implanted Silicon

7.1 Introduction

Photoluminescence is a process where above band gap light generates electron hole pairs known as excitons, which recombine and can produce radiation. These excitons diffuse freely through the substrate and can bind to dopants and other impurities. Photoluminescence spectroscopy is a sensitive and non-destructive probe of dopants in silicon. Donor and acceptor species can be identified and concentrations measured.

The study of interacting donors was possible using photoluminescence, as the presence of a nearby donor affected the energy levels of the bound excitons. In this chapter, the photoluminescence experiments performed to measure donor interactions will be presented. Photoluminescence spectroscopy was also used to measure the background impurity level of the silicon, and the presence of any other defects arising from the sample production process.

This chapter begins with a discussion on the physical processes of photoluminescence, then provides a review of the literature. The use of photoluminescence to measure concentrations of donors in bulk crystals and thin layers, and spectroscopy of implanted donors and highly doped samples will be covered. Measurements on the bulk crystals and implanted donors will be discussed. Results on the doping density of crystals, and the identification of defects and impurities in the implanted samples will then be presented. Finally, the experiments on measuring the interactions of phosphorus in silicon will be examined, focusing on the results from the atomic ion implanted samples.
7.2 Theory

Excitons are stable two particle complexes in solids [141], made up of a correlated electron and hole. The application of above band gap illumination onto the crystal produces excitons, whereby an electron from the valence band is excited into the conduction band leaving a hole in the valence band. The electron makes its way to the conduction band minimum by exchanging energy with phonons, and the hole moves to the valence band maximum, this free exciton (FE) is able to diffuse throughout the sample. Their separation in $k$ space results in a low probability for recombination. A photon can be emitted with the recombination of the exciton, a phonon is also emitted to conserve crystal momentum (see Figure 7.1). The phonons which contribute to the decay are the following: $E_{TA} = 18.4 \text{ meV}$, $E_{LO} = 56.2 \text{ meV}$ and $E_{TO} = 58.0 \text{ meV}$ [37].

The probability that the exciton will be trapped by a crystal defect is significant, be they impurities or structural defects. These traps usually have states within the band gap of silicon. Excitons bind to the neutral states of shallow donors and acceptors forming four particle complexes. The

![Figure 7.1: Schematic of the photoluminescence free exciton formation and recombination process. An electron from the valence band (VB) is excited to the conduction band (CB) leaving a hole in the valence band. The electron makes its way to the conduction band minimum through interactions with phonons. The electron then recombines with the hole releasing light. The free exciton recombination is phonon assisted to conserve crystal momentum, with the phonon gaining some of the transition energy.](image)
binding energies of these bound exciton (BE) complexes are about 10% of the binding energies of the electrons to the donor or acceptor [62]. For phosphorus the donor electron binding energy is 45.5 meV and the exciton binding energy is 4.7 meV. As the shallow donor and acceptor states sit at the band extrema, the recombination of bound excitons is usually phonon assisted, however the presence of the impurity atom breaks the crystal symmetry which allows the recombination to proceed directly without the assistance of a phonon (NP). Self annihilation of the electron-hole pair usually proceeds via an Auger process, with only about 0.01% of the recombination luminescent.

The energy levels of the shallow dopant bound exciton complex can be modelled through a shell model [109, 142]. The two electrons in the bound exciton complex form a spin singlet and orbit around the positive core of the hole attracted to the screened donor ionic core through the electron pair bond, see Figure 7.2. The hole can recombine with either of the electrons in the complex. In this way more than one exciton can build up on a neutral donor, forming a bound multi exciton complex (BMEC).

The line widths of the phonon replicas of the photoluminescence lines in natural silicon are set by phonon broadening, while inhomogeneous isotope broadening limits the linewidth of the no phonon transitions. Inhomogeneous isotope broadening occurs as the measurement takes place over an ensemble of donors, each placed in a region of silicon with a slightly different isotope composition giving a slightly different band gap. By purifying the isotope composition of a crystal

Figure 7.2: Schematic representations of an exciton bound to a phosphorus donor atom. (a) The phosphorus atom is incorporated into the tetrahedral structure of the silicon host crystal with the extra outer shell electron bound to the P⁺ ionic core at low temperatures. The valence band hole (h⁺) takes the place of a bonding electron and binds to the phosphorus core with the electrons orbiting. (b) A shell model of the exciton binding to a donor atom. The hole binds to the phosphorus ionic core with the two electrons orbiting in the same energy shell. The two electrons form a spin singlet in the ground state, with the same symmetry as the P electron ground state, 1s(A₁). In this way bound multi-exciton complexes can build up.
the linewidth can be reduced. For example, studies in isotopically enriched $^{28}$Si reveal sharper no-phonon bound exciton widths than natural silicon, with widths narrower than the interferometer instrument line width of 0.014 cm$^{-1}$ [41].

In pure silicon, without any defects and impurities, the excitons have been predicted to have a lifetime of $\sim$60 $\mu$s and diffuse up to $\sim$430 $\mu$m. In crystals doped with boron to a density of $1 \times 10^{13}$ cm$^{-3}$, capture by the impurity reduces the diffusion to $\sim$150 $\mu$m [37]. The result of the large diffusion of excitons is the collection of luminescence from a larger volume of the crystal than just the spot illuminated by a visible wavelength laser with a penetration depth of $\sim$1 $\mu$m or so.

### 7.2.1 Silicon and Shallow Dopant Luminescence Peaks

The photoluminescence transitions observed in silicon at low temperatures (at $\sim$4.2 K and below) have been tabulated in Table 7.1. Figure 7.3 shows the photoluminescence spectrum for a sample doped with phosphorus and boron.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (meV)</th>
<th>Peak</th>
<th>Position (meV)</th>
<th>Peak</th>
<th>Position (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{NP}$</td>
<td>1150.01</td>
<td>$B_{NP}$</td>
<td>1150.70</td>
<td>$FE_{TA}$</td>
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<td>$B_{NP}'$</td>
<td>1148.51</td>
<td>$FE_{LO}$</td>
<td>1098.51</td>
</tr>
<tr>
<td>$P_{NP}''$</td>
<td>1143.71</td>
<td>$B_{NP}''$</td>
<td>1146.41</td>
<td>$FE_{TO}$</td>
<td>1096.96</td>
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<td>$B_{TA}$</td>
<td>1132.00</td>
<td>$Al_{NP}$</td>
<td>1149.53</td>
</tr>
<tr>
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<td>$B_{TA}'$</td>
<td>1129.80</td>
<td>$Al_{TO}$</td>
<td>1091.49</td>
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<td>$B_{TA}$</td>
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<td>$As_{TO}$</td>
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<td>$Sb_{NP}$</td>
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</tr>
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<td>1092.37</td>
</tr>
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<td>$B_{TO}'''$</td>
<td>1086.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_{TO}''''$</td>
<td>1085.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.1: Table listing the peak positions of free exciton and shallow donor and acceptor bound exciton photoluminescence lines in silicon. Definitions of abbreviations: FE - free exciton, NP - no phonon, TA - transverse acoustic phonon, TO - transverse optical phonon, LO - longitudinal optical phonon. A superscript indicates the number of excitons in a bound multi-exciton complex. From spectroscopy performed at liquid helium temperatures [109, 143, 144].
CHAPTER 7. PHOTOLUMINESCENCE OF PHOSPHORUS IMPLANTED SILICON

7.3 Literature Review

A review of the literature of photoluminescence in silicon follows. The use of photoluminescence to measure the concentrations of donors and acceptors in silicon will be covered. As will be studies on samples of thin doped layers and implanted silicon, with a discussion on the complications which arise in their measurement. The effect produced by interactions between impurity atoms on the photoluminescence lines in highly doped silicon will also be discussed.

7.3.1 Dopant Measurements

Photoluminescence developed into a technique to measure the concentrations of donors and acceptors in silicon from the work of Michio Tajima [63, 144]. He noted that sample resistivity related to the peak heights of the observed photoluminescence, through the ratio of the bound exciton peak intensities to the free exciton peak intensities. As the concentration of dopants increased, the intensity of the bound exciton peaks increased, and the free exciton peaks reduced in intensity correspondingly. Calibration curves for converting peak height ratios to donor and acceptor concentrations were published [63], with the trends almost linear in concentration, see Figure 7.4 (a). Doping densities as low as $1 \times 10^{10}$ cm$^{-3}$ were able to be measured and quantified. The measurement of the concentration of both the donors and acceptors within the sample was possible, unlike with resistivity measurements where only the number of uncompensated carriers are measured. Tajima’s calibration curves can be used when the sample is saturated with excitons, such as when

Figure 7.3: Photoluminescence spectrum of phosphorus and boron doped silicon showing the position of the main lines, from Kosai and Gershenson [143]. Lines correspond to those in Table 7.1, with the labels a and b represent the bound multi-exciton complexes. The broad electron hole droplet is shown in the TO region [143].
an argon ion laser with sufficient power to observe the electron hole droplet, and is known as the high excitation density condition. The use of the ratios negates the need for exact control over experimental conditions.

When using low laser powers of weakly absorbing light, under the so called low excitation density conditions, the bound multi-exciton complexes are suppressed, and the calibration curves for peak height ratios to concentrations were found to be linear. Broussell et al. [65], using the weakly absorbed laser light from a Nd:YLF laser, working at 1047 nm (1.184 eV), published calibration curves for phosphorus, boron and arsenic under these conditions (see Figure 7.4 (b)). These curves are limited to concentrations of dopants below $1 \times 10^{16}$ cm$^{-3}$, the point where donor interactions start to broaden the lines, and were capable of measuring the background doping of the silicon substrates used in this work.

**Thin Layers**

The implantation of low energy phosphorus ions produces a thin layer of doping density different to the larger bulk of the crystal, and methods to separate the signals from the implanted layers and the bulk were required. For samples of silicon comprised of a thin layer attached to a large bulk with a different doping density, the diffusion of the excitons through both layers complicates the separation of the photoluminescence signal arising from the different layers. For example, the majority of the samples used in this work had phosphorus implanted layers of between 20-100 nm thick. With the excitons capable of diffusing further than 100 $\mu$m into the bulk, a large background signal would be expected. One experimental approach we used was to try microscopy techniques to reduce the influence of the background. Various other techniques have been developed to overcome this difficulty and are presented here.

In epitaxial layers of silicon doped with different chemical species to that of the bulk substrate, Tajima [145,146] was able to separate the signal from the two layers. As long as the doping density in the bulk substrate was the same across samples, calibration curves for the doping concentration in the epi-layer were calculated by comparing the ratio of peak heights of the dopants in the epi-layer to the peak heights of the predominant dopant in the bulk (rather the the free exciton). These curves had to be calibrated through electrical measurements of the resistivity of the epi-layers. A variation on this method [147, 148] using indium doped bulk substrates led to detection of doping levels in an epi-layer down to $> 5 \times 10^{11}$ cm$^{-3}$. Indium doping suppressed all other shallow dopant luminescence. Using layers doped with different chemical species had proved to be a good method for separating the signal from each layer, but required an independent measure of doping density, such as electrical measurements, to calibrate the ratios. Calibration had to be redone for each batch of samples produced on a new substrate, or the thickness of the epitaxial layer was changed.
Figure 7.4: (a) Calibration curve for the calibration of peak height ratio to dopant concentration for the high excitation density condition [63]. (b) Calibration curve for peak height ratio to dopant concentration for the low excitation density conditions [65].
For samples where the dopant of interest is present in both layers, complicated formulas involving equations of diffusion and capture of excitons have been attempted [149] to separate signals, but are not practical for laboratory use. Etching studies, where layers of material are removed and comparisons between spectra are used to separate the signals, have also proved popular [150, 151] but have the disadvantage of being destructive to the samples.

7.3.2 Highly Doped Samples and Donor Interactions

With the increase in concentration of dopants in silicon, the luminescence lines from bound excitons have been observed to broaden, and shift to lower energies. Nishino et al. [112] studied these shifts for concentrations of phosphorus doped silicon in the range of $5 \times 10^{13}$ to $3 \times 10^{17}$ cm$^{-3}$ and speculated that these shifts were caused by excitons bound to more than one impurity, and not from the bound multi-exciton complexes which show up in the same region of the spectrum. Parsons [30] observed such shifts in samples with concentrations of $1 \times 10^{16}$ to $2 \times 10^{18}$ cm$^{-3}$. He stated that the temperature dependence of the line shape could be due to excitons bound to clusters of dopant atoms.

Narita [64] modelled the shifts in the shallow donor photoluminescence line positions observed

Figure 7.5: *Observed shift of the phosphorus TO replica bound exciton peak (BE$_{TO}$) for various concentrations from Shiraki and Nakashima [152]. The electron hole droplet is also shown for comparison (EHD$_{TO}$). Spectra collected at 4.2 K [152].*
in the experimental data of Shiraki and Nakashima [152] (see Figure 7.5), from samples with phosphorus doping levels from $7 \times 10^{15}$ to $3 \times 10^{18}$ cm$^{-3}$. The hopping of an exciton between two donors was assumed to lead to the observed energy shift. The presence of the second donor at a distance $R$ from the first, perturbed the binding energy of the exciton ($E_0 = 4.7$ meV for phosphorus) bound to the first via the following formula:

$$\Delta E(R) \sim -2E_0 e^{-R/r_0}$$

(7.1)

with $r_0 = 5 + 2 = 7$ nm being the combined Bohr radius of the exciton [92] and donor electron. Assuming a random distribution of donors in a sample with concentration $N$, the nearest neighbour separations $R$ follow Chandrasekhars formula [108]:

$$R = 0.554 N^{-\frac{1}{3}},$$

(7.2)

and the model did not provide sufficient energy shift to match the data. Narita overcame this discrepancy by assuming that the exciton would hop between pairs and recombine from the pair which had the largest binding energy. The modelling of excitons bound to larger clusters of interacting donors was not performed, but could also lead to the required energy shift.

Gorbunov and Kaminskii [92, 153] studied photoluminescence spectra of silicon doped from $1 \times 10^{16}$ to $8 \times 10^{17}$ cm$^{-3}$. Their analysis of the strain effects on the bound exciton peak, and the nearest neighbour and next-nearest neighbour statistics, suggested the shift and width of the bound exciton lines originate from a band of excitons bound to single donors and donor pairs. They suggested that these exciton complexes were not isolated, and that the exciton could hop from one to another. The linewidth was said to be due to pairs of donors of differing separation. No calculations were made of the expected shift.

A theoretical calculation of the concentration broadening of acceptor bound exciton spectral lines performed by Pan et al. [154] found the broadening to be due to wavefunction overlap of neighbouring acceptors. At concentrations of $5 \times 10^{17}$ cm$^{-3}$ the broadening was calculated to be 1 meV with an asymmetric tail to lower energies. They did not specify a shift to the peak energy and also believed it was generally hard for a bound exciton to hop between neutral impurities, thus discount this as a mechanism for the change in the transition energies observed.

In samples doped above the metal insulator transition, $3 \times 10^{18}$ cm$^{-3}$, an impurity band forms. Such samples studied by photoluminescence [113, 155, 156], showed recombination of impurity band electrons and holes. The optical band gap was also able to be inferred through photoluminescence [157]. As the doping concentration in a sample increased, the band gap narrowed, shifting the photoluminescence lines to lower energies. The optical measurements of this band gap narrowing match those measured through electrical techniques [158].
7.3.3 Ion Implanted Samples

Studies of donor and acceptor ion implanted silicon using photoluminescence have been few. Studies have focused on the implantation and annealing conditions and their affects on the luminescence spectrum, such as changes to the room temperature luminescence [159, 160] from damage caused by high implantation fluence. Wagner et al. [161] compared the low temperature luminescence from silicon, caused by shallow dopants implanted at 40–50 keV with fluences from $1 \times 10^{14}$ to $1 \times 10^{15}$ cm$^{-2}$, and laser or rapid thermal annealed. They found the laser annealed samples produced a lot of structural defect related luminescence, whereas the RTA processing produced more structurally sound samples. They also observed broad dopant band peaks in the implanted and rapid thermal annealed samples, whose luminescence shape compared well to that of highly bulk doped silicon. Terashima et al. [162] performed photoluminescence studies on samples of 0.5 keV B$^+$ implanted and rapid thermal annealed silicon. The observed spectrum included a peak related to a boron band, whose signal increased with the use of UV excitation. As the dopants all sat within 20 nm of the surface, the small penetration of the UV laser preferentially illuminated this implanted region, and this increased the signal.

The literature reviewed indicates that active dopants sitting close to a silicon surface have been observed using photoluminescence, in samples implanted with low energy ions, and annealed with a RTA. The fluences of the implanted ions considered in the literature were higher than those used in our study, and no mention was made of the sample surface termination. No literature has reported on photoluminescence studies of silicon implanted with phosphorus ions of energies 70 keV and below and fluences of $1 \times 10^{13}$ cm$^{-2}$ and below.

7.3.4 Conclusion

The measurement of the concentration of donors and acceptors in bulk silicon is possible using photoluminescence. Phosphorus is always present in detectable quantities in silicon, and difficulty in separating the signal due to the implanted ions and those in the bulk could be achieved by comparing to the boron peaks (as these are also present in silicon). The use of this method to measure the activation of the implanted donors requires a calibration with some other measure of the donor concentration, such as by electrical measurements. As resistivity measurements of the implanted layers proved difficult, only a qualitative understanding of the activation trends with implantation energy and fluence were possible. This would still be of use as no other studies have reported on the photoluminescence of phosphorus ions implanted into silicon at the fluences and energies used in this thesis.

The concentration broadening and shift of the shallow impurity bound exciton lines in silicon was generally thought to being due to excitons bound to more than one impurity. The exciton can
hop within and between clusters. The lineshape and shift of the peaks at the various concentrations have not been fully modelled, as Pan’s calculation did not report on the shift in the line, and Narita’s used a simple two donor model. The impurity band narrowing models were usually applied to samples doped above the metal insulator transition, when the shift was also observed for samples doped below this level. Assuming the simple energy shift model of Narita’s, the difference between the spectra of ensemble atomic, and ensemble molecular implanted samples could be detected. Narita’s theory calculated a shift of \( \sim 2 \text{ meV} \) for an \( R = 10 \text{ nm} \) separation between donors in a pair, easily resolvable from the isolated donor bound exciton no phonon line with the interferometer (resolution of 0.06 meV).

### 7.4 Materials and Methods

A detailed description of the materials, methods and equipment used in the following experiments is included in Chapter 3. Samples used in the photoluminescence studies were \( \text{P}^+ \) and \( \text{P}_2^+ \) implants at energies from 5 to 14 keV and fluences of \( 1 \times 10^{11} \) to \( 5 \times 10^{12} \text{ cm}^{-2} \) implanted on the Colutron at the University of Melbourne. Implants at 15 to 70 keV \( \text{P}^+ \) and \( 1 \times 10^{12} \) to \( 5 \times 10^{13} \text{ cm}^{-2} \) implanted at ANU were also studied. The base material was the TopSil silicon. Samples of \( ^{28}\text{Si} \) epi-layers were also measured.

Experiments were performed at the University of Melbourne using a dispersion grating instrument with sample cooling provided by the cold finger type cryostat. Measurements at Simon Fraser University were performed on the Fourier transform instrument with samples cooled by immersion in a helium bath cryostat.

### 7.5 Measurements of Bulk Silicon Samples

Bulk silicon samples were measured with both the dispersion grating instrument and the Fourier transform instrument. The results from the dispersion grating instrument indicated laser heating of the samples. Measurements using the Fourier transform instrument provided background doping concentrations for the bulk silicon wafers, the Blank silicon samples.

#### 7.5.1 Dispersion Grating Instrument Measurements

Spectra obtained with the dispersion grating system of the blank high resistivity Topsil silicon are shown in Figure 7.6. A large peak was observed at 1.1 eV, with smaller peaks at 1.04 eV, 1.14 eV and 1.16 eV. The samples were measured in a cryostat while attached to a cold finger held at 4.2 K, but the spectra matched those from samples measured at or above 25 K [62,163] rather than
those measured at 4.2 K [143]. The luminescence observed was broader than the luminescence measured at the lower temperature (see Figure 7.3), but was in the regions of the phonon replicas. This indicated local laser heating of the sample. The reduction of laser power so as to reduce the effects of laser heating resulted in a signal too weak to detect with the single point InGaAs detector.

The peaks in the spectra were identified as the phonon assisted free exciton recombination. The peak at 1.1 eV was a combination of the TO and LO phonon assisted peaks, at 1.14 eV the TA phonon assisted peak, and at 1.04 eV the $2\times$ optical phonon peak. No luminescence was observed from the region expected of bound exciton no-phonon transitions. To resolve any bound exciton or free exciton peaks which may have been broadened by the spectrometer rather than by thermal processes, the spectrometer entrance slit was narrowed. Reducing the slit width reduced the intensity of the lines, but did not resolve any components, confirming the sample heating hypothesis. For example, using a 500 $\mu$m slit width the resolution of the instrument was 1.5 meV, whereas the half width at half maximum of the 1.1 eV peak was 6 meV. The reduction in peak intensity limited the usable slit width to a minimum of 250 $\mu$m, with a resolution of 0.7 meV.

The peak observed at 1.16 eV did not originate from the silicon sample. The photolumines-
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Figure 7.7: Photoluminescence spectrum of a $^{28}$Si epitaxial layer compared to the laser focused onto a mirror, obtained with the dispersion grating system, and showing the lines origination from the laser. (5 mW laser power at 514.5 nm, 600 g/mm grating, 1.5 mm slits, 500 ms/point collection time, $T_{\text{cryo}} = 4.2$ K). Identification of lines in text. Spectra offset vertically for clarity.

The photoluminescence instrument at the University of Melbourne did not employ a plasma line filter in place to remove the plasma lines from the argon ion laser operating at 514.5 nm. The laser line rejection filter in place before the entrance to the spectrometer did not remove all of the reflected laser intensity. Plasma lines in the spectra were identified by comparing the spectrum from a $^{28}$Si epitaxial layer doped at $1 \times 10^{15}$ cm$^{-3}$ with the spectrum of the laser focused onto a mirror, see Figure 7.7. The phonon assisted recombination lines were clearly observed in the spectrum from the silicon, with no corresponding lines at these positions in the mirror spectrum. The strongest lines observed in both were the lines at 1.16 eV, confirming this was a plasma line from the laser, and the line at 1.21 eV (1029 nm) which was the second order diffraction of the 514.5 nm laser line. The lines which did not originate from the silicon were second order diffraction lines from the laser emission.

7.5.2 Fourier Transform Instrument Measurements

The photoluminescence spectra taken of the blank Topsil silicon samples using the Fourier transform instrument, are shown in Figure 7.8. All the relevant free exciton and bound exciton transitions from shallow dopants are clearly resolved by the instrument (see and compare to Table 7.1...
Figure 7.8: Fourier transform photoluminescence spectra of unprocessed high resistivity TopSil silicon samples Blank 1 and Blank 2. Measurement of background doping concentration for both samples used the high excitation density conditions. (20 mW laser power at 532 nm, 3.5 mm aperture, and 1.5 K). Spectra offset vertically for clarity.

and Figure 7.3). The upper spectrum in the figure originated from a sample with a higher background doping level than the lower, indicating two qualities of silicon substrate were used to produce samples. Both were quoted as high resistivity by the manufacturer, and photoluminescence measurements were the first to distinguish the differences between the two. Labels on the blank silicon substrates were introduced at this point to distinguish between the two qualities.

Dopant densities were measured from the peak height intensities of the photoluminescence spectrum, by taking the ratios: $P_{TO}/FE_{TO}$ and $B_{TO}/FE_{TO}$ and comparing them to the calibration curve for the high excitation density conditions of Reference [63], see Figure 7.4 (a). The doping concentrations of the two samples follows:

- The doping density of Blank 1 was: $9 \times 10^{12}$ P cm$^{-3}$ and $1 \times 10^{13}$ B cm$^{-3}$
- The doping density of Blank 2 was: $2.5 \times 10^{12}$ P cm$^{-3}$ and $1.3 \times 10^{12}$ B cm$^{-3}$.

The silicon in Blank 1 was closely compensated. Electrical resistivity measurements, such as the four point probe, which measure the free carriers, the difference in the number of carriers from the donors ($N_D$) and the acceptors ($N_A$), would find a similar resistivity for both samples. For both the the above silicon samples, $|N_D - N_A| \approx 1 \times 10^{12}$ cm$^{-3}$, a resistivity of about 7000 Ohm-
cm, which was in the range quoted by the silicon manufacturer. While mobility measurements can identify compensated samples via ionised impurity scattering, the technique requires the use of specialised structures for the conduction paths, resulting in complicated sample preparation. Here we see the power of photoluminescence to be able to measure the concentration of both donors and acceptors in silicon, concurrently and non-destructively.

The photoluminescence measurements of the implanted samples produced with the above wafers had to contend with some background phosphorus in the spectra. The lower background doping level in Blank 2 silicon made signals originating from the implanted phosphorus ions in this silicon easier to observe than in samples produced in Blank 1 silicon.

The only other bulk samples measured on the Fourier transform instrument were the \( ^{28}\text{Si} \) epitaxial layers. It was expected that donors in the epitaxial layer would produce sharper bound exciton, \( P_{\text{NP}} \) lines than in the natural silicon, but this was not observed. The broadening of the lines was probably due to a large strain on the \( ^{28}\text{Si} \) epitaxial layers from a bad epitaxial growth.

### 7.6 Measurements of Processed Silicon Samples

#### 7.6.1 Sample Production Process Quality

The spectra obtained from all the implanted and annealed samples contained various degrees of copper luminescence, which was observed in both spectroscopy systems. Photoluminescence spectra of these processed silicon samples obtained with the dispersion grating system are shown in Figure 7.9, and those obtained using the Fourier transform instrument in Figure 7.10. As well as the luminescence originating from shallow dopants and free excitons, copper luminescence was observed in the region from 1.03 eV to 0.9 eV. The spectrum included the \( \text{Cu} \) centre, consisting of a zero-phonon 1.014 eV line with anti-Stokes and Stokes phonon replicas of 7.05 meV and a continuum to lower energies [37]. The peaks are more clearly observed with the Fourier transform instrument than the dispersion grating instrument as the later suffered due to laser heating. The spectra from the dispersion grating instrument could be compared to those in the literature measured at 30 K [164].

Luminescence from a second copper centre was also observed in processed silicon samples using the Fourier transform instrument. As well as the \( \text{Cu} \) centre at 1014 meV the spectra also included the \( \text{Cu}^* \) centre at 943.7 meV. Subsequent investigations of these centres in isotopically enriched \( ^{28}\text{Si} \) led to the identification of the composition of these centres to include four atom complexes [165, 166]. The \( \text{Cu} \) centre was made up of 4 × Cu atoms and the \( \text{Cu}^* \) centre from 3 × Cu and 1 × Ag atoms.

A copper and silver contamination in one part of the production process would have been
7.6. MEASUREMENTS OF PROCESSED SILICON SAMPLES

Figure 7.9: Dispersion grating photoluminescence spectra of 10 keV P$^+$ and P$^{2+}$ implanted samples, showing the Cu centre. (8 mW laser power at 514.5 nm, 600 g/mm grating, 1 mm slits, 500 ms/point collection time, $T_{\text{cryo}} = 4.2 \text{ K}$). Spectra offset vertically for clarity.

Figure 7.10: Fourier transform photoluminescence spectra of silicon samples showing the 1014 meV Cu centre and the 943.7 meV Cu$^*$ centre. (20 mW laser power at 532 nm, 3.5 mm aperture, and 1.5 K). Spectra offset vertically for clarity.
incorporated into the silicon during the rapid thermal anneal (RTA). Copper and silver are fast diffusers in silicon and only trace amounts were required to produce the strongly luminescent centres. At 1000 °C copper has a diffusion coefficient of $5.8 \times 10^{-5}$ cm$^2$/s, and within five seconds a surface contamination would have travelled up to 170 µm into the sample. Rapid thermal quenching of the silicon is also required to form these centres, again provided by the RTA. Once the support wafer in the RTA was contaminated, copper and silver would have easily been passed on to other samples. Changing the support wafer removed this contamination from further samples, and more care in cleaning the samples prevented further contamination.

Dislocation luminescence was observed in the ANU implanted sample set, the higher energy and higher dose implants, see Figure 7.11. Dislocations were produced inadvertently by scribing a label on the back of each sample before the rapid thermal anneal. The large temperature gradients within the sample induced by the RTA processing, propagated the dislocations from the scratch throughout the crystal [35]. The line at 807 meV in the spectrum was from the centre $D1$ and that at 874 meV from the centre $D2$ [37]. These are near surface dislocations and have a larger intensity when illuminated with the 532 nm laser than the 1047 nm laser.

A peak at ~820 meV with ~5 meV phonon replicas was observed in the photoluminescence spectra from some of the samples but was not able to be identified.

Figure 7.11: *Fourier transform photoluminescence spectrum of processed P⁺ implanted silicon sample showing dislocation and copper luminescence.* (20 mW laser power at 532 nm, 3.5 mm aperture, and 1.5 K).
7.6.2 Strain

The splitting of the $P_{NP}$ peak observed in the $1 \times 10^{13}$ cm$^{-2}$ P$^+$ implants and shown in Figure 7.12 was due to strain in the samples. The high doping density in the layer of implanted ions caused a change in the lattice constant within the layer, and the slight lattice mismatch with the bulk crystal produced a strain within the lattice. The strain split the $P_{NP}$ peak by lifting a degeneracy in the donor electronic levels. Another process which could broaden the lines was the dopant interactions as discussed by Pan et al. [154]. Donor interactions are expected in these samples and the presence of the strain introduced difficulties in separating the two processes. An interesting observation from this sample set was that the sample with the smallest splitting of the $P_{NP}$ peak, the 15 keV P$^+$ implant into silicon with the thermal oxide, also produced the most dislocation luminescence. The formation of the dislocations may have relaxed the strain out of the crystal lattice.

The strain in the samples could be quantified in terms of both depth and magnitude using double crystal X-ray diffraction. Pesek [167], in a study on Ge ions implanted into silicon at peak concentrations and projected ranges similar to those used in these phosphorus doped samples, measured the strain due to both the damage caused by the ions and the ions themselves. He found

![Figure 7.12: Fourier transform photoluminescence spectra of silicon implanted with $P^+$ at various energies at the fluence of $1 \times 10^{13}$ cm$^{-2}$, zooming in on the $P_{NP}$ region. Samples showed peak splitting due to local strain. (60 mW laser power at 532 nm, 3.5 mm aperture, and 4.2 K). Spectra offset vertically for clarity.](image-url)
that the damage related strain disappears after a rapid thermal anneal at 800 °C for 15 sec, while the strain due to the ions themselves was still observed at 1050 °C.

Concern for metallic contamination and as a process control step, the prototype quantum computer device DP5 used for microwave spectroscopy experiments, and fabricated at the Semiconductor Nanofabrication facility at UNSW was studied by photoluminescence. This device passed through the University of Melbourne facilities, where two single phosphorus ions were implanted. Measurements on the bulk of the device showed no metallic impurity contamination or dislocations. What was observed was splitting of the P_{NP} peak due to strain caused by the highly doped regions and metallised surfaces produced as electrical contacts to the device. The photoluminescence bound exciton signal originated from the bulk of the substrate, indicating that the engineered surface contacts produced a strain field felt throughout the substrate.

7.7 Phosphorus Ion Implanted Samples

Measurements were performed on samples implanted with phosphorus ions with the aim of observing interactions between the donors. Also studied was the activation of the phosphorus atoms, and of note was that no previous photoluminescence studies had focused on the implantation of phosphorus in the energy range and fluences used in this work. The study of implanted donor activation is relevant to address concerns about the possible yield of low energy phosphorus ion implanted qubits, in close proximity to an oxide.

The measurements of dopant activation after implantation and annealing by photoluminescence were hampered by the background phosphorus doping in the silicon and an anomalous disappearance of phosphorus signal the closer an implant was to the surface. The 14 keV and below, P^+ and P^{+2} ion implanted samples were produced with the higher background doped silicon of Blank 1, whose significant background doping masked the expected increase in the P bound exciton peaks. The background signal also masked any broadening of the peaks. These spectra are not reported here.

The 70 keV P^+ implants into Blank 1 silicon did show an increased P_{TO} peak as well as a broad peaks from a high P concentration region, at lower energies to both the P_{TO} and P_{NP} peaks, see Figure 7.13. This broad peak was comparable to those in Figure 7.5 from bulk doped silicon samples, which were expected to arise from the formation of clusters of donor atoms, and shifted in energy away from the isolated donor peak as the concentration increased. In the implanted samples, the spectrum from the background doping in the bulk of the crystal was observed as well as the broad cluster peak from the implanted layer. This broad cluster peak in the TO region of the spectrum could be confused with the free exciton process of the electron-hole droplet, but as the peak was also present in the NP region it must have originated from a bound exciton process and
not from free excitons.

The high fluence samples implanted at ANU into Blank 2 silicon also produced this broad luminescence peak attributed to a high doping level, see Figure 7.14. The 35 keV implant showed a larger shift in the broad cluster peak compared to the 70 keV implant. As both had the same implanted fluence, the smaller depth of the 35 keV implant produced a higher doping concentration in the implanted layer. The 15 keV P$^+$ implants, the shallowest of the set, were expected to have the highest density of donors, thus the largest peak shift, but these samples did not show the P cluster peak. The lack of the P cluster peak in these implants raised concerns about the quenching of the luminescence signal due to the vicinity to the surface. Mechanisms for the surface interfering with the bound excitons will be discussed shortly. Note that these 15 keV P$^+$ implanted samples did produce the largest P cluster resonance in the electron paramagnetic resonance measurements (see Figure 3.5).

These implanted samples also showed an increase in the isolated donor peaks over the background level. Isolated donors were a result of the non-uniform depth distribution brought on by the implantation. These observations were aided by the use of the Blank 2 silicon as the substrate,
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Figure 7.14: Fourier transform photoluminescence spectra of P$^+$ implants of various energies into silicon at a fluence of $1 \times 10^{13}$ cm$^{-2}$. A broad peak originating from clusters of donors can be seen in some of the samples. (60 mW laser power at 532 nm, 3.5 mm aperture, and 4.2 K). Spectra offset vertically for clarity.

which had a lower doping level than Blank 1. The background doping, even at such low concentrations, poses issues for the measurement. The implanted donors sat within a couple of hundred nanometers of the surface at most, and the penetration depth of the 532 nm laser was a micron or so, but the excitons may have diffused hundreds of microns within the silicon. In this way the luminescence from the implanted layer was superimposed on the luminescence from the whole bulk of the crystal.

### 7.7.1 Implanted Ion Activation

Analysis of the spectra collected was undertaken so as to ascertain the extent of implanted donor activation. The implanted donors which were activated by the anneal increased the intensity of the phosphorus peaks. If the donors were “isolated”, that is they were not interaction or only weakly interacting with other donors, they would increase the height of the P$_{NP}$ and P$_{TO}$ peaks. The donors which were in clusters would increase the intensity of the P cluster peaks. All of the bound excitons reduce the intensity of the free exciton luminescence, but as we do not know the
efficiency of the P cluster peak in producing radiation we cannot use the bound exciton peak in the calibration ratios. By comparing the ratio of the peak heights $P_{TO}/B_{TO}$, a qualitative look at the change in the number of isolated P donors introduced via the implantation was undertaken. The boron peak was chosen as it was always present and variations in the height of the peak across samples from the same batch of wafers was expected to be small. The measured trends were compared to the proportion of implanted donors expected to be isolated from ion implantation simulations.

Activation was compared across implanted samples produced with the same base silicon substrate so as the boron doping level would be similar. The ratio of peak heights for samples produced in Blank 1 silicon are shown in Figure 7.15. The large background doping hid any effects from the implanted ions, but of concern was that most of the implants show smaller $P_{TO}/B_{TO}$ ratios than the unimplanted Blank 1 silicon, with no strong trend to the data in terms of implanted fluence or energy. This loss of $P_{TO}$ signal remains a mystery, but it may be due to larger than expected variations in the background doping of both P and B, as samples did not all originate from the one wafer. In any case, the trends for the implants of energy 14 keV and below did not show anything which could be claimed to be above background.

The only implants to show an increase in the isolated $P_{TO}/B_{TO}$ ratio in Blank 1 silicon were from ions implanted deeper into the silicon, the 70 keV P$^+$ ions (the three points furthest to the right in Figure 7.15). The ratio was approximately constant between these samples even with the order of magnitude increase in the fluence, from $1 \times 10^{12}$ to $1 \times 10^{13}$ cm$^{-2}$. A comparison of the $P_{TO}/B_{TO}$ ratio for the samples with implants into Blank 2 silicon is shown in Figure 7.16. The lower background doping density helped in identifying the trend of an increase in the number of isolated donors with the increase in implantation energy.

The trends observed in the $P_{TO}/B_{TO}$ ratio were reproduced in the ion implantation simulations. In this case, atoms were assumed to be isolated if they had a separation from their nearest neighbour greater than 20 nm. Changing this value would change the absolute number of isolated atoms but not the trend. Figure 7.17 shows the number of isolated atoms expected for samples with various implantation energies and fluences. Firstly, for implants of the same energy, an increase in the fluence increases the number of donors in the system, but since the volume of the system is kept constant (projected range doesn’t change) the concentration increases and the separation between donors decreases, leaving less isolated donors at higher fluences. For the 70 keV implants, an order of magnitude increase in the fluence results in only a factor of two decrease in the number of isolated donors, reflected in the small change in the data.

For implantation at a constant fluence, higher implantation energies led to an increase in the volume of the implanted layer (longer projected range of ions), increasing the separation between donors which resulted in more isolated donors. The data followed this expected trend. Note that
for the $1 \times 10^{13}$ cm$^{-2}$ implants, at 70 keV only about 1 % were expected to be isolated, and at 15 keV about 0.1 %, which highlights the concern about the lack of an observed P cluster peak in the 15 keV sample. The rest of the donors would have been in interacting clusters, with the expectation that the proportion in clusters increased with a reduction of the implantation energy. This trend was observed in the EPR experiments, see Figure 3.5, with the central line increasing as the implant energy decreased, but not in the PL experiments, where the magnitude of the P cluster peak decreased, and was not seen in the 15 keV sample.

The loss of signal from implanted phosphorus ions has been noted in previous studies, and caused some concern regarding the suitability of lower energy ion implanted donors as qubits in a solid state quantum computer device. Schenkel et al. [168,169] studied the activation of low energy implanted phosphorus ions at low fluences and found a decrease in activation as the energy and fluence were reduced. Activation was measured by the electrical technique of spreading resistance analysis (SRA). At $1 \times 10^{13}$ cm$^{-2}$, the 30 keV implant had an activation of 80 % whereas for 10 keV, activation dropped to 40 %. For the 10 keV implant, the activation was 0 % at $1 \times 10^{11}$ cm$^{-2}$. The quality of the oxide also played a part in donor activation, with the thermal oxide showing higher activation rates than the native oxide. The loss of activation was said to be due to interstitial diffusion of the phosphorus to the interface, aided by transient enhanced diffusion, during the annealing of the sample.

![Figure 7.15: $P_{TO}/B_{TO}$ peak height ratio for implanted samples in Blank 1 silicon. Energy in keV and fluence in cm$^{-2}$. (532 nm at 60 mW, 4.2 K. 3.5 mm aperture).](image-url)
Contrary to the previous studies by Schenkel, McCamey et al. [170] measured the activation of 16 keV P\textsuperscript{+} implants into silicon to be almost 100 %. This was achieved by performing room temperature I-V measurements on silicon MOSFETs implanted with \(2 \times 10^{12} \text{cm}^{-2}\) P\textsuperscript{+} ions through a 5 nm thermal oxide, with the measured the changes to the threshold voltage matching that expected from 100 % activation. This paper also noted that spreading resistance analysis was not an appropriate technique for measuring donors in such a thin layer and at such low densities. The large surface probes and high oxide trap density made the results of SRA inherently uncertain.

In further studies Schenkel et al. [27, 87] admitted that the SRA technique was inadequate to measure the activation of implants in a thin layer close to the surface. Here they used antimony implants and found that secondary ion mass spectrometry measurements matched the simulated implantation profile, while the results of the SRA did not. The authors still insisted that the phosphorus diffuses interstitially. Electron paramagnetic resonance experiments on the antimony implanted samples, showed an improvement in signal strength when the donors were photo-neutralised with white light illumination. Ionisation of donors was said to occur due to band bending from charge traps at in the oxide and interface. These charge traps coupled with the donor electron spins resulting in a reduction of the bound electron \(T_2\) times. Removal of the oxide before measurements increased the \(T_2\) times of the donors, by removing the charge traps at the interface.
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Figure 7.17: The number of isolated donors in a cm$^2$ area from implantation simulations described in Chapter 4, for various fluences and energies. An isolated dopant is defined as having a separation from its nearest neighbour greater than 20 nm.

Measurements on the number of charge traps at the silicon–silicon dioxide interface for silicon capped with a thin thermal oxide, and both with and without ion implantation and processing were performed by McCallum et al. [70] using deep level transient spectroscopy (DLTS). At best, interface trap densities of $\approx 1 \times 10^{10}$ cm$^{-2}$ were achieved even after implantation of 15 keV P$^+$ ions at fluences of up to $1 \times 10^{12}$ cm$^{-2}$ and rapid thermal annealing, indicating that the implantation of the low energy ions did not increase the trap density. They also note that in some cases of larger trap densities to begin with, the implantation helped improve the oxide quality.

At their worst, native oxides can have interface trap densities many orders of magnitude larger than those of the thermally grown oxides. Many of the samples produced in Blank 1 silicon did not have the optimal oxide, which would have contributed to the reduction in signal for ions implanted close to the surface, and especially for lower fluence implants where the number of traps may have been larger than the number of implanted ions. While the ionisation of the donors by the charge traps would have been countered by the application of above band gap illumination in the photoluminescence experiments, the proximity of the traps to the donors could have opened up non-radiative recombination pathways. Stripping the oxide before measurement would have elim-
inated the interactions between the donors and the interface traps, but given the high background doping in the Blank 1 silicon substrate, no improvement in signal would have resulted.

The high background doping of the Blank 1 silicon substrate meant that no judgement could be made on the activation of donors in the low energy and low fluence samples. For the $1 \times 10^{13} \text{ cm}^{-2}$ fluence $P^+$ ion implants into Blank 2 silicon, the intensity of the P cluster peaks reduced as the ions were implanted closer to the surface, with the cluster peak disappearing in the 15 keV samples. The loss of PL signal was not due to loss of active donors atoms as the EPR measurements showed a consistency in the number of spins across these samples. The EPR also showed a resonance from the $P_b$ defects, interface trap states. The reduction in the $T_2$ times of implanted antimony donors in the EPR experiments of Schenkel et al. [87], indicated interactions between the states at the interface and the donor electrons. The interface states could open up non-radiative recombination pathways for excitons bound to donors close-by. This drop in the intensity of the photoluminescence signal does not imply that the phosphorus atom is “ruined” as a donor and a qubit (e.g. by ionisation), but just that the extra requirement of radiative recombination to observe the donor bound exciton signal in the PL spectra was not met.

### 7.7.2 Ion Implanted Dopant Interactions

Changes to the photoluminescence spectra from interactions between donors were not observed in the $P^+$ implanted samples, with only the high dose atomic implants showing effects due to interactions. These interactions manifested themselves as the broad P cluster peak in Figure 7.13 and Figure 7.14. This peak shifted in energy away from the isolated donor peak with increasing donor density, and was fitted well by a Gaussian. For each sample and for both the NP and TO replicas of the cluster peak, the magnitude of the shift away from the isolated donor peak to the fitted centre of the cluster peak was calculated. The donor distribution within the implanted layer of each sample was characterised by the mean nearest neighbour separation calculated with the implantation simulations. Figure 7.18 shows the magnitude of the energy shift of the P cluster peak versus the mean nearest neighbour separation of the donors in each sample. An exponential trend in energy shift with nearest neighbour separations was observed, with the NP peak having a larger energy shift than the TO phonon assisted peak.

By converting the simulated mean nearest neighbour separation to an associated bulk concentration via Equation 7.2, comparisons were made between the observed shift in the P cluster peak energy from the implanted layers, with the shifts observed in bulk doped silicon reported in the literature. The sample with the largest mean donor separations, the 70 keV $P^+$ $1 \times 10^{12} \text{ cm}^{-2}$ with an $R_{\text{mean}} = 14.2$ nm, and a bulk doped silicon equivalent concentration of $\sim 5 \times 10^{16} \text{ cm}^{-3}$, had an energy shift in the P cluster peak of about 1 meV. The sample with the smallest mean separation from which a cluster peak was observed, the 35 keV $P^+$ $1 \times 10^{13} \text{ cm}^{-2}$ implant, with an
Figure 7.18: Magnitude of the energy shift of the P cluster peak versus the mean dopant separation. The centre of the P cluster peak was found by fitting a Gaussian and the energy shift was taken from the isolated donor peaks. The mean separation of nearest neighbours in the samples was calculated using large area implant simulations. The plotted trends are of the Narita equation (Equation 7.1), and the Openov equation (Equation 7.3) using measured physical parameters, and fits to the data using both these equations with the parameters free to vary.

\[ R_{\text{mean}} = 5.5 \text{ nm} \] equivalent to a bulk doped concentration of \( \sim 1 \times 10^{18} \text{ cm}^{-3} \), had a peak shift of about 13 meV. The implanted samples were doped to a concentration range just below the silicon metal insulator transition, a range where dopant interactions have been previously observed. The P cluster peak in silicon bulk doped with such a concentration range had an observed energy shift of magnitude equivalent to that observed in the implants. For example, Shiraki and Nakashima [152] observed a 1 meV shift from the isolated P case in their \( 8 \times 10^{16} \text{ cm}^{-3} \) bulk doped sample up to a shift of 18 meV shift in their \( 3 \times 10^{18} \text{ cm}^{-3} \) phosphorus doped sample (see Figure 7.5). The interaction processes between the donors in these ensemble atomic phosphorus ion implants were the same as those in the bulk doped crystals.

The positions of the bound exciton photoluminescence lines were influenced by the energy of the band gap, the exciton binding energy, and the energy of any phonon involved in the transition. Thus, the processes which could have caused the observed shift and broadening of the P cluster peaks are: a change in the exciton binding energy or a change in the energy levels of the P donor
electron states, a local change in the band gap of the crystal, or changes to the phonon energy. Analysis of the trend in the cluster peak energy shift was performed using three different models:

1. The Narita model [64] based on the study of bulk doped silicon. The shift in peak energy was modelled via Equation 7.1 as a shift in the exciton binding energy due to hopping of the exciton between two donors. This model assumes excitons bound to only two donors and the energy levels within the phosphorus donor staying constant.

2. The shift in the energy of the P cluster peak caused by a shift in the phosphorus electronic levels from the coupling of two donors. In this model the presence of the exciton is ignored.

3. A many particle interaction model of the formation of the donor band in the implanted region. The shift in peak energy follows the narrowing of the band gap, and the peak shape is due to the density of states of the donor band associated to the size and distribution of the donor clusters.

The three models were tested against the data using the measured physical values of the phosphorus electrons and bound excitons. Figure 7.19 shows a conceptual schematic of the system assumed by Models 1 and 2. The system comprises of two neutral phosphorus donors a distance $R$ apart with an exciton bound to them. Model 1 assumes that the exciton can hop between the two P atoms increasing the binding energy as the separation decreases. Model 2 assumes that the vicinity of the second P donor to the first shifts down the energy levels of the donor electrons, with the binding of the exciton following this shift. The models were used so as to simplify the system from that of the two shielded phosphorus ionic cores, three electrons and the lack of an electron (the hole) within the silicon matrix, and the complications of all their associated interactions.

**Model 1: Exciton Hopping**

The simple two donor exciton hopping model of Narita, Equation 7.1, did not reproduce the cluster peak shift data well when using the measured binding energy and Bohr radius (see Figure 7.18).
The trend was correct, with an increase in the shift as the mean donor separation was reduced, but the magnitude was not large enough. As was mentioned in Narita’s paper, the model did not adequately reproduce the shifts in the bulk doped silicon either. Narita had to extend the model to include hopping between clusters and to clusters of more than two atoms. The same arguments could be applied here, as the samples studied were atomic implants and not molecular implants, clusters of more than two atoms were expected to form. The clustering simulations performed on these samples will be discussed shortly. By extending the model to include clusters greater than two, the fit to the observed energy shift should improve as the exciton would bind more strongly to larger numbers of donors.

Using Equation 7.1 and least squares fitting to the peak shift data with $E_0$ and $r_0$ as free parameters, the expression fit the data with a reduced $\chi^2 = 1.03$. The parameters of the fit were $E_0 = 34.8 \pm 8.3 \text{ meV}$ and $r_0 = 3.4 \pm 0.4 \text{ nm}$. The energy scale parameter was seven times the binding energy of the bound exciton, which could represent an exciton bound to a large cluster of donors.

Model 2: Phosphorus Donor Energy Shift

As neighbouring donors interact the electronic levels of the phosphorus donor change through hybridisation, forming molecular states. The bound exciton could have followed the energy shift of the lowest energy of the split P ground state. The process was modelled using the equation from Openov [171] for the hydrogenic approximation to the symmetric to anti-symmetric splitting of the ground state of the two phosphorus donors. The system Openov was investigating was that of two ionised phosphorus donors and a single electron. This system may be compared to our case of the two neutral phosphorus donors and a neutral exciton. The equation had the following form:

$$E(R) = 4E \frac{R}{a} \exp \left( -\frac{R}{a} - 1 \right)$$  \hspace{1cm} (7.3)

where $E$ (meV) is the ground state energy of the isolated phosphorus electron, and $a$ (nm) is the effective Bohr radius of this state, or the energy and size of the potential well respectively. $R$ is the separation between the donors. For phosphorus in silicon, $E = 45.5 \text{ meV}$ and $a = 2.5 \text{ nm}$ [47], and this equation is plotted in Figure 7.18 with a trend and magnitude surprisingly close to the experimental data. Fitting the energy shift data with the Openov equation provided the following parameters: $E = 42.3 \pm 6.1 \text{ meV}$ and $a = 2.3 \pm 0.2 \text{ meV}$, with a reduced $\chi^2$ of 0.82, also shown in Figure 7.18. These values are within error of the ionisation energy and Bohr radius of a phosphorus donor electron, and this model predicts the observed shift of the peak as changes in the donor levels for an exciton bound to a pair of donors.
Calculation of P Cluster Peak Shape

Reproduction of the P cluster peak was attempted using the Narita (Equation 7.1) and Openov (Equation 7.3) equations, shown in Figure 7.20. The models assume the peak as made up of luminescence from excitons bound to donor pairs of various separations. The distributions of nearest neighbour pair separations within a sample was modelled with the ion implantation simulations described in Chapter 4. For an example of such a distribution see Figure 4.14. These separations were convoluted with the equations modelling the peak shifts versus separations, converting the distributions to the proportion of donors within a sample which produce certain energy shifts. The calculation was then plotted as a comparison to the P cluster peak spectrum. As expected the Narita equation did not provide the magnitude of shift required to fit the cluster peak, but reproduced the right shape. The magnitude of the shift from the Openov equation was adequate, but the shape was not. The larger peak shift values, those furthest from the P\textsubscript{70} peak are produced by atoms with the closest separations. The hydrogenic approximation was expected to break down at separations smaller than two Bohr radii, in the regime of strong coupling, which was observed. For separations $R < a$ and approaching zero, Equation 7.3 tends from a maximum in the energy shift towards a zero energy shift. This region was not included in the reproduction of the cluster peak using the Openov equation in Figure 7.20. As a comparison the P cluster peak was fitted by a Gaussian, which reproduced the peak well, and will be discussed shortly in terms of the formation of a donor band.

Many Donor Clusters

When modelling the atomic ion implanted systems, both the Narita equation and the Openov equation suffered from the simplification to a two donor system. These equations may still adequately model the energy shifts from pairs of donors produced by molecular ion implantation, but could not adequately reproduce the peak shape or shift for our implanted samples.

The samples from which the P cluster peak was observed contained predominately clusters larger than four atoms. An analysis of the simulated cluster size expected for the 70 keV P\textsuperscript{+} implants is shown in Figure 7.21. For the lowest dose 70 keV implanted sample around half of the donors were isolated, whereas at the highest dose this dropped to 10%. Not many of the atoms were in clusters of two or three, and the number in clusters larger than four increased from 40% at the lower dose to 90% at the higher dose. For these samples, the clusters while large, were still isolated from one another, and the doped region had not yet formed into a continuous metallic region. The clustering calculations also matched the EPR experimental results, where the resonance due to clusters of phosphorus increased in intensity as the density of atoms increased.

The simulations of the size of the clusters indicated that for the atomic ion implanted samples,
the energy shift must be modelled through interactions between more than two donors. The Narita model of interactions can be extended to more than two atoms and still fit the data. The Openov equation on the other hand, provided the correct energy shift using only two donor and thus can not be extended to higher numbers of donors. This would only make sense if there was some process limiting the interactions to two donors, for example, a directional dependence to the interaction.

Extending the models to clusters of more than two donors introduces additional complexity to the modelling. A study of interactions between three impurities conducted by Nagasaka and Narita [172], calculated the effects of the three donor molecule on the photoconductivity response of germanium. They had to construct the three donor molecule for three spatial configurations, and had to estimate the statistics of each within a random distribution of donors in germanium. The extension of the calculation to more than two donors does not only increase the number of interactions that require calculation, but also adds an extra degree of freedom in terms of the relative donor orientation. This would increase the complexity of the calculation, which would become very computationally intensive. Increasing the number of donors in the calculation to three or even four, while increasing the accuracy of the modelling, would not have been sufficient.
to properly account for the expected size of the clusters in our samples. The effort required was not thought necessary.

**Model 3: Formation of the Donor Band and Band Gap Narrowing**

Interactions between two donors could not adequately reproduce the P cluster spectra obtained from the atomic phosphorus ion implanted samples. Interactions between the many particles expected within the donor clusters must be examined, but such calculations are complicated and a simplification was required. The many donor interactions expected within the clusters led us to consider a model of impurity band formation providing the P cluster peak width, and the narrowing of the band gap due to the additional implanted changes leading to the shift in the peak position.

The wavefunction overlap of neighbouring donor electrons broadens the energy levels of donor electron states leading to the formation of an energy band, the impurity band, similar to the formation of the silicon bands discussed in Chapter 2. Bergersen et al. [113] considered the formation of the impurity band as the mechanism leading to the broad peaks in the photoluminescence spectra from highly phosphorus doped silicon. They calculated the density of states using a Hubbard band, which simplified the many particle interactions by considering the donors to sit on a regular array. The separation of the donors on the array was related to the doping density. The width of
the donor band they calculated using this model was of the right order of magnitude as the peak widths they observed, but did not adequately account for the tails in the peak. They speculated that these tails were the result of the randomness of the donors within an actual sample. They also used an $H_2^+$ molecular model of band formation (similar to the Openov model) which resulted in a calculated width broader than that measured.

A study by Altermatt et al. [91] which re-examined the Bergersen et al. data, as well as other donor band density of states data, found the donor band to be Gaussian in shape. This matched our data, where the P cluster peak was fit well by a Gaussian (see Figure 7.20). The half width of the 70 keV $P^+$ $5 \times 10^{12}$ cm$^{-2}$ sample was 4 meV. While we did not find a trend between the width of the peak and the nearest neighbour separation in our samples the observed width did compare well to the Bergersen et al. data. While we expected the implanted samples to be doped below the metal-insulator transition (the implanted layer was not continuously metallic), the donor interactions leading to the broadening of the density of states and thus the cluster peak were occurring within the randomly distributed clusters.

The shift of the P cluster peak was due primarily to two processes: the narrowing of the band gap due to the extra charges implanted into the sample, which shifted the peak to lower energies, and the shift of the donor states closer to the conduction band which accompanied the formation of the impurity band, a shift of the peak to higher energies.

The dominant mechanism leading to the shift in the P cluster peak to lower energies was the band gap narrowing, where the interactions between all the charged particles in the implanted region of the semiconductor (both mobile and fixed) led to the narrowing of the band gap [91]. As the doping density increased, this process led the energy between the top of the valence band and the bottom of the conduction band to decrease, an effect independent of any changes to the impurity energy levels, and only relies on the presence of the extra charges. A phenomenological band gap narrowing expression was provided by Klaassen [173]:

$$\Delta V_{g0}(N) = V_1 \left\{ \ln \left( \frac{N}{N_2} \right) + \sqrt{\left[ \ln \left( \frac{N}{N_2} \right) \right]^2 + C_2} \right\}$$

with $V_{g0}(N)$ the change in the band gap, $N$ the doping concentration in cm$^{-3}$, $N_2 = 1.3 \times 10^{17}$ cm$^{-2}$, $V_1 = 6.92$ meV, and $C_2 = 0.5$. The above equation had been converted from dopant density to mean nearest neighbour distribution via Equation 7.2, and plotted in Figure 7.22 as the energy shift away from the intrinsic band gap.

The shift of the energy of the donor states relative to the conduction band due to donor-donor interactions was a secondary effect. The energy between the donor ground states and the conduction band (45.5 meV for isolated P donors) stays constant until concentrations reach those close...
The band gap narrowing was measured in our spectra as an energy shift away from the isolated donor peak, representing the region of intrinsic band gap. Generally measurements of the band gap narrowing would measure the energy difference between the top of the valence band and the edge of the impurity/conduction band. In our spectra this point would be at the low energy edge of the P cluster peak, and it was to this point, where the cluster peak met the background as shown by the arrow in Figure 7.20, that the energy shift was calculated. Due to the presence of other peaks in the spectrum and the noise in the background, the confidence in the measurement of the band gap narrowing was 2 meV.

The magnitude of the observed energy shift (to the low energy side of the peak) versus the mean donor nearest neighbour separation in the sample was plotted as squares in Figure 7.22. This data does not only include the band gap narrowing, but also the shift in the P donor states to the metal insulator transition ($3 \times 10^{18}$ cm$^{-3}$), where the donor band approaches, and then merges with the conduction band. Our samples were affected by this process. Altermatt et al. [91] have parameterized this effect, which would be seen as a shift to higher energies in luminescence spectra.

![Figure 7.22](image)

Figure 7.22: The band gap narrowing as inferred from photoluminescence measurements. The data taken as the difference in energy from the low energy edge of the $P_{NP}$ cluster peak to the $P_{NP}$ peak (squares), as shown by the arrow in Figure 7.20. For the triangles, the shift in the $P$ energy levels ($E_P$) was added to the data, leaving the band gap narrowing. The solid line is Equation 7.4, a phenomenological model of band gap narrowing.
towards the conduction band. This effect was removed from the trend by adding the parameterized shift to the P donor states [91] to the measured data, with the resultant band gap narrowing plotted as the triangles. The energy shift to the P<sub>NP</sub> cluster peak are shown in this figure. The data from the P<sub>TO</sub> cluster peaks (not shown) are consistently 4 meV larger than those of the P<sub>NP</sub> peaks, probably due to a phononic effect.

When the shift in the donor states towards the conduction band was considered, the shift in the energy of the P cluster peak followed the band gap narrowing of the implanted region over the range of doping in this study. Further studies over a larger range of doping densities should be performed to see if this trend continues. Also, implantation of other shallow dopants would clarify if the trend is species independent.

The consequence of this model for the use of photoluminescence to measure coupling between two donors is that the donor pairs would be required to be relatively isolated from other impurities to avoid the band gap narrowing effects of many impurity systems.

### 7.8 Conclusion

Photoluminescence in silicon is a process whereby above band gap illumination produces electron hole pairs which upon recombination produce near infra-red radiation. Spectroscopy of samples was possible because these excitons bind to donors, acceptors, impurities and dislocations, revealing their presence in the silicon lattice. The spectra obtained using the dispersion grating system suffered from laser heating issues whereas the Fourier transform instrument had no such problems.

Photoluminescence is a powerful tool for probing silicon. The background donor and acceptor concentrations of the silicon substrate used to produce the implanted samples was measured to an accuracy capable of distinguishing between a truly low doped crystal and one which was highly compensated. Resistivity measurements could not provide this information. Photoluminescence proved capable of identifying issues in the sample production process, by identifying the presence of copper and silver contamination, and of dislocations. Recent experiments in isotopically enriched <sup>28</sup>Si indicated that the Cu and Cu* centres contained at least four metal atoms.

Experiments on the phosphorus ion implanted samples revealed the presence of both isolated and interacting donors. Measurements on low energy atomic and molecular phosphorus ion implanted samples were not able to separate any effects due to the implanted ions from the higher background doping of the substrate. Higher energy and higher fluence implants showed an increase in the isolated donor photoluminescence signal as well as a broad peak originating from donor clusters. The trend in the intensity of the isolated donor signal indicated activation of the implanted ions, and was consistent with implantation simulations. Traps at the silicon–silicon dioxide interface were said to interact with the implanted phosphorus, opening up non-radiative
recombination pathways and quenching the bound exciton luminescence.

The P cluster peak shifted further away and to lower energies from the isolated donor peak as the density of the implanted donors increased. The trend in the energy shift was exponential to the mean nearest neighbour separation of the donors. The two donor models did not adequately reproduce the obtained data. The shift in the position of the P cluster peak was due to band gap narrowing from the charge carriers in the implanted region, and the peak shape followed the density of states from the formation of the donor band within the clusters. This model is consistent with the expectation of clusters larger than two dominating the atomic ion implanted samples. Measurement of two donor interactions may still be possible using photoluminescence on molecular ion implanted samples, but as the changes in the spectra due to the interactions would be small, samples with no background doping would be required, and the pairs would have to be relatively isolated so as not to form a many donor system and narrow the band gap.

Production of isolated donor pair samples would be required to properly study the two donor interactions experimentally. The use of low energy molecular ions in the future requires a better understanding of the effects which the oxide and any change traps at the interface exert on the bound excitons on donors in the vicinity of the interface, as closely couple pairs produced using this method would sit close to the surface. More care to eliminate these oxide defects by passivating or removing the oxide may also help. Samples could also be produced using the “bottom-up” method of STM lithography, though a large reduction in the sampling volume of the collecting optics would be required to measure the small areas produced using this technique. The use of a confocal-microscopy instrument could achieve the required sampling volume if the sensitivity is sufficient.
Chapter 8

Conclusion and Future Work

8.1 Conclusion

The primary goal of this thesis was to study the methods and techniques required to measure the exchange coupling between pairs of interacting phosphorus donors in silicon. This included the production and characterisation of implanted samples, the electronic Raman scattering technique, and the accurate measurement of sample temperature.

The research in this thesis was conducted in the context of an effort by the Centre for Quantum Computer Technology to build a quantum computing device in silicon (a system with the potential for the scale-up required to perform large scale and useful computations), and to answer specific concerns regarding the exchange coupling of phosphorus donors in silicon in the Kane type architecture. The study of molecular systems in the solid state was also of particular concern with the decrease in the size of transistors in integrated circuits, where interactions between a small number of impurities can drastically affect the properties of devices.

The interactions between donors in silicon were studied with the experimental techniques of electronic Raman scattering, electron paramagnetic resonance and photoluminescence spectroscopy. The ionisation energy of the phosphorus donor electron being $E = 45.5$ meV meant that samples had to be cooled by cryogenics. Samples of interacting donors were produced via ion implantation of atomic and molecular phosphorus ions followed by a rapid thermal anneal. Molecular implantation led to the production of samples containing isolated pairs of donors, whose intra-pair separation was controllable via the implantation energy.

The following is a summary of the conclusions from the work in this thesis.
8.1. CONCLUSION

8.1.1 Ion Implanted Samples and Simulations

To measure the exchange coupling between pairs of donors, samples with isolated pairs of closely separated donors had to be produced. This was achieved through the implantation of dimer molecular ions, where the implantation energy controlled the separation within the pair, and the implantation fluence controlled the distance between pairs. Calculations of the separation between atoms within both the atomic and molecular ion implanted samples, the number of implanted donors capable of interacting, and the size of the expected interacting donor clusters were performed and presented in Chapter 4. Simulations of the ion implantation process led to the following conclusions:

- Molecular dynamics simulations showed that the simulation of the low energy $\text{P}_2^+$ molecular ions were consistent with the simulation of two independent $\text{P}^+$ ions at half the total energy, and SRIM simulations gave consistent results with molecular dynamics simulations which led to the confident use of SRIM.

- Low energy implantation of $\text{P}_2^+$ ions produced samples of closely coupled pairs of atoms capable of measurable intra-pair interactions. The distribution of the atoms implanted as dimer molecules was substantially different from the atomic ion implants at low fluence, but indistinguishable at high fluence. The lower energy ion implantation would suffer from a loss of atoms into the oxide.

The characterisation of the samples using electron paramagnetic resonance was used to identify the existence of coupled donors. No coupled donors were detectable in the lower energy and low fluence molecular ion implants, the samples expected to show such interactions the strongest. The presence of isolated implanted donors was detected in all the samples. Measurements of the higher fluence atomic ion implants indicated the presence of coupled donors, with uncertainty as to the size of the clusters of donors involved.

8.1.2 Electronic Raman Scattering of P in Si

Chapter 5 reported on the attempt to measure the strength of the exchange coupling between pairs of donors with the use of electronic Raman scattering spectroscopy. Samples cryogenically cooled were measured in the visible and near infra-red.

- Electronic Raman scattering was observed from both donor doped and acceptor doped silicon for the first time in approximately 30 years using near infra-red Raman spectroscopy.
The effect of wavefunction overlap from donors in bulk doped silicon followed the trend reported previously, a broadening of the ERS peak and the peak energy tending to lower energies. For acceptors, the ERS peak was observed to broaden and shifted to higher energies, which was the first report of this behaviour.

Laser heating of the samples during measurement was identified, and the sample temperature was estimated from changes to the observed luminescence spectra. The heating did not adversely affect the observed ERS peak. Electronic Raman scattering from silicon close to 4.2 K was achieved with the use of low laser powers.

No electronic Raman scattering was observed from any of the phosphorus ion implanted silicon samples. This was due to the instrument lacking the sensitivity to the relatively few donors in these samples, and the possibility of ionisation of donors close to the surface. Thus, no measurements of the exchange coupling between two phosphorus donors in silicon was possible.

Electronic Raman scattering was not observed in the visible wavelengths, raising uncertainty in regards to the position of the virtual intermediate state used in Jain et al.’s theory. As well as the reduction in the scattering volume, the illumination of the sample with above band gap light would have produced an overwhelming number of bound excitons. The ERS would not have been possible due to this change in the electronic structure of the donors. The scattering process competes with the more efficient process of exciton generation and binding to donors.

A new path was proposed for the electronic Raman scattering transition, directly between the top of the valence band and the phosphorus donor states (both at the same point in $k$ space), which could lead to a resonance enhancement of the scattering cross section for excitation at this transition energy (1.15 eV), or the possibility of an excitonic resonance. The transition energy is in the near infra-red and close to the frequency of the Nd:YAG laser. The nature of this transition is still to be determined.

8.1.3 Silicon TO Phonon as a Local Temperature Probe

The proposal by Koiller et al. to measure the exchange coupling between neighbouring phosphorus donors requires the precise knowledge of the sample temperature, and as laser heating was an issue in the electronic Raman scattering experiments, an accurate local temperature probe of silicon was highly desirable. The changes to the silicon TO phonon with temperature due to crystal anharmonicity were studied so as to be used as a local temperature probe, with the possibility of concurrent use with other laser based measurements. Chapter 6 reported on experiments
performed on a high resolution instrument, measuring the changes to the shift and width of the phonon spectrum with temperature.

- An anomaly was observed in the frequency shift of the phonon with temperature which did not have a corresponding change in the width, and was not properly accounted for by the anharmonic phonon models. The phonon frequency shift consisted of an increase in the frequency of the phonon with an increase of the temperature from 4 to 60 K, and a decrease in the frequency with an increase in the temperature for temperatures above 60 K.

- The frequency shift in the low temperature region was fit to an empirical model in terms of the specific heat of a phonon mode. As the specific heat and thermal expansion of the crystal are closely linked through the Grüneisen parameter, this model fits in with the changes to the phonon dynamics of silicon occurring at these temperatures. The maximum in the frequency shift matches the minimum in the bulk Grüneisen parameter.

- The measured shift in the silicon TO phonon mode can be used as a local probe of temperature down to liquid helium temperatures, using an appropriate high resolution spectrometer.

### 8.1.4 Photoluminescence Spectroscopy of P in Si

A study of the silicon samples with photoluminescence spectroscopy was included in Chapter 7. The measurement of interactions between donors in silicon was attempted using photoluminescence spectroscopy. Photoluminescence was sensitive to defects and impurities in silicon, and was also used to gain information on the substrates and processing of the samples.

- Photoluminescence was found to be a useful method of sample production process quality control, with the observation of dislocations, and copper and silver contamination in the processed samples.

- The background phosphorus doping of the silicon substrates used for sample production was measured accurately for the first time showing variations in the impurity levels of substrate which were quoted as the same resistivity by the manufacturer. One had a higher doping level than the other, but the phosphorus donors and boron acceptors were closely compensated matching the resistivity of the purer sample. The background doping of the purest sample was measured to be: $2.5 \times 10^{12} \text{P cm}^{-3}$ and $1.3 \times 10^{12} \text{B cm}^{-3}$.

- Due to exciton diffusion, the background doping of the silicon posed a problem for the low energy and low fluence ion implanted samples, as the presence of the implanted atoms could not be observed above the background, hampering both the study of donor activation and
donor interactions. The loss of bound exciton luminescence signal was said to proceed via more efficient non-radiative recombination through interactions of the donors with interface states.

- For the higher energy and higher fluence samples, the photoluminescence measurements were the first time this technique has been applied to samples produced in this range. The number of isolated donors increased with an increase in the implantation energy consistent with the simulations. A broad peak due to phosphorus clusters was also observed which shifted away in energy from the isolated donor peak with respect to the increase in density of donors in the implanted layer.

- The observed donor interactions in the atomic phosphorus implanted samples produced an energy shift of the P cluster peak which followed an exponential trend. Modelling of the shift was performed with three different models: the Narita model of exciton hopping, the Openov model of a shift in P states, and the band gap narrowing. The two donor models did not adequately reproduce the shift and width of the peak. Clusters of more than two interacting donors were expected in our samples. Expanding the calculation to more than two donors would have been too complex, but was also not necessary as the multi-particle model of band gap narrowing and donor band formation adequately explained the data.

8.1.5 Summary

In summary, the observation of the effects of donor interactions (between many donors) was possible using optical techniques, but the scaling down of the measurement to the few atom level, and the measurement of ensembles of isolated pairs of donors proved to be difficult.

8.2 Future Work

8.2.1 Electronic Raman Scattering of P in Si

- In the short term further work should continue on the measurement of electronic Raman scattering of phosphorus in silicon, with the aim of applying Koiller et al.’s proposal to measure the strength of the exchange coupling between donors in an ensemble of pairs. The observation of the transition, with the new Renishaw spectroscopy instrument, for the first time in approximately thirty years shows the measurement of the exchange coupling between ensemble of pairs should be achievable, as long as the relevant samples can be produced, and with the use of surface enhancement techniques.
8.2. FUTURE WORK

- Samples of low energy molecular implants, while problematic due to a loss of signal, could prove useful if the causes of the loss of signal were identified. Study of the interaction between the donors and the charge traps at the silicon–silicon dioxide interface should be attempted. A low temperature epitaxial overgrowth of silicon may also help to improve the signal from these samples, as this would put a distance between the donors and the interface states. In the long run, samples of isolated pairs produced with STM lithography should be used to study interactions between donors.

- Further study of the possible resonance of the ERS with the dopant states in the near infrared should be attempted.

- Further theoretical study on the shift in the energy of the boron acceptor ERS peak with increasing concentration should be attempted.

8.2.2 Silicon TO Phonon as a Local Temperature Probe

- Measurements of the temperature dependence of the zone centre optic phonon with Raman scattering should also be attempted on other diamond type semiconductors, at high resolution, and down to 4 K to search for any similar anomalous behaviour to that observed in silicon. Further modelling should also be undertaken to better understand the observed trend in the frequency shift of the silicon TO phonon with temperature.

8.2.3 Photoluminescence Spectroscopy of P in Si

- Photoluminescence spectroscopy scaled down with the use of confocal microscopy would provide a way of reducing the number of donors sampled, and also hopefully reduce the influence of the background doping of the substrate. Confocal microscopy is selective in depth, so the influence on the spectrum of the bulk of the silicon substrate would greatly be reduced. The new Renishaw instrument including the array detector could be used. With the recent development of InGaAsP avalanche photodiodes, the collection of weak signals at wavelengths close to 1 µm is possible [174] and could be attempted.

- The influence of the background phosphorus signal on the photoluminescence study donor activation and interacting donors could be eliminated by the implantation of other donor species less prevalent in silicon such as arsenic ions.

- Difficulty in optically detecting the signal from the donors limits how few donors can be measured. Ultimately, to measure donors at the few atom level, electrical detection could be applied. Photoluminescence excitation spectroscopy can directly populate excitons onto the
donors, and with a magnetic field, directly onto the nuclear spin state of choice as demonstrated by Yang et al. [32]. The predominant decay path for the bound excitons is the production of electrons via the Auger process, making the electrical detection of the decay of a single bound exciton a tantalising prospect. The formation and recombination of a bound exciton on a phosphorus donor could be measured via a silicon single electron transistor, which can work at temperatures up to 4.2 K [175] compatible with optical cryostats.
Appendix A

More Electronic Raman Scattering Experiments

Reported in this appendix are the electronic Raman scattering experiments performed on silicon doped with phosphorus using the visible wavelength Dilor system, and the near infra-red system using the single channel detector. While their results were negative and were not included in Chapter 5, they are included as an appendix as a record of the work performed.

A.1 Visible Wavelength Raman Spectroscopy

The first Raman spectroscopy instrument available and used in this work was a Dilor XY micro-Raman system operating in the visible wavelengths, and described in Chapter 3. Experiments were performed at liquid helium temperatures using a cold finger type cryostat on samples of: blank 5–7 kOhm-cm silicon, bulk phosphorus doped silicon of 1–10, 0.1 and 0.001 Ohm-cm resistivity and bulk boron doped silicon of 20–70, 4–8 and 0.8–1.2 Ohm-cm resistivity. The phosphorus doping concentration range of the sample set was from about \(1 \times 10^{15} \text{ cm}^{-3}\) to \(1 \times 10^{17} \text{ cm}^{-3}\) in semiconducting silicon, and \(7 \times 10^{19} \text{ cm}^{-3}\) in metallic silicon. The boron doped samples had a doping density of about \(5 \times 10^{14}\) to \(2 \times 10^{16} \text{ cm}^{-3}\). Samples were aligned with their [001] axis along the polarisation directions of the laser. Experiments were performed with 514 nm and 488 nm illumination using various laser powers and integration times.

Evidence of the donor or acceptor electronic Raman scattering peak was not observed in any of the measured spectra. Figure A.1 displays spectra taken at long integration times and high laser powers (488 nm with 100 mW of illumination and 2400 s of integration time). Compared is the 0.1 Ohm-cm phosphorus doped silicon with the blank silicon and a reflection off the gold cryostat stage providing a “mirror” spectrum. The laser was polarised either “vertically” or “horizontally”
A.1. VISIBLE WAVELENGTH RAMAN SPECTROSCOPY

Figure A.1: Visible wavelength Raman spectra of 0.1 Ω cm Si:P, Blank silicon and the gold cryostat stage. (100 mW laser at 488 nm, 2400 s integration time, $T_{\text{cryo}} = 4.2$ K). Spectra displaced vertically for clarity.

(parallel or perpendicular) to the sample axis. The silicon TO phonon peak was large and well resolved in each spectrum and at least two orders of magnitude larger than anything associated with noise. Figure A.2 is a close-up of the low wavenumber region. The tail of the laser was clearly observed, on top of which were oscillations that match up at the same energy on all of the silicon samples as well as the gold stage. A peak at close to 105 cm$^{-1}$ was observed in both the phosphorus doped silicon and the blank silicon, thus ruling out the possibility of this peak originating from the electronic Raman scattering transition. It was possible these oscillations were due to thin film interference by reflections of the laser from the sample surface and the quartz cryostat window. The above measurements pushed the instrument to the limits of its detection.

It is worth noting that the experimental conditions shown in the figures used a very high laser power, with the potential to heat the silicon. The ERS transition was also not observed with lower laser powers.

Comparing these spectra with that in Figure 5.1 from Jain’s work using the 1064 nm laser, we would have expected to see a peak at 105 cm$^{-1}$ at least half as large as the TO phonon peak (ignoring the $\omega^4$ increase in phonon scattering cross section). The theory on electronic Raman scattering discussed earlier contains a resonance enhancement factor, $R_{12}$ (Equation 2.9), where illumination in the visible spectrum should provide advantages in cross section over the near infra-
APPENDIX A. MORE ELECTRONIC RAMAN SCATTERING EXPERIMENTS

Figure A.2: Visible wavelength Raman spectra of 0.1 Ω cm Si:P, Blank silicon and the gold cryostat stage. (100 mW laser at 488 nm, 2400 s integration time, $T_{cryo} = 4.2 \, K$). Spectra displaced vertically for clarity.

red. The direct band gap at the conduction band minimum has an energy of $E_G = 3.8 \, eV$, the Ar-ion laser had an energy of $E_{488\, \text{nm}} = 2.54 \, eV$ and the Nd:YAG laser $E_{1064\, \text{nm}} = 1.165 \, eV$, giving the Ar-ion laser a resonance advantage $R_{12} = 1.8$ over the Nd:YAG with an $R_{12} = 1.1$. These results are consistent with the fact that there have been no reports in the literature of the observation of Raman scattering using above band gap excitation.

In classical scattering, the frequency to the power of four dependence of the scattering cross section, gives an advantage to scattering in the visible wavelengths over the near infra-red, but this is not the case in scattering from electronic states. The resonance enhancement factor should have also improved the signal in the visible wavelength measurements. As no previous work had observed the transition outside of the near infra-red it is to these wavelengths that the experimentation on donor states in silicon turned. Thoughts on why the ERS transition was not observed in the visible spectrum are discussed Section 5.4.

A.2 Near Infra-Red Raman Spectroscopy

Once the (single channel) near infra-red Raman instrument (described in Chapter 3) was commissioned, experiments on silicon samples cooled by liquid helium were performed. The samples
measured were those of the bulked doped silicon described in the previous section, as well as a set of phosphorus implanted silicon including $P^+$ and $P_2^+$ implanted ions at energies from 5 to 15 keV and fluences from $1 \times 10^{10}$ to $1 \times 10^{13}$ cm$^{-2}$. This provided ensemble distributions of isolated atoms, close pairs and metallic samples.

The valley-orbit electronic Raman scattering transition from phosphorus in silicon was not observed in the spectra from any of the samples measured with this instrument, neither bulk doped nor implanted phosphorus. The following is a discussion of the difficulties encountered in the Raman spectroscopy measurement. These difficulties included instabilities in the instrument during the long scanning times the single point detector required, laser heating of the samples and the associated luminescence, and spectral artefacts from the laser emission.

A.2.1 Instrument Stability

The detector employed was a cooled InGaAs single point detector, which limited collection to a single point in the spectrum at each time step. Unlike a silicon CCD or an array detector where, say 512 points in the spectrum are collected simultaneously, the single point detector must measure each of these points separately. To cover the same section of the spectrum at the same resolution and collection time as a 512 point array, the single point detector would take 512 times as long. This disadvantage severely limited the collection time per sample, especially when running with expensive cryogenics.

Figure A.3 shows the spectra collected from a phosphorus ion implanted silicon sample. The lower spectrum was taken with 100 ms/point integration times and normalised to the upper scan taken at 1500 ms/point with $3 \times$ averaging at each point. The TO phonon peak area scaled linearly with integration time. The lower scan, at a shorter integration time, had larger background noise than the longer scan when considering the higher frequency noise. The longer scan shows larger ‘drift’ in the baseline, not quick changes in baseline level but changes over a longer time scale such as the drop between 150 - 200 cm$^{-1}$ and then a rise up to 270 cm$^{-1}$. The higher frequency component to the background noise was relatively smaller for the longer scan than for the shorter scan. Comparison of the noise level between the samples was achieved by taking the ratio of the TO peak height to the root mean square (RMS) noise of the background. The TO-signal to RMS noise of the lower (less time) scan was 29 and the upper was 166. By taking into account the baseline drift of the longer scan the ratio of TO signal to drift became 33. The averaging of the signal at each point had reduced the noise, but the longer scan time had resulted in a drift to the baseline which was comparable to the noise in the shorter scan. RMS noise was measured over a short range of background data. The baseline drift was taken as the larger jumps in what presumably should have been a flat background. The structure of the upper scan did not match any peaks expected from a Raman scattering measurements of silicon.
Figure A.3: Near-IR Raman spectra of silicon implanted with 7 keV $P^+_2 \times 10^{11} \text{ cm}^{-2}$ at various integration times. Lower spectrum: 100 ms/point integration time with no averaging and scaled $15\times$. Upper spectrum: 1500 ms/point integration time and $3\times$ averaging. (450 mW at 1064 nm laser illumination, 600 g/mm grating, 250 µm slits, and $T_{\text{cryo}} = 4.2 \text{ K}$). To save time, upper spectrum was collected over two separate ranges. Spectra displaced vertically for clarity.

A particularly bad example of instability during a long scan is shown in Figure A.4. The lower scan had been taken at 100 ms/point with $3\times$ averaging and the upper scan at 2000 ms/point with $3\times$ averaging. The shorter scan had been scaled by $20\times$ to aid in comparison. The slope in the spectrum was due to silicon luminescence produced by laser heating of the sample. The silicon TO phonon line is clear in the lower (shorter) scan but is obscured in the upper (longer) scan. The ratio of the TO phonon intensity to RMS noise for the shorter scan was 20 and for the longer scan 24, both are comparable and no advantage was gained by using a longer scanning time. The total scanning time for the spectra shown were: lower, $t \approx 1 \text{ minute}$ and upper, $t = 60 \text{ minutes}$. During the time taken for the longer scan, the temperature of the sample may have been fluctuating leading to the jumps in the luminescent baseline, and the microscope focus could have drifted due to movements in the sample or stage. These results led to questions over the stability of the instrument during long scans, thus limiting the sensitivity of the instrument to resolve small signals by limiting the collection time of each scan.
A.2. NEAR INFRA-RED RAMAN SPECTROSCOPY

Figure A.4: Near-IR Raman spectra of 0.1 Ωcm phosphorus doped silicon at various integration times. Lower spectrum: 100 ms/point integration time with 3× averaging, and magnified 20 times. Upper spectrum: 2000 ms/point integration time and 3× averaging. (40 mW at 1064 nm laser illumination, 600 g/mm grating, 250 μm slits, and $T_{\text{cryo}} = 4.2$ K). Spectra displaced vertically for clarity.

A.2.2 Laser Heating

Illumination of a silicon sample held at 4.2 K with a 1064 nm Nd:YAG laser produces a minimal amount of band edge luminescence since the energy of the laser $E_{1064} = 1.165$ eV is sub-silicon band gap, $E_G(4 \text{ K}) = 1.17$ eV. The absorption of this laser by silicon is minimal, at approximately 4 cm$^{-1}$ [51], but still enough to increase the temperature of the sample at sufficient laser powers. As the temperature increased, the band gap decreased increasing the absorption of the laser, and increasing luminescence. Figure A.5 shows the effect of an increase in laser power illuminating a blank silicon sample attached to a liquid helium cold finger type cryostat. As the laser power was increased, the intensity of luminescence produced increased. The magnitude of the silicon TO phonon Raman scattering peak also increased, but the luminescence increase masked some of the intensity of the TO phonon peak. The Nd:YAG laser became above band gap excitation at silicon sample temperatures of > 100 K (see Figure 2.7). This band edge luminescence is broad, at least 500 cm$^{-1}$, and matches the line position and width seen in the literature for silicon samples held at approximately 100 K [176].

Our experimental setup was susceptible to local heating of the samples by the laser because of
Figure A.5: Near-IR Raman spectra of blank silicon at various laser powers. From the lower to upper spectrum: 45 mW, 105 mW, 250 mW and 500 mW. The broad luminescence background is an indication of laser heating of the sample. (1064 nm laser illumination, 100 ms/point integration time, 600 g/mm grating, 250 µm slits, and $T_{\text{cryo}} = 4.2$ K).

the cold finger type cryostat design. As discussed in Chapter 3, a large temperature gradient can develop between the front surface of the sample, where the laser was illuminating, and the back which is in thermal contact with the cold finger. Other factors that contributed to the rise in the sample temperature were: the cooling power of the helium (related to its flow), the thermal contact between the sample and the cold finger mediated by either thermal grease or indium, the focusing of the laser, and the sample size. The presence of such broad luminescence indicated an elevated sample temperature but the absence of luminescence did not necessarily mean no laser heating as luminescence can be quenched by various defects and surface conditions. Luminescence in our experimental setup could be eliminated by working at lower laser powers, which also reduced the intensity of any ERS signal, and necessitated longer collection times.

Comparing the spectra by scaling to laser power, Figure A.6 shows an improvement in signal to RMS noise from the increase in incident light. The 45 mW spectrum had a S/N ratio of 13, the 105 mW 17, the 250 mW 26 and the 500 mW 36, but when the jumps in the baseline were taken into account the TO phonon signal to baseline jump ratio was 10 for all the spectra.

Elevated temperatures thermally depopulated the ground state of the phosphorus donor electron and thus reduced the intensity of the peak. Jain et al. [51] saw signals from samples at
A.2. NEAR INFRA-RED RAMAN SPECTROSCOPY

Figure A.6: Near-IR Raman spectra of blank silicon at various laser powers. From lower to upper spectrum: 45 mW, 105 mW, 250 mW and 500 mW. Each spectrum has been scaled by dividing by the laser power. (1064 nm laser illumination, 100 ms/point integration time, 600 g/mm grating, 250 µm slits, and $T_{\text{cryo}} = 4.2$ K). Spectra displaced vertically for clarity.

temperatures estimated to be up to 62 K, and since no luminescence was observed in their spectra the samples were most likely measured at less than 100 K.

A.2.3 Laser Emission

The misalignment of the collection optics and filters could leak lines into the spectrum which were not of sample origin. These lines normally originate from the laser and were reduced in intensity, and hopefully completely removed by the inclusion of laser line filters as discussed in Chapter 3. Figure A.7 shows an artefact signal at around 105 cm$^{-1}$, the position of interest for electronic Raman scattering from phosphorus in silicon. As this line was observed in both the spectrum from the blank silicon sample and off the gold stage, it was not the ERS line, and most likely a reflection of a line originating from the laser. This same line was observed from the spectrum of a phosphorus ion implanted sample, shown in Figure A.8. Focusing of the microscope objective deeper into the sample reduced the intensity of the line, most likely by reducing the reflection of the laser off the sample surface. As this line was the same order of magnitude as the TO phonon line and in the right spectral range for the ERS transition, care was taken to discount this artefact signal by comparing the signal at the time to the silicon blank and a mirror. Re-alignment of the
Figure A.7: Near-IR Raman spectrum of blank silicon and gold cryostat stage showing spurious signal (artefact). (50 mW laser at 1064 nm unpolarised, 300 ms/point integration time, 600 g/mm grating, 0.5 mm slits, and $T_{\text{cryo}} = 4.2 \text{ K}$).

optics removed this signal as did rotation of the stage, again indicating this artefact from the laser entered the spectrometer through a reflection.
Figure A.8: Near-IR Raman spectrum of silicon implanted with 5 keV $P_2^+$ ions showing spurious signal (arrestact), as the objective is focused deeper into the silicon. (50 mW laser at 1064 nm, 300 ms/point integration time, 600 g/mm grating, 0.5 mm slits, and $T_{\text{cryo}} = 4.2$ K). Spectra displaced vertically for clarity.
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