
Donor activation and isotopic enrichment of silicon via ion implantation for quantum computing

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Abstract

Quantum computers are set to revolutionise technology by harnessing the immense promise of quantum mechanics, the law governing nature on the atomic scale, to enable a dramatically increased efficiency for certain algorithms over their classical counterparts. By storing and manipulating information on quantum bits (qubits), which can exist in a superposition of 0 and 1 at the same time and can be entangled with each other, instead of classical bits, which are strictly 0 or 1, certain problems that are intractable with classical computation can be solved. To realise a qubit, a quantum system that exists in two or more states, such as a spin in a magnetic field, is required. Group V donors in silicon (Si) are promising qubit candidates that can store quantum information in both the spin of the donor nucleus and the donor electron that it binds by the Coulomb potential. Si offers an ideal platform due to its isotopic composition of predominantly spin-zero nuclei (over 92% is ^{28}Si with nuclear spin $I = 0$), that can provide a noise-free host lattice, and the wealth of knowledge accumulated in the microelectronics industry. The most versatile method for introducing donors in Si is ion implantation, a foundational technique of the information technology industry that has already demonstrated the production of long-lived phosphorus (P) donor qubits. This method is explored in this thesis.

The bismuth (Bi) donor offers some useful properties for quantum devices, such as an increased quantum memory, clock transitions and the potential to couple to superconducting flux qubits. To fabricate a quantum device that employs Bi, it is necessary to implant and activate a Bi donor in Si. Here, the optimum implantation and thermal annealing strategy is determined to maximise the operational yield of near-surface Bi donor qubits by repairing the Si crystal damage and electrically activating the donor, evidenced by the measurement of Bi

donor electron spin resonance. A further critical issue in donor qubit fabrication is the depletion of the nuclear spin-1/2 ^{29}Si isotope to extend coherence times, which would be beneficial to be performed routinely. Accordingly, a method of isotopically enriching a surface layer of natural Si via sputtering during the high fluence implantation of $^{28}\text{Si}^-$ ions was developed. This technique increases the accessibility of producing spin-free ^{28}Si material by requiring only a conventional ion implanter and naturally abundant sources. The successful recrystallisation of this ^{28}Si layer and the demonstration of increased coherence times for implanted P donors make this a promising technique for integrating into the fabrication of implanted donor qubits. Finally, the measurement of the full extent of the ^{29}Si depletion on the coherence time requires a low concentration of donors implanted into this ~ 100 nm thick surface layer of ^{28}Si . Therefore, a high sensitivity technique capable of probing a small number of spins is essential. This challenge is addressed by the design and implementation of a low-temperature electrically detected magnetic resonance (EDMR) system, capable of measuring spin transitions of donor electrons in Si with a sensitivity at least 5 orders of magnitude greater than for conventional electron spin resonance systems. In future, this will allow for the coherence times of donors implanted into our enriched ^{28}Si layers to be determined from the linewidth of EDMR signals. This thesis lays the foundations for exploiting Bi donor clock transitions in qubit devices and addresses the challenge of providing an isotopically enriched ^{28}Si matrix for donor qubits that is shown to extend qubit coherence times and thus makes progress towards the scalable fabrication of a donor spin quantum computer.

Statement of Originality

This is to certify that:

- This thesis comprises only of the author's original work, except where indicated otherwise.
- The thesis is no more than 100,000 words.

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List of Acronyms

AFM Atomic Force Microscopy

CMOS Complementary Metal-Oxide-Semiconductor

CVD Chemical Vapour Deposition

CW-ESR Continuous-Wave Electron Spin Resonance

EBL Electron Beam Lithography

EDMR Electrically Detected Magnetic Resonance

ESR Electron Spin Resonance

FFT Fast Fourier Transform

FIB Focussed Ion Beam

FWHM Full Width at Half Maximum

HPC High Performance Computer

HRTEM High-Resolution Transmission Electron Microscopy

IBIC Ion Beam Induced Charge

MBE Molecular Beam Epitaxy

NISQ Noisy Intermediate-Scale Quantum

NMR Nuclear Magnetic Resonance

PAI Pre-Amorphisation Implant

RBS Rutherford Backscattering Spectrometry

RTA Rapid Thermal Anneal

SEM Scanning Electron Microscope

SET Single Electron Transistor

SIMS Secondary Ion Mass Spectrometry

SNICS Source of Negative Ions by Caesium Sputtering

SPE Solid Phase Epitaxy

SQUID Superconducting Quantum Interference Device

SRIM Stopping and Range of Ions in Matter

TEM Transmission Electron Microscopy

TOF-SIMS Time-Of-Flight Secondary Ion Mass Spectrometry

TRR Time-Resolved Reflectivity

UHPS Uniform High Purity Silicon

UHV Ultra High Vacuum

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Chapter 1

Introduction to Quantum Computing with Donor Spins

1.1 Introduction

The fundamental theory describing the behaviour of particles and their interactions on the atomic and subatomic scale is given by quantum mechanics. This theory is radically different to the classical description of nature on the macroscopic scale. Exploiting these differences in new quantum technologies is a key motivation for this thesis. The properties of a bound quantum system are quantized into discrete values, for example electrons orbit the nucleus with discrete energy levels in the Bohr model of the atom which can explain the lines in atomic absorption and emission spectra [1], as opposed to the continuous spectrum we are familiar with in our human-scale existence. Wave-particle duality [2] describes how atomic and subatomic ‘particles’ have wave-like properties, as evidenced by the interference pattern created by electrons [3] and atoms [4] travelling through Young’s double slits, and how light waves behave as if composed of particles, as demonstrated in the photoelectric effect [5] in which individual photons impart energy onto electrons allowing them to escape the surface of a metal. Indeed, Heisenberg’s uncertainty principle [6] states that there is a fundamental limit to how precisely we can predict the values of certain pairs of physical quantities, such as position and momentum, from a complete set of initial conditions. Instead of being able to predict the

exact location of a quantum particle, as allowed in classical mechanics using Newton's laws of motion, one can only predict its probability distribution, described by the wavefunction, using the time-dependent Schrödinger equation [7].

The linearity of the Schrödinger equation implies that any linear combination of solutions is also a solution. This leads to the quantum principle of superposition, in which a quantum system can exist in more than one state at the same time prior to measurement. The juxtaposition of this with classical physics is made obvious by the famous thought experiment in which Schrödinger's cat is both dead and alive at the same time [8]. Quantum entanglement is another key phenomenon which arises in quantum mechanics but is absent in classical mechanics. Entanglement is generated when a pair of quantum particles are produced or interact such that the quantum state of each particle cannot be described independently of the other. Upon measurement, this leads to a correlation between the physical properties of each particle, even if they are separated by vast distances such that it would be impossible for information, limited by the speed of light, to travel between the two. Einstein referred to this as 'spooky action at a distance' as it violates the local realism view of causality [9].

In 1982, Richard Feynman suggested harnessing these features of quantum physics to make a new type of computer, capable of simulating quantum systems [10], summarised with his famous quote "Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical". Along with David Deutsch [11] and others, he inspired physicists to pursue the development of quantum computers. In quantum computation, sophisticated gymnastics are routinely performed on the physical properties of quantum systems, for example spin, during the running of a quantum algorithm. This provides the best real-world application for shining a light on the complexities of the quantum realm and holds the key to advancing our understanding of quantum systems through simulation.

The realisation of classical bits has rapidly progressed from the on/off states of vacuum tubes, through semiconductor transistors and integrated circuits to microprocessors where 14 nm technology is commonplace [12], with the miniaturisation of transistors following Moore's Law [13]. This miniaturization opens a pathway to devices of a size necessary to exploit quantum phenomena in the solid state. Quantum computing would revolutionise technology, with

quantum algorithms, such as Shor’s Factorisation [14] and Grover’s Search algorithm [15], capable of performing with quantum speedup over their classical counterparts. This increased computational efficiency opens up new possibilities for solving certain problems that were previously intractable due to their heavy demands on computational time. Modelling complex molecules to aid drug discovery, optimising multi-variable problems, predicting the progression of chaotic systems with increased accuracy and artificial intelligence via machine learning are just a few examples of promising quantum computing applications.

Donors in silicon have attracted a large amount of attention in recent years as a platform for quantum computers due to their long coherence times, atomic scale qubit confinement, the wealth of knowledge on silicon fabrication techniques collected by the multi-billion dollar Complementary Metal-Oxide-Semiconductor (CMOS) industry and the fact that they comprise a two-for-one qubit system, with both the orientation of the donor electron and nuclear spins with respect to the applied magnetic field storing quantum information. The full initialisation, control and readout of near-surface phosphorus donors implanted in silicon has been demonstrated using surface nanocircuitry [16, 17]. Deterministic ion implantation offers a promising fabrication solution for donor qubits as it could produce scalable arrays of donor qubits by implanting single ions in a step-and-repeat fashion and making use of conventional ion implanters, commonplace in the semiconductor doping industry [18]. The scalability of this technique will become increasingly important in the future when error correction, requiring many physical qubits to make one logical qubit robust to noise-induced decoherence, can be implemented to develop a large-scale fault-tolerant quantum computer which requires millions or billions of qubits to solve practical problems [19].

Ion implantation is also compatible with the implantation of all 4 of the stable group V donors in silicon. Although phosphorus in silicon has received the most attention, the use of alternative donor species offer increased possibilities over phosphorus, with bismuth offering the largest number of energy levels for increased quantum memory [20], clock transitions for increased coherence times [21], the possibility of coupling to superconducting flux qubits to form a hybrid qubit system and an increased placement precision. However, when implanted in silicon, the large mass of bismuth results in an increased amount of silicon crystal lattice

damage and requires an appropriate post-implantation thermal annealing strategy to repair the damage and activate the donor such that it is substitutional in the lattice with the donor electron bound to the nucleus by the Coulomb potential [22].

Quantum systems are incredibly fragile to noise in their environment which causes a loss of quantum information through decoherence. The ‘semiconductor vacuum’ provided by a single crystal of ^{28}Si , an isotope with zero nuclear spin, offers an ideal noise-free environment for donor qubits to reside in. The dominant decoherence mechanism in natural silicon is due to the presence of the ^{29}Si isotope, with a natural abundance of around 5% and a nuclear spin of $1/2$, which causes variations in the local magnetic field experienced by the donor due to dipole-induced fluctuations [23]. The isotopic enrichment of silicon has demonstrated dramatically increased donor coherence times for both the electron and nuclear spins [24]. This offers promise for the high fidelity operation of silicon donor qubits with the decreased error rate reducing the overhead in the number of physical qubits required to implement error correction.

1.2 Thesis Structure

The main topic of this thesis concerns the ion implantation of donors into silicon, with the overarching aim of developing this technique for quantum computing applications. A group V dopant is required to be electrically activated in Si, with its unpaired electron bound to its nucleus by the Coulomb potential, in order to form an operational qubit with the donor electron. To this end, post-implantation annealing strategies were investigated to maximise the electrical activation yield of donors in silicon, to maximise the qubit fabrication yield in future quantum computing devices. In order to increase qubit coherence times for high fidelity quantum computing, donors require the noise-free surrounding environment of the ‘semiconductor vacuum’, consisting of a single crystal of the spin-free isotope ^{28}Si . A method of isotopic enrichment of Si, requiring only conventional ion implantation technology and natural silicon, was developed in this work. A low-temperature quantum measurement system capable of probing donor electron spin transitions was designed and implemented and the sensitivity was characterised by measuring transitions from P donors in a background-doped Si substrate. This electrically

detected magnetic resonance system should allow for the future extraction of coherence times for donors implanted into the isotopically enriched layers of ^{28}Si produced by our method.

The structure of this thesis is as follows:

Chapter 1 provides a brief introduction to quantum computers and their potential to revolutionise modern technology. Donor spins in silicon are introduced as a promising qubit candidate along with the challenges involved in fabricating such a quantum system. The work undertaken in this thesis towards this aim is summarised.

Chapter 2 gives an overview of the theory behind this topic of quantum computing, with donors in silicon given as a promising method of qubit realisation. Relevant experimental results for milestone achievements in the initialisation, control and readout of phosphorus donor spins in silicon are given, including a selection of quantum computing architectures for this platform. Ion implantation is introduced as the method of choice for fabricating donor qubits in silicon, along with thermal annealing to repair the crystal lattice damage and activate the donors. Finally, the theory behind electron spin resonance and nuclear magnetic resonance is given, as both are important for donor qubit control and the former is used in this work to probe the magnetic environment of the donor electrons. The relevant background theory, along with a review of previous experimental work, is expanded upon in each of the experimental chapters 4-6.

Chapter 3 describes the main experimental methods utilised in this work. The processes involved in fabricating donor in silicon samples and devices, including ion implantation, annealing and surface oxide growth, are described. Principles behind the characterisation techniques used to assess the material properties post ion implantation, including composition, recrystallisation kinetics, electrical properties and crystal quality, are given, along with the quantum measurement of donor electron spin transitions using electron spin resonance and electrically detected magnetic resonance. All of the experimental parameters used in this thesis are given in the relevant experimental chapters 4-6.

Chapter 4 details the experimental work undertaken in this thesis towards assessing the viability of bismuth as a donor spin qubit in silicon for quantum computing applications. The

optimum implantation and annealing strategy was determined for near-surface Bi implanted at fluences above and below the Si amorphisation threshold by determining the electrical activation yield, substitutional fraction and diffusion of Bi donors. Electron spin resonance was used to confirm that a substantial fraction of near-surface implanted Bi donors were electrically activated following a post-implantation anneal.

Chapter 5 develops a new technique for the isotopic enrichment of silicon for the purpose of providing a low-noise environment for donor qubits to extend their coherence time. The surface layer of a natural Si substrate is isotopically enriched by sputtering during the high fluence implantation of $^{28}\text{Si}^-$ ions. TRIDYN simulations were used to predict the level of isotopic enrichment achieved by the implantation of ^{28}Si at various energies and fluences and to investigate various sources of contamination during this process. The depletion of the ^{29}Si and ^{30}Si isotopes and level of impurities introduced by high fluence $^{28}\text{Si}^-$ ion implantation were measured, along with the crystal quality of this isotopically enriched layer after solid phase epitaxy. The coherence time of P donors implanted into an enriched ^{28}Si layer was determined using a Hahn echo pulsed Electron Spin Resonance (ESR) measurement.

Chapter 6 reports on the design and implementation of an electrically detected magnetic resonance system that is capable of measuring donor spin flips via a change in substrate photoconductivity with high sensitivity. Electrically Detected Magnetic Resonance (EDMR) devices with an on-chip microwave stripline and source and drain electrodes were fabricated on background-doped Si:P to optimise the measurement by maximising the EDMR signal to noise ratio by adjusting various experimental parameters. The phenomenon of donor freeze out was observed by measuring at a range of temperatures and the dependence of the EDMR signal amplitude and linewidth on the microwave power and modulation amplitude, used for lock-in amplification, were determined. This work makes advances towards being able to probe the coherence time of donors implanted into the isotopically enriched ^{28}Si layers produced in chapter 5.

Chapter 7 concludes with the key achievements and provides suggestions for further work for each of the areas of experimental research undertaken in chapters 4-6. Finally, the progress this research contributes towards the ultimate goal of fabricating a scalable quantum computer

using the ion implantation of donors in silicon is given.

Chapter 2

Background Theory

This chapter provides a theoretical standing to provide context to the key results of this thesis. Quantum computing is introduced, with the donor in silicon qubit highlighted as a promising method of realisation from a zoo of alternative qubit candidates. The spin Hamiltonian, from which energy levels are derived, operational procedure, decoherence mechanisms and possible quantum computing architectures are described for the donor system. The procedures for fabricating such a system, using donor ion implantation and annealing, are outlined. This chapter is concluded with the principles of electron spin resonance; a method used for quantum measurement of donor spin transitions in this thesis. Additional theory is given in the experimental chapters 4, 5 and 6 that provides more specific information on the Bi donor spin qubit system, isotopically enriched ^{28}Si and electrically detected magnetic resonance of P donors in Si, respectively.

2.1 Quantum Computing

Moore's Law, the trend in miniturization of microprocessors that sees the transistor count approximately double every two years, is coming to an end as we are reaching the limits to how small we can make transistors before heat dissipation and quantum effects significantly disrupt their operation. Fortunately, we can look towards quantum mechanics to allow for the future solving of problems which are currently intractable. Quantum technology is not the next

step in Moore’s Law, but a whole new journey [25]. Quantum computers were first proposed in the 1980s, with Paul Benioff giving the first description of a quantum mechanical Turing machine [26], Richard Feynman proposing a basic model of a quantum computer that would have the power to simulate quantum systems more efficiently than a classical computer [10] and David Deutsch describing the first universal quantum computer [11]. Since then, much effort has been put into the physical realisation of a quantum computer, with many different types of quantum hardware suggested. Companies such as Google and IBM have already made headway by producing quantum computing chips with over 50 superconducting qubits but only time will tell what form a large-scale universal quantum computer will ultimately take.

2.1.1 The Qubit

Classical computers process and store information as a binary string of 0s and 1s using classical bits. Mathematically, the classical bit can be represented by one of the two states:

$$0 \text{ or } 1 \tag{2.1}$$

Analogously, quantum information is stored on quantum bits, or ‘qubits’, which can exist as a linear superposition of both states of a two-level quantum system, the ground state $|0\rangle$ and the excited state $|1\rangle$, at the same time. The normalised qubit state can be represented using complex numbers as:

$$|\Psi\rangle = \cos \frac{\theta}{2} |0\rangle + e^{i\phi} \sin \frac{\theta}{2} |1\rangle \tag{2.2}$$

The space encompassed by the states described by the two degrees of freedom, the real numbers θ and ϕ , corresponds to the surface of a unit sphere; known as the Bloch Sphere. By convention, the $|0\rangle$ state is represented by the $+\hat{z}$ unit vector, while the $|1\rangle$ state is represented by the $-\hat{z}$ unit vector [27].

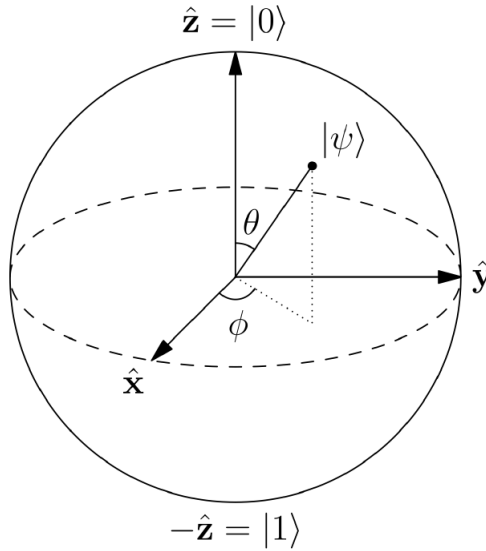


Figure 2.1: Bloch sphere representation of a qubit state.

The power of quantum computers over classical computers is realised by entangling multiple qubits. A classical register of N bits has 2^N possible configurations, however, only 1 of these configurations can be stored at one time. Similarly, a quantum register of N qubits has 2^N different basis states. However, this register can store superpositions of all of these states simultaneously. Entanglement of the qubits can produce states that are difficult to create on a register of N classical bits, leading to certain algorithms with increased efficiency over their classical counterparts. Put mathematically, the logical operations available to N qubits is described by a special unitary group known as $SU(2^N)$ (a Lie group of $2^N \times 2^N$ unitary matrices with determinant 1), which contains more elements (including those which create entanglement) than the comparable group $SU(2)^{\otimes N}$ (a group of $2^N \times 2^N$ matrices formed from the Kronecker product of N 2×2 unitary matrices with determinant 1) for N unentangled qubits [28]. In other words, the group of possible operations that act simultaneously on up to N of the N entangled qubits is much larger than the group of single qubit rotations performed on N qubits.

The requirements for the physical implementation of quantum computation are summarised in the DiVincenzo Criteria [29]:

1. A scalable physical system with well-characterized qubits
2. The ability to initialize the state of the qubits

3. A universal set of quantum gates
4. Long relevant coherence times
5. A qubit-specific measurement capability

Experimental realisation of all 5 criteria is extremely challenging and has driven research into many rival qubit systems. Simple quantum operations and algorithms have been demonstrated on few qubit systems with various fabrication methods, with some demonstrating all but DiVincenzo's first criteria of scalability.

2.1.2 Qubit Realisation

Since all that is required to make a qubit is a quantum system with at least 2 well-defined energy levels, there are many possible types of physical platforms for quantum computers, each with their own advantages and disadvantages. The competition is fierce between rival quantum computing groups researching into different types of qubit and methods of experimental realisation, each aiming to pull ahead from the others in demonstrating all 5 of DiVincenzo's Criteria. A selection of the most popular types of qubit are given here.

Photon-based quantum computers [30] utilize the polarization states of the photon, e.g. horizontal and vertical or clockwise and anticlockwise circular polarization, as the qubit basis states. Photonic qubits are appealing due to their long coherence times and single qubit gates are easy to implement using waveplates to rotate the polarization. The transportation of photonic qubits also offer the most practical method for quantum communication. However, achieving coupling between photons for two-qubit gates is difficult due to the weak interaction strength and requires strong non-linear optics. Cavity quantum electrodynamics, where atom-photon interactions are enhanced by an optical cavity, may be required to mediate interactions [31]. A breakthrough in demonstrating a simple quantum algorithm using single photon sources, detectors and linear optical circuits was achieved with the KLM scheme [32]. This scheme relies on quantum interference with auxiliary photons at a beamsplitter and single photon detection to induce interactions nondeterministically. Presently, the efficiency of single photon sources and

detectors, implementing deterministic photon interactions and shrinking waveguide quantum circuits to be fabricated on-chip pose the major challenges of photonic quantum computing.

The energy levels of cold trapped atoms [33] or ions [34] form reliable qubits that are attractive for their record-holding T_1 and T_2 coherence times. Atomic qubits can be initialised by optical pumping and measured with state-dependent optical fluorescence. Inter-qubit interactions can be induced by lasers through a collective mode of harmonic motion in the trap. The major difficulty with trapped atom qubits comes with scaling up, as laser-cooling becomes less efficient, qubits become more susceptible to noise and quantum gate fidelity decreases. Methods to overcome this challenge include coupling qubits between different small collections of trapped ions through photonic interactions or physically shuttling ions.

Superconducting circuits offer three different types of qubit: the charge qubit [35], where the presence or absence of excess Cooper pairs in a superconducting island represent the basis states, the flux qubit [36], where the basis states are symmetric and antisymmetric superpositions of clockwise and anticlockwise loop current states, and the phase qubit [37], where the basis states are defined by the phase difference across a Josephson junction. Single qubit gates can be implemented by applying resonant RF pulses and two qubit gates can be implemented by direct capacitive or inductive coupling or through photons in a transmission line. The macroscopic nature of these circuits has lead to rapid initial development of qubit systems with tens of qubits by companies such as IBM and Google. The first demonstration of a quantum advantage was announced by Google in 2019 using a programmable superconducting processor [38]. However, these macroscopic systems suffer from faster decoherence than other microscopic systems and their size may also lead to a major hurdle for future scale-up due to the large spatial overhead at cryogenic temperatures.

The spin or charge states of electrons in quantum dots [39], localised by surface electrodes, or the electronic or nuclear spin states, localised by single dopants [40], in semiconductors are attractive qubits due to their long coherence times, particularly in isotopically enriched ^{28}Si . Single qubit rotations can be performed using microwave magnetic or electric fields and two qubit gates can be achieved through the exchange interaction or through the electric dipole interaction. Longer range coupling through photons in microcavities [41] is also possible. Mea-

surement and initialisation of the electron spin state has been achieved by spin-dependent coupling to a single electron transistor for both quantum dots [42] and donors [16]. Fabrication of these quantum dots or dopants can benefit from the well-advanced semiconductor microelectronics industry and offer scalable platforms for quantum computers.

In addition to these types of qubit, bulk nuclear magnetic resonance [43] has demonstrated quantum control, nitrogen-vacancy centres in diamond have long-lasting spin coherence at room temperature [44] and topological anyons are proposed to provide fault-tolerant universal quantum computation through non-abelian braiding [45]. The examples given in this section give a flavour of the diversity of the experimental and theoretical progress towards quantum computers.

Quantum computing development is approaching the Noisy Intermediate-Scale Quantum (NISQ) technology era, in which quantum computers with 50-100 qubits may be able to perform tasks with superior efficiency than our most powerful classical computers, but noise in quantum gates will constrain the depth of quantum circuits that can be executed reliably [19]. In fact, some may say that we have now well and truly entered the NISQ era, with the demonstration of a quantum advantage for the checking of outputs from a quantum random number generator with Google's 54 superconducting qubit Sycamore processor in 2019 [38]. Quantum computing milestones are being achieved at an increasingly rapid pace with many different research institutions and industries harnessing a plethora of physical platforms. The work in this thesis is focused on just a single qubit candidate; the promising quantum system of the donor spin in silicon.

2.2 Donors in Silicon

Elements from group V of the periodic table, the stable of which include phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi), serve as shallow donors in silicon (Si) as they introduce electron states into the band gap of Si, with binding energies as shown in Fig. 2.2a. At low temperatures, the hydrogenic donor electron will be bound to the donor nucleus, partially shielded by inner electronic shells, as shown in Fig. 2.2b, with a Bohr radius much larger

than that of the hydrogen atom due to the effective mass of the electron and the dielectric screening from Si. Donors in Si offer a two-for-one qubit system since both the donor electron and nuclear spins have multiple projections onto an externally applied magnetic field. For both the donor electron and nucleus, this spin degree of freedom defines the state of the qubit, upon which operations can be performed. Silicon is a particularly attractive host for spin qubits [46]. It offers long spin coherence times due to its low spin-orbit coupling and small natural abundance of non-zero nuclear spin isotopes (only 5% is the nuclear-spin carrying ^{29}Si ($I = 1/2$) which can be removed by isotopic enrichment). A unique benefit of silicon is the fact that the fabrication of these spin qubits is supported by a wealth of knowledge from the advanced silicon microelectronics industry and that these qubits can be integrated with classical circuitry.

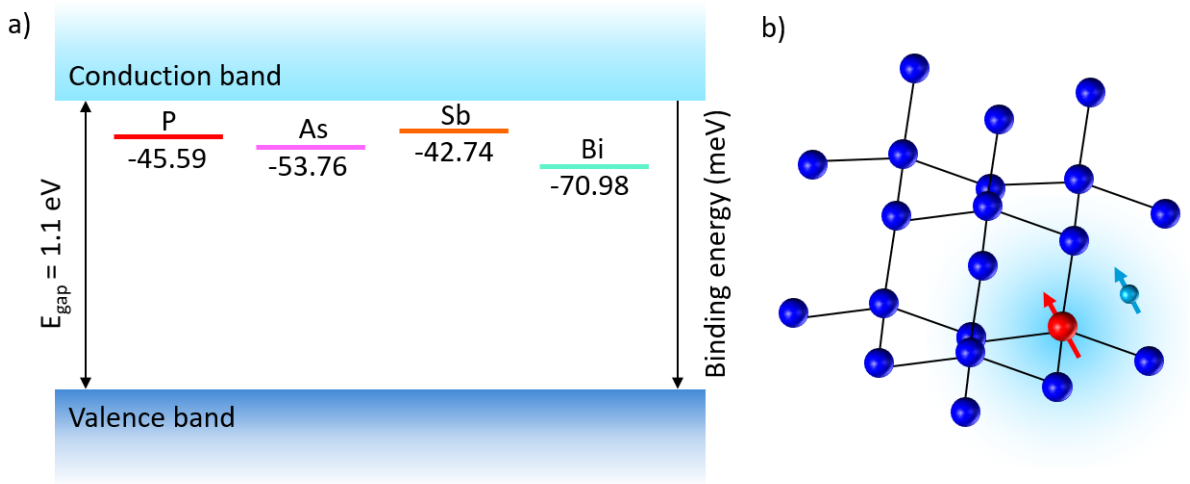


Figure 2.2: a) Group V donor energy levels in Si [47] (not to scale). b) An electron spin (light blue) is bound to a donor nucleus (red), substitutional in the Si lattice (blue), by the Coulomb potential.

Donors have some key differences to their silicon-based spin qubit cousins, quantum dots, both of which are suitable for fabricating solid-state quantum computing devices. Whereas electron spins in quantum dots are confined by lithographically-defined surface electrodes (hence the alternative term ‘artificial atoms’), donors provide a natural mechanism for trapping single electrons via the Coulomb potential of the donor nuclei. Donors therefore do not require additional gates for electron confinement, on top of those gates required to electrostatically shift the donor Fermi level, reducing the overhead for leads during scale-up engineering. Donor systems have the additional degree of freedom from the donor nuclear spin, accessible via the electron-nuclear hyperfine interaction, allowing donors to be operated as a two-for-one

qubit system. Additionally, the exceptionally long coherence time of an ionised donor nuclear spin can be exploited for storing quantum information [24]. The atomic scale of donor qubit systems has posed fabrication challenges in engineering the coupling strength between qubits to perform two-qubit gates and between qubits and nanocircuitry for readout. Conversely, the spatial location of electrons in quantum dots is highly tuneable with gate voltages and thus hybrid donor-dot architectures are actively pursued [48].

The two leading methods for fabricating donor qubits by placing ^{31}P nuclei within the silicon lattice are referred to as the ‘bottom-up’ and ‘top-down’ approaches. The bottom-up method involves the placement of small clusters of phosphorus donors onto the surface of silicon using a scanning tunnelling microscope and phosphine (PH_3) gas [49]. The donor is then encapsulated at a given depth by epitaxial overgrowth of silicon. This bottom-up method achieves near atomic precision placement of donors, however, it is difficult to control and measure how many phosphorus nuclei are adsorbed per placement site. The top-down method involves ion implantation of single P donors into Si and is the area of research for this thesis. Deterministic ion implantation, resulting in donors located in a specific region of a device, can be achieved by methods discussed in section 2.3.2. Since ion implantation is a semiconductor doping industry standard technique, this deterministic implantation is both scalable and compatible with current semiconductor technology. This provides a promising fabrication method for producing arrays containing large numbers of physical qubits required to encode a logical qubit that is robust to errors.

2.2.1 The Spin Hamiltonian

The Hamiltonian is a quantum mechanical operator that expresses the total energy of a quantum system. It can be solved to find the possible states in which the quantum system can exist and their corresponding energy levels. The spin Hamiltonian of a single donor nucleus and bound electron in an externally applied magnetic field can be approximated to the three relevant terms:

$$\hat{H} = \hat{H}_{EZI} + \hat{H}_{NZI} + \hat{H}_{HFI} \quad (2.3)$$

where $\hat{H}_{EZI}$ describes the electronic Zeeman interaction (EZI) between the electronic spin, S , and an external magnetic field, $\mathbf{B} = (B_x, B_y, B_z)^T$, $\hat{H}_{NZI}$ describes the nuclear Zeeman interaction (NZI) between the nuclear spin, I , and the external field and $\hat{H}_{HFI}$ describes the hyperfine interaction (HFI) that depends on the orientation of the electron spin in the magnetic field generated by the nuclear spin. These three terms can be expanded to:

$$\hat{H} = \mu_B \mathbf{B}^T \mathbf{g} \hat{\mathbf{S}} - \mu_n \mathbf{B}^T \mathbf{g}_n \hat{\mathbf{I}} + \hbar \hat{\mathbf{S}}^T \mathbf{A} \hat{\mathbf{I}} \quad (2.4)$$

where μ_B is the Bohr magneton given by $\mu_B = e\hbar/2m_e$, μ_n is the nuclear magneton given by $\mu_n = e\hbar/2m_p$, $\mathbf{g}$ and $\mathbf{g}_n$ are the electron and nuclear Landé g-factor matrices, the electron spin is described by the vector of operators $\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)^T$, the nuclear spin is described by the vector of operators $\hat{\mathbf{I}} = (\hat{I}_x, \hat{I}_y, \hat{I}_z)^T$ and $\mathbf{A}$ is the hyperfine interaction matrix.

For the case of a group V donor in Si, a number of simplifications can be made. The electron and nuclear Landé g-factor matrices can be replaced by a scalar as they are isotropic due to the bulk Si cubic inversion symmetry. The hyperfine interaction is described by a scalar hyperfine coupling constant A , given in frequency units, due to the cubic site symmetry in a silicon crystal lattice retaining only the isotropic component (the Fermi-contact interaction) of the hyperfine interaction. The isotropic approximation weakens for donors in close proximity (< 10 nm) to an interface that are subjected to electric fields from surface gates [50], however, measurements in this thesis were taken with the magnetic field aligned in one direction only. The Hamiltonian of an electronic spin $\hat{S}$ and a nuclear spin $\hat{I}$ in a magnetic field B_0 along the z-direction is given by:

$$\hat{H} = \mu_B g_e B_0 \hat{S}_z - \mu_n g_n B_0 \hat{I}_z + \hbar A \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \quad (2.5)$$

In frequency units, this Hamiltonian can be expressed as:

$$\frac{\hat{H}}{\hbar} = g_e \frac{e}{4\pi m_e} B_0 \hat{S}_z - g_n \frac{e}{4\pi m_p} B_0 \hat{I}_z + A \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \quad (2.6)$$

Where e is the elementary charge and m_e and m_p are the electron and proton mass, respectively.

From this donor spin Hamiltonian, we can determine the possible states and corresponding energy levels of the qubit. This will enable the determination of the qubit resonance frequency between different spin states which corresponds to the microwave frequency required to perform qubit rotations, as we shall see in section 2.2.3.

2.2.2 Donor Qubit Energy Levels

The number of basis states, and hence energy levels, of a donor spin qubit is given by $(2S + 1)(2I + 1)$. In order to determine these eigenstates and eigenenergies, the Hamiltonian must first be expressed as a matrix in a particular basis state before the characteristic equation can be solved. In the limit of a very small or very large external magnetic fields, different assumptions can be made that provide convenient basis states to simplify the mathematics of the system to aid the determination of the energy levels of the donor spin qubit.

In the weak magnetic field regime ($g_n\mu_n B_0 < g_e\mu_B B_0 < hA/2$), the hyperfine interaction dominates over the Zeeman terms, therefore $\hat{S}$ and $\hat{I}$ are not separately conserved, only the total angular momentum, $\hat{F} = \hat{S} + \hat{I}$, is. $\hat{F}$ and its projection onto the external magnetic field, $m_F = -F, -F + 1, \dots, F - 1, F$, are good quantum numbers as the hyperfine interaction is diagonalised and the Zeeman terms can be treated as a perturbation in the $|F, m_F\rangle$ basis.

In the high magnetic field regime ($g_e\mu_B B_0 \gg g_n\mu_n B_0 \gg hA/2$), the Zeeman interaction will dominate the hyperfine interaction. The electron and nuclear angular momentum, S and I , and their projections, m_S and m_I , will be good quantum numbers. Since S and I are constant within any given energy level, the $|m_S, m_I\rangle$ basis can be used to uniquely classify an energy level. The Zeeman terms are diagonalised and the hyperfine interaction can be treated as a perturbation in the $|m_S, m_I\rangle$ basis.

The intermediate magnetic field regime is explored in the ESR and EDMR measurements performed in this work. Therefore, the following section calculates the energy levels of a donor

spin system for an arbitrary magnetic field strength.

Breit-Rabi Formula

To provide a full picture, including intermediate magnetic field strengths, we must consider eigenstates which are superpositions of the $|F, m_F\rangle$ and $|m_S, m_I\rangle$ basis states. For total electron angular momentum $J = S + L = 1/2$, the Hamiltonian can be solved analytically, resulting in the Breit-Rabi formula for energy levels of the system. Since donor electrons in the ground state have spin angular momentum $S = 1/2$ and orbital angular momentum $L = 0$, this formula is applicable and is derived here.

First, the hyperfine interaction term is expanded and written using quantum mechanical ladder operators:

$$\frac{\hat{H}_{HFI}}{h} = A(\hat{\mathbf{S}} \cdot \hat{\mathbf{I}}) = A(\hat{S}_x \hat{I}_x + \hat{S}_y \hat{I}_y + \hat{S}_z \hat{I}_z) = A(\hat{S}_z \hat{I}_z + (\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+)/2) \quad (2.7)$$

Where the ladder operators $\hat{S}_\pm$ and $\hat{I}_\pm$ are:

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y \quad (2.8)$$

$$\hat{I}_\pm = \hat{I}_x \pm i\hat{I}_y \quad (2.9)$$

The electron and nuclear spin ladder operators act on the states to raise or lower the angular momentum projection by 1:

$$\hat{S}_\pm |S, m_S\rangle = \sqrt{S(S+1) - m_S(m_S \pm 1)} |S, m_S \pm 1\rangle \quad (2.10)$$

$$\hat{I}_\pm |I, m_I\rangle = \sqrt{I(I+1) - m_I(m_I \pm 1)} |I, m_I \pm 1\rangle \quad (2.11)$$

providing the resulting m_S and m_I values lie within the ranges $-S, \dots, S$ and $-I, \dots, I$, respectively, otherwise the result returns zero.

The full Hamiltonian can now be expressed as:

$$\frac{\hat{H}}{h} = \gamma_e B_0 \hat{S}_z - \gamma_n B_0 \hat{I}_z + A \hat{S}_z \hat{I}_z + \frac{A}{2} (\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+) \quad (2.12)$$

Where $\gamma_e = g_e e / 4\pi m_e$ and $\gamma_n = g_n e / 4\pi m_p$ are the electron and nuclear gyromagnetic ratios, respectively, in units of Hz/T. We can now see that the total angular momentum projection, $m_F = m_S + m_I$, is conserved, with both S_z and I_z leaving states with definite m_S and m_I unchanged, while $S_+ I_-$ and $S_- I_+$ increases m_S and decreases m_I or vice versa, leaving the sum constant. Since $S = 1/2$, $m_S = \pm 1/2$ and therefore, for each value of m_F there are only two possible states, defined by the basis:

$$|\pm\rangle = |m_S = \pm 1/2, m_I = m_F \mp 1/2\rangle \quad (2.13)$$

The matrix elements of the Hamiltonian can be determined in this basis as:

$$\frac{\hat{H}}{h} = \begin{array}{cc} & \begin{array}{c} |+\rangle \\ |-\rangle \end{array} \\ \begin{array}{c} \langle +| \\ \langle -| \end{array} & \left(\begin{array}{cc} \frac{1}{2}\gamma_e B_0 - \gamma_n B_0(m_F - \frac{1}{2}) + \frac{A}{2}(m_F - \frac{1}{2}) & \frac{A}{2}\sqrt{(I + \frac{1}{2})^2 - m_F^2} \\ \frac{A}{2}\sqrt{(I + \frac{1}{2})^2 - m_F^2} & -\frac{1}{2}\gamma_e B_0 - \gamma_n B_0(m_F + \frac{1}{2}) - \frac{A}{2}(m_F + \frac{1}{2}) \end{array} \right) \end{array}$$

The eigenenergies $E_{\pm}$, corresponding to eigenstates $|\pm\rangle$, of the Hamiltonian can be found by solving the time-independent Schrodinger equation:

$$\hat{H} |\pm\rangle = E_{\pm} |\pm\rangle \quad (2.14)$$

The eigenenergies, in frequency units, are found by solving the characteristic equation:

$$\det \left(\frac{\hat{H}}{h} - E_{\pm} \hat{I} \right) = 0 \quad (2.15)$$

Solving the quadratic equation yields the eigenenergies given by the Breit-Rabi formula:

$$E_{F=I \pm 1/2} = -\frac{A}{4} - \gamma_n B_0 m_F \pm \frac{\Delta W}{2} \sqrt{1 + \frac{4m_F x}{2I + 1} + x^2} \quad (2.16)$$

Where x is the dimensionless field strength parameter and ΔW is the energy splitting, in units of Hz, between the two hyperfine sublevels at zero magnetic field, B_0 :

$$x = \frac{(\gamma_e + \gamma_n)B_0}{\Delta W} \quad (2.17)$$

$$\Delta W = \frac{A}{2}(2I + 1) \quad (2.18)$$

For the maximum F value, i.e. when $F = I + 1/2$, there are two energy levels which are linear in the magnetic field, B_0 . These energy levels correspond to $m_F = \pm(I + 1/2)$ for which the expression under the square root in the Breit-Rabi formula is an exact square and so the last term should be replaced by $+\frac{\Delta W}{2}(1 \pm x)$.

The energy levels (eigenvalues) of different nuclear and electron spin states (eigenvectors) as a function of external magnetic field for the spin Hamiltonians of Bi and P donors in Si will be given in the relevant theory sections of chapters 4 and 6, respectively. From this, we will be able to interpret the ESR and EDMR spectra collected in the corresponding experimental work in terms of spin transitions between donor energy levels.

2.2.3 Initialise, Control, Readout

The ability to control the state of a qubit is required for single qubit rotations, that form part of a universal set of quantum gates; DiVincenzo's 3rd criterion for quantum computation. An advantage of using the spin of a donor electron or nucleus to encode quantum information is the ability to manipulate the spin using standard ESR or Nuclear Magnetic Resonance (NMR) techniques, respectively. An external magnetic field is applied to polarise electron and nuclear spins. Resonant microwave fields, with a frequency such that their energy matches the Zeeman splitting between electron or nuclear spin states, are used to drive transitions between spin eigenstates. The length of the microwave pulse controls the angle with which the electron or nuclear spins rotate around the single qubit Bloch sphere. Single qubit gates (rotational operations) can be implemented by applying an appropriate sequence of microwave pulses. Dynamic decoupling can also be implemented using microwave pulses to reduce the effects

from random fluctuations in the qubit environment, thus extending coherence times. Large ensembles of donor spins can be addressed by applying global microwave pulses, however, most quantum computing architectures require individually addressable spins. This can be achieved by supplying spatially restricted microwave fields with an on-chip shorted coplanar waveguide carrying an alternating current located above each individual qubit, electrically isolated with a gate oxide [16], as shown in Fig. 2.3. Alternatively, the bias of electrodes located above individual donors can be used to distort the donor electron wavefunction, altering the hyperfine interaction via the Stark shift, to tune the donor into or out of resonance with the globally applied microwave field.

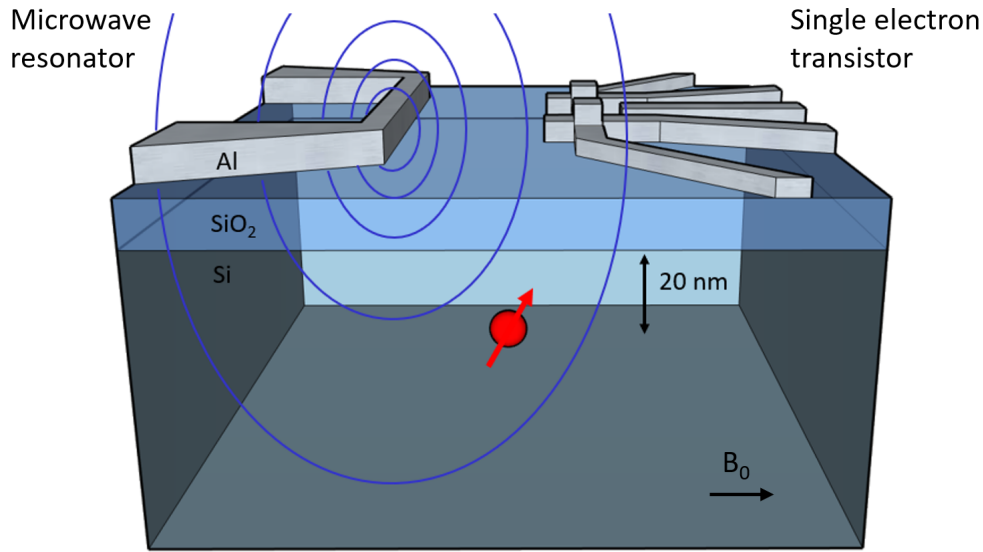


Figure 2.3: The electron and nuclear spin state of a donor can be controlled by an on-chip microwave resonator and initialised and measured by spin-to-charge conversion by tunnel coupling to the island of a single electron transistor [16]. The donor is required to be ~ 20 nm below the surface electrodes and electrically isolated by a high quality thin gate oxide with a low density of interface traps and fixed oxide charge.

Readout of the state of individual qubits, DiVincenzo's 5th criterion, is required in order to measure the result of a quantum computation. Conventional electron spin resonance measurement using magnetic induction, while commonplace in bulk spin systems, is impractical for single spins due to their extremely small magnetic signal. A more sensitive method of spin-to-charge conversion can enable the readout of individual spins. This can be achieved by spin-dependent tunnel coupling of a donor electron to the island of a Single Electron Transistor (SET), approximately 20 nm away [51]. A Scanning Electron Microscope (SEM) image of a donor qubit device is shown in Fig. 2.4. Biased surface electrodes are used to tune the

system such that the spin-up state of the donor electron lies above the Fermi level of the SET island while the spin-down state lies below it. As a consequence of the Pauli exclusion principle, the spin-down electron is forbidden to tunnel from the donor as it is blocked by occupied electron states in the SET island. Conversely, a spin-up donor electron will readily tunnel into an empty electron state in the SET island, resulting in an ionised donor. The positive charge of this ionised donor is detected by a change in current flowing through the nearby SET, sensitive to the detection of a single electron tunneling in real-time with a bandwidth of ~ 100 kHz [51]. Using this method, the spin state of a donor electron can be read out in a single shot with high fidelity (typically $> 90\%$) if the thermal broadening of the SET island is less than the Zeeman splitting of the donor electron, which can be achieved with high magnetic fields, $B_0 > 1$ T, and very low electron temperatures, $T \approx 200$ mK [51].

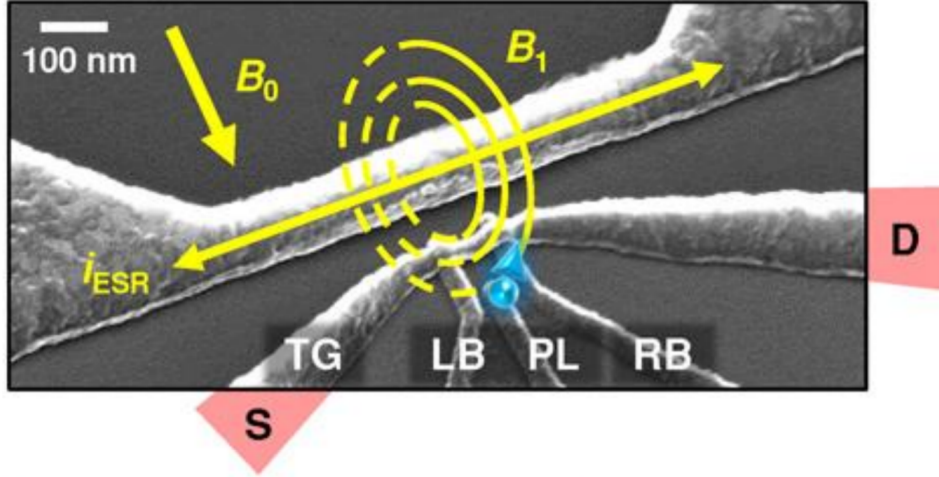


Figure 2.4: Scanning electron micrograph of a donor qubit device [16]. The spin of the donor (blue) is controlled by an oscillating magnetic field B_1 from the microwave transmission line, perpendicular to the in-plane external field B_0 . Readout of the donor spin is performed by spin-to-charge conversion using an SET consisting of a top gate (TG), plunger gate (PL), left and right barrier gates (LB and RB) and source/drain contacts (S and D).

The ability to initialise the state of a qubit, the 2nd of the DiVincenzo criteria, is a fundamental computing requirement as the initial state of a register must be known before starting any computation. A highly desirable by-product of the spin-to-charge readout method is that the donor electron will always be reset to the spin-down state at the end of the measurement. This is due to either the electron being in the spin-down state to begin with, in which case it would not leave the donor, or the spin-up electron tunneled from the donor and was replaced by a spin-down electron extracted from below the SET island Fermi level.

The donor nuclear spin state can be readout by using the donor electron spin as an ancilla qubit [17]. The resonant frequency of the electron depends on the nuclear spin state due to the hyperfine coupling. The nuclear spin will be projectively measured in a particular state if the electron spin, initialised in the spin-down state, is flipped to a spin-up state by a π -pulse at the corresponding frequency, detected by a current pulse through the SET. Since the Zeeman interaction dominates the hyperfine interaction, this method of nuclear spin measurement is almost perfectly quantum non-demolition [52]. This means repetitive measurements of the nuclear spin can be performed to increase the readout fidelity, with $> 99.8\%$ fidelity achieved for 100 repeated measurements [17].

The complete set of qubit control, that includes Rabi oscillations to prepare arbitrary superposition states of the qubit, Ramsey decay fringes to yield the pure dephasing time T_2^* , Hahn echo decay to yield the qubit coherence time T_2^H and dynamical decoupling sequences to extract the ultimate limit of the coherence time, has been demonstrated with donor electrons and nuclei [24].

This work performed over the last decade has shown that the initialisation, control and readout of a donor spin qubit using surface nanocircuitry is highly compatible with the ion implantation of donors, a fabrication technique discussed in section 2.3. We will now take a look at donor spin coherence times, which strongly affect the fidelity of qubit operations.

2.2.4 Qubit Coherence

Quantum systems are extremely fragile compared to classical bits. Small perturbations in their surrounding environment cause quantum information to leak out or decohere. The length of time that a qubit can store quantum information for is given by two time constants, T_1 and T_2 . The spin-lattice relaxation time (T_1) is referred to as the longitudinal relaxation time and describes spin relaxation from the excited state $|1\rangle$ to the ground state $|0\rangle$ (or a loss of classical information stored in θ in the Bloch sphere). T_1 can be measured with an inversion recovery pulse sequence, as shown in Fig. 2.5a. The spin coherence time (T_2) is referred to as the transverse relaxation time and describes spin decoherence (or a loss of quantum phase

information stored in ϕ in the Bloch sphere). T_2 can be measured with a Hahn echo pulse sequence, as shown in Fig. 2.5b. Dynamical decoupling builds upon the two-pulse Hahn echo technique by including multiple refocusing pulses that can decouple the qubit from a greater frequency range of noise and measure the ultimate limit of T_2 . T_1 sets an upper bound for T_2 ($T_2 \leq 2T_1$) as a rotation that aligns the spin completely along the z-axis of the Bloch sphere necessarily destroys the coherence of the transverse spin polarisation. Coherent single and two qubit operations are required during the progression of a quantum algorithm and thus, the spin coherence time, T_2 , achieved by dynamical decoupling must be much longer than the operation time, T_{op} , (ranging from $T_2/T_{op} \sim 10^2 - 10^5$ depending on the topology of the quantum architecture and error-correcting code) for fault-tolerant operation.

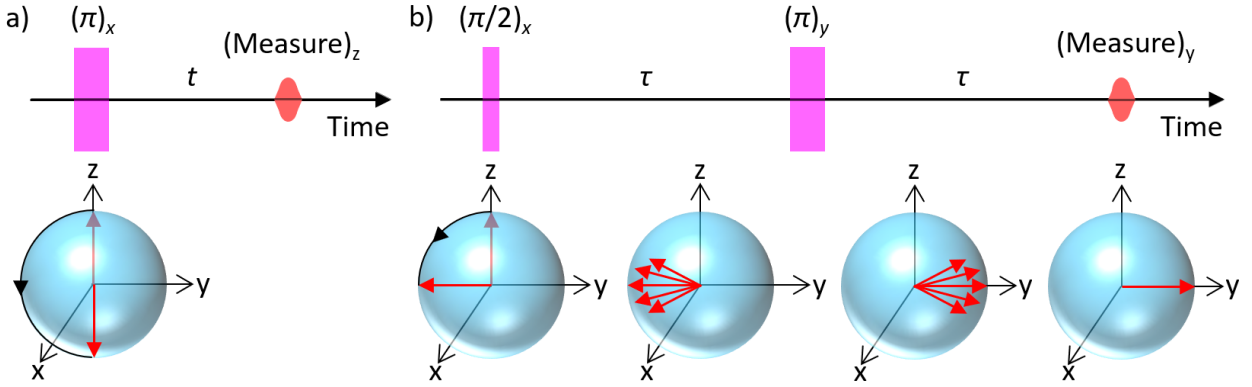


Figure 2.5: Measuring qubit coherence: a Bloch sphere representation. a) T_1 is measured with an inversion recovery pulse sequence in which the ground state $|0\rangle$ is transformed into the excited state $|1\rangle$ by a π rotation and the state probability is measured along the z-axis after a time t . b) T_2 is measured with a Hahn echo pulse sequence in which the ground state $|0\rangle$ is first mapped onto the xy-plane by a $\pi/2$ rotation. The spins of different qubits (or the spin of the same qubit measured at different times) diverge, due to varying local magnetic field strengths resulting in a variation of precession speeds, for a time τ . A π rotation is then applied such that the slower spins are now in the lead and the faster ones trail behind. After the same time delay τ , the spins will refocus and an echo signal is measured along the y-axis.

For donor spin qubits in a semiconductor crystal, longitudinal relaxation is related to a loss of energy from the spin that is absorbed by the crystal lattice via phonons; hence the term spin-lattice relaxation for T_1 . In contrast, transverse relaxation is caused by interactions of the spin with other surrounding fluctuating spins; hence the spin coherence time, T_2 , is referred to as a spin-spin interaction. T_2 can be considerably shorter than T_1 for donors in Si.

In the solid state, the relaxation time T_1 depends on the coupling strength between the

donor electron spin and lattice phonons, governed by the spin-orbit interaction. Fortunately, the spin-orbit coupling in Si is weak, due to the large band gap and the absence of piezoelectric phonons [53]. Above a few kelvin, T_1 is limited by thermal excitation to the valley-orbit excited state of the donor. The spin-lattice relaxation time of electrons in Si at low temperature, governed by phonon scattering, is exceptionally long (minutes to hours) and does not limit the encoding of quantum information in spin states.

Natural Si is composed of 92.2% ^{28}Si , an isotope with zero nuclear magnetic dipole (nuclear spin $I = 0$) which does not contribute to donor qubit decoherence. However, 4.7% of natural Si is composed of ^{29}Si , an isotope with a magnetic dipole (nuclear spin $I = 1/2$) which does contribute to donor qubit decoherence. The dynamics of surrounding ^{29}Si nuclear spins generate perturbations in the magnetic field of the donor spin and randomise its phase. This ‘spectral diffusion’ is the main limiting factor for the spin coherence times T_2^* and T_2 in natural Si. A donor environment of isotopically enriched ^{28}Si is required to achieve the low decoherence ‘semiconductor vacuum’ environment. Extremely long T_2 coherence times (> 30 s for ionised P donors) have been reported for single near-surface implanted donors in isotopically enriched Si with a residual ^{29}Si concentration of 800 ppm [24], enabling a single qubit control fidelity of $> 99.99\%$. A new method for isotopically enriching Si to just 250 ppm residual ^{29}Si is provided in chapter 5.

In isotopically enriched Si, donor-donor interactions become a dominant decoherence mechanism, which can be minimised by reducing the concentration of donors present. The Hahn echo measurement adds a decoherence source known as ‘instantaneous’ diffusion, in which the simultaneous flipping of all resonant donor electron spins changes the local magnetic field of each individual donor [54]. Dipole interaction-induced flip-flops of nearby donor electrons also result in spectral diffusion. This mechanism can dominate decoherence at low temperatures in the presence of low ^{29}Si concentrations when instantaneous diffusion is eliminated with a modified Hahn echo pulse scheme [55]. These decoherence mechanisms are expanded upon in the theory section of chapter 5 when discussing the effects of the isotopic enrichment of Si.

The T_2 of near-surface donors integrated into single qubit devices can be shorter than bulk donors due to the proximity of paramagnetic centres at interfaces and defects introduced during

the fabrication method. The unpaired electrons in dangling bonds (P_{b0} centres) at the Si/oxide interface are an example of spin defects that will couple to donor spins [56]. Antimony donors implanted 50 nm below a native oxide interface were found to have their donor electron spin T_{2e} limited to 0.3 ms at 5.2 K, which was increased to 0.75 ms upon hydrogen termination of the surface [57]. These coherence times were significantly shorter than for antimony donors implanted 150 nm below the interface with a T_{2e} of 2.1 ms. Paramagnetic defects introduced in Si during the ion implantation of donors [58] can also interact with donor spins, causing an additional decoherence mechanism which can be alleviated by a suitable annealing strategy to repair the lattice damage. Fluctuating electric fields associated with surface charge traps or gate voltages can couple to the donor spins by Stark shifting the hyperfine coupling constant [59] or the g -factor [50].

However, these decoherence mechanisms applicable to near-surface ion implanted donors have been mitigated by the growth of a high quality thermal SiO_2 layer with a low P_{b0} concentration and fixed oxide charge interfaced with Si and post-implantation annealing. These fabrication strategies have enabled the donor electron coherence time to be extended to $T_{2e} = 0.95$ ms for P donors implanted to less than 20 nm below the Si surface, a value which was found to not be limited by the proximity of the interface [24]. Methods to further extend qubit coherence times and increase gate fidelities are actively pursued, with the tuning of donors to clock transitions where the system is less sensitive to noise [21] and the dynamical correction of gate pulses to cancel noise [60] having already been demonstrated.

2.2.5 Quantum Computing Architectures

Due to the sensitivity of quantum systems to noise, computational processes, such as initialisation of the qubit state, one and two qubit gate operations and readout of the qubit state at the end of an algorithm, all introduce errors that result in a fidelity of $< 100\%$. Therefore, in order for a large-scale quantum computer to perform useful operations with a quantum advantage over their classical counterparts, the protection of quantum systems against noise using quantum error correction will be necessary. In this, one logical qubit is encoded in many physical qubits that can be corrected for errors by determining the error syndrome via the measurement

of ancilla qubits. In fault-tolerant quantum computation theory, in which qubits are encoded in a quantum error-correcting code, a quantum computer will be able to perform arbitrary algorithms provided the error rate per physical gate or time step is below some constant threshold value [61]. In the NISQ era, quantum error correction may be impossible to implement as many physical qubits will be required to make one logical qubit robust to errors, leading to large overheads. However, clever design of noise-resilient algorithms are being developed to extend the computational power of NISQ devices.

Focusing on the use of donors in Si as the physical hardware of the quantum computer, there are still many ways to initialise, control and readout qubits. The interconnection topologies and floor planning of the qubits in quantum computing architectures are important for determining the error correction threshold for future large-scale technologies. In this section, three different types of quantum computing architecture based on the donor spin qubit in Si will be discussed.

The Kane Architecture

In 1998, Bruce Kane made the seminal proposal for a quantum computing architecture using the nuclear spin of single phosphorus donors embedded in a silicon crystal lattice as the qubit [40]. An applied magnetic field B_0 polarises the nuclear spins into the ground state $|0\rangle$ or the excited state $|1\rangle$. Single qubit rotations can be performed by bringing specific nuclear spins into resonance with an applied oscillating magnetic field B_{AC} . This shift in nuclear resonance frequency is achieved by altering the electric potential of ‘A-gates’ above each donor which control the strength of the hyperfine interaction, A , proportional to the probability density of the electron wavefunction at the nucleus. Two qubit logic gates can be performed by coupling neighbouring nuclear spins via the donor electron exchange interaction. These interactions can be switched on or off using the electric potential of ‘J-gates’ located between the donors to control the exchange interaction, J , which depends on the degree of overlap of electron wavefunctions. A schematic of the proposed layout of the Kane architecture is shown in Fig. 2.6. Nuclear spins are measured by transferring the nuclear spin state to the electron spin state by adiabatically increasing J and then determining the electron spin state by its effect on the orbital wavefunction of an exchange-coupled two-electron system, which can be probed using

capacitance measurements between adjacent gates. Initialisation of the nuclear spin is achieved through measurement and then spin flipping if necessary.

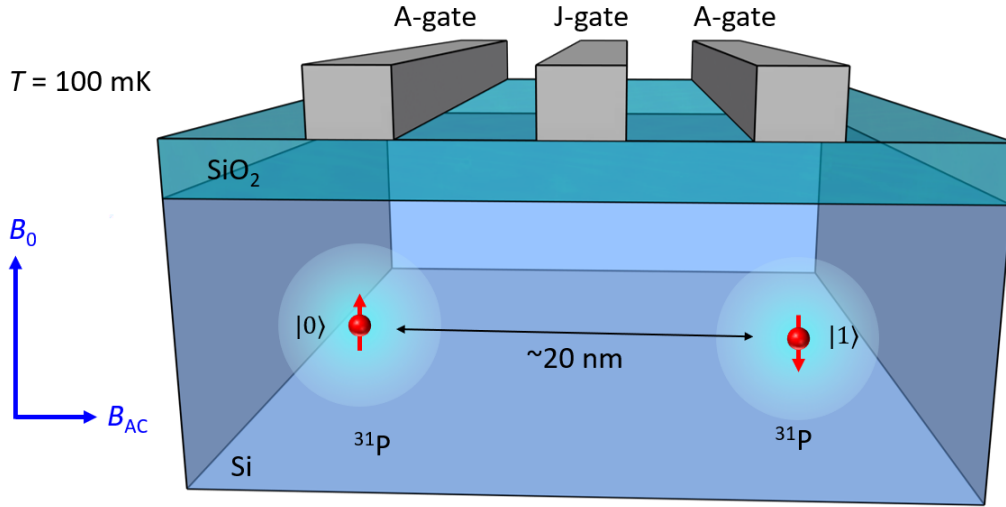


Figure 2.6: The Kane architecture consists of a one-dimensional array of ^{31}P donors in a Si substrate, separated by an oxide barrier from surface electrodes. ‘A-gates’ control the nuclear resonance frequency and ‘J-gates’ control the electron-mediated coupling between neighbouring nuclear spins for implementing single and two qubit gates, respectively.

While elegant, the Kane architecture has its flaws. The control of the nuclear spin qubits can only be achieved by applying a global microwave field B_{AC} , which places the impractical necessity for the quantum computer to be located inside a homogeneous AC magnetic field. The one dimensional architecture places unrealistic requirements on qubit gate fidelity and the number of ancilla qubits; making fault-tolerant scaling difficult to achieve.

The Surface Code Architecture

A significant improvement on Kane’s proposal was made by Charles Hill et al. in 2015 [62] who presented an architecture for a two-dimensional lattice of phosphorus donor nuclear spin qubits in silicon sandwiched between 2 control layers forming a mutually perpendicular crisscross gate array. Again, control of the spin of the P nuclei or donor electrons can be achieved by tuning them on resonance with a global oscillating magnetic field. The three dimensional silicon chip architecture, taken from the original paper [62], is shown in Fig. 2.7.

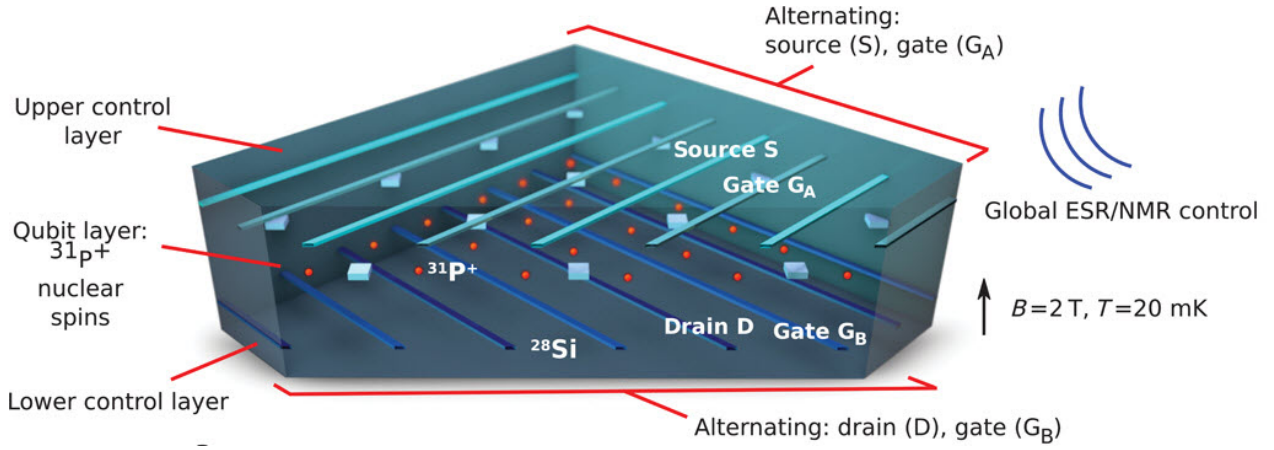


Figure 2.7: The surface code architecture consists of a two-dimensional array of ^{31}P donors in Si between 2 gate layers for control, initialisation and measurement. This figure is reprinted from reference [62].

This surface code architecture with a 2D array of qubits, capable of operating synchronously and in parallel, allows for high threshold topological quantum error correction which greatly reduces the stringent requirements on gate error rates. However, since the exchange interaction strength, J , varies by an order of magnitude with atomic lattice site [63], achieving atomic-precision placement of the P qubits in Si is perhaps the greatest drawback to large-scale Kane-inspired architectures.

The Flip-Flop Qubit Architecture

The ‘flip-flop’ qubit architecture proposed by Andrea Morello et al. in 2017 [64] makes use of longer-range qubit interactions, and hence relaxes the requirement for atomic precision of donors in silicon. This flip-flop qubit architecture envisions a two-dimensional array of ^{31}P donors embedded in isotopically pure ^{28}Si at a depth of ~ 20 nm below the interface with a thin SiO_2 layer. The orbital donor electron wavefunction can be controlled by a vertical electric field, E_z applied by a biased surface gate above the donor. At low applied electric fields, the electron cloud surrounds the donor nucleus in a ‘bulk-like’ donor state. At high applied electric fields, the electron cloud is drawn away from the donor nucleus and towards the Si/SiO₂ interface in an ‘interface-like’ state. The hyperfine interaction, $A(E_z)$, through which the donor electron and nucleus are coupled, is proportional to the amount of overlap between the donor electron and nuclear wavefunctions. Therefore, the strength of the hyperfine interaction can be

controlled by the applied electric field, E_z .

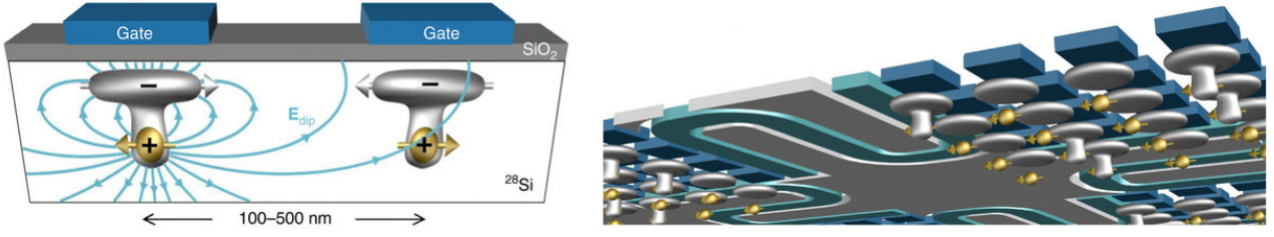


Figure 2.8: The flip-flop qubit architecture consists of a 2D array of ^{31}P donors in Si below biased top gates to operate and couple through the electric dipole interaction. A large-scale flip-flop qubit architecture is proposed, in which qubits can interact over long ranges by coupling with microwave resonators [64].

The donor systems operate in the ‘flip-flop’ qubit mode, where the spin of the donor electron ($|\uparrow\rangle$ or $|\downarrow\rangle$) is in the opposite direction to the spin of the nucleus ($|\uparrow\rangle$ or $|\downarrow\rangle$), i.e. transitions occur between the basis states $|\downarrow\uparrow\rangle$ and $|\uparrow\downarrow\rangle$. High-fidelity one-qubit gate operations can be achieved by electrically driving the flip-flop qubit. Electric Dipole Spin Resonance (EDSR) transitions can be induced between these flip-flop qubit basis states by electrically modulating the hyperfine interaction, $A(E_z)$, at the resonance frequency corresponding to the energy splitting between states $|\downarrow\uparrow\rangle$ and $|\uparrow\downarrow\rangle$.

Two-qubit gates can be achieved through the electric dipole interaction, as shown on the left in Fig. 2.8. When the donor electron wavefunction is drawn towards the interface, charge polarization occurs, which creates an electric dipole. This induced electric dipole moment introduces a coupling term in the Hamiltonian of a nearby donor if it is also in the interface-like state. The interaction strength between two electric dipoles is $V_{\text{dip}} \propto 1/r^3$, where r is the separation distance between them. The coupling between two interface-like donors is extended even further than this due to the enhancement by the metallic interface on top of the vertical dipoles. This interaction is much longer range than the exchange interaction, J , proposed in the Kane architecture. The electric dipole interaction could also be used to couple flip-flop qubits to microwave resonance cavities to extend entanglement to millimetre-distances, as shown on the right in Fig. 2.8. The microwave resonator could also be used for interfacing with photonic links.

Readout of the qubit state can be achieved by spin-dependent tunnelling into a single elec-

tron transistor. Long coherence times for the storage of quantum information can be achieved by mapping the state of the flip-flop qubit onto the donor nuclear spin qubit by applying an ESR π -pulse. While in ‘idle-mode’, this donor can then be ionised in the interface-like state to extend the nuclear spin coherence time to $T_{2n}^{CPMG} > 30$ s [24]. Certain bias points, or sweet spots, can also be used to make the qubits robust to charge noise up to second order. This would allow for fault-tolerant quantum computing with error rates below quantum error correction thresholds.

The nature of the long-range interaction in this architecture does not require atomically precise donor placement and allows inter-qubit distances to be 100-500 nm. This makes donor placement by ion implantation, a method which causes some uncertainty in the final resting position of the ion, a viable option and allows plenty of space for classical readout and control circuit components in between qubits. This quantum computing architecture therefore shows a great deal of promise for large-scale fabrication using semiconductor industry standard techniques, discussed in the following section.

2.3 Donor Ion Implantation

A promising strategy for constructing large-scale devices capable of demonstrating the flip-flop qubit architecture involves placing individual donor spins in silicon using ion implantation, followed by electron beam lithography to define the surface electronics for initialisation, control and readout of the spin qubits. Ion implantation is a standard industry process for introducing dopants into semiconductors that is versatile in its ability to introduce different species of dopant atoms to any depth up to a few micrometers into a device [65]. The finite precision of the donor placement is limited by the size of the aperture through which the ion is implanted and the straggle in the substrate. However, this is compatible with the relaxed requirements for spatial precision in the flip-flop qubit architecture which uses longer-range coupling through the electric dipole interaction.

2.3.1 Timed Poisson Implantation

The species of the implanted ion is selected by the choice of source, typically a solid-state cathode containing a significant fraction of the desired species, and filtering ions with a desired mass-to-charge ratio using mass spectrometry. The mean resting depth of the implanted ion below the surface of the target substrate is selected by the implantation energy. The implantation fluence, or number of ions implanted per cm^2 of the target substrate, is selected by adjusting the ion beam current and implantation time to obtain, on average, the desired number of donors in an active region of a device by Poisson statistics. Demonstrations of single donor qubit devices have successfully been achieved using this method [16, 17, 24]. However, a deterministic approach to ion implantation is required to demonstrate multi-qubit coupling and scale-up to quantum computing architectures.

2.3.2 Deterministic Single Ion Implantation

In order to overcome Poisson statistics with the stochastic process of ion implantation, various methods are under investigation to register the implantation of single ions either before or after they impact the substrate [18]. Pre-implantation detection methods include the development of a laser-cooled linear Paul trap used as a single ion source [66, 67, 68] and image charge detection of single ions during their flight [69]. Post-implantation methods include the detection of secondary electrons emitted from the surface by the impact of a single ion from a focused ion beam [70, 71] and the detection of drain current modulation upon the implantation of a single donor into the channel of a Si nanoscale metal-oxide-semiconductor field-effect-transistor [72].

A promising method that can be integrated into the fabrication process flow of a large scale quantum computing device involves the detection of the charge induced in the substrate produced by single ions implanted through a nanostencil [73]. This method of Ion Beam Induced Charge (IBIC) can achieve the placement of single donors to the technologically useful depth of ~ 20 nm in specific locations of the active region of a device. When an ion is implanted into silicon, it dissipates a fraction of its kinetic energy into nuclear stopping processes which produce phonons and undesirable lattice damage. The remaining fraction of the kinetic energy of the

implanted ion is dissipated into electronic stopping processes, generating ionisation desirable for the IBIC detection method. This energy lost to electronic stopping generates electron-hole pairs in the substrate which can be collected by biased detector electrodes. Sensitive charge detection electronics (comprising low-noise external preamplifier circuitry and a silicon detector substrate with low levels of impurities and a high quality gate oxide to minimise leakage current) are required to detect the displacement current generated by the implantation of a single ion. The single ion is localised by implanting through a nanostencil, fabricated by ion milling an aperture in an Atomic Force Microscopy (AFM) cantilever. The IBIC signal generated from a single ion implant event is used to trigger the blanking of the ion beam and repositioning the nanostencil to the next implantation site, thus constructing an array of donors required for a large-scale device in a step-and-repeat fashion. Using this IBIC method, with the setup as shown in Fig. 2.9, a detection fidelity of 99.87% has been achieved for the implantation of 14 keV $^{31}\text{P}^+$ ions into Si at near room temperature [74].

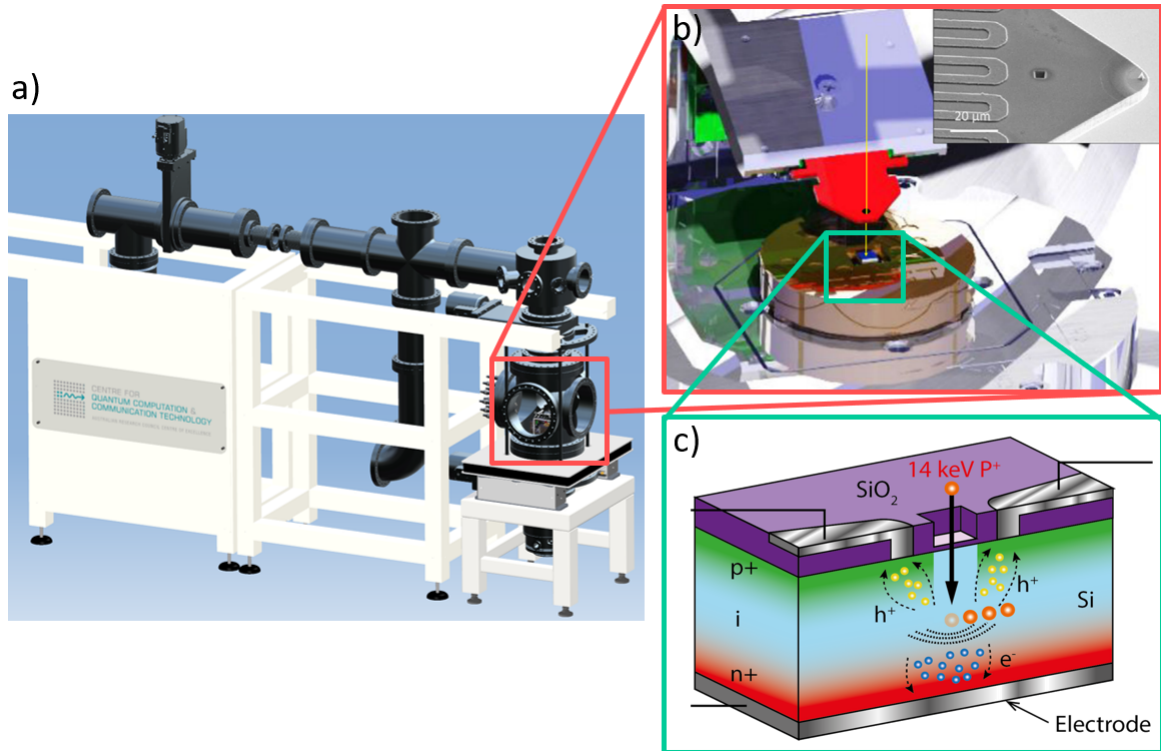


Figure 2.9: Deterministic ion implantation. a) A colutron implanter accelerates and steers a beam of donor ions towards the target. b) The colutron has been integrated with an atomic force microscope with a nanostencil in the AFM cantilever through which the ion beam is collimated onto a precise location on the Si substrate. c) If the substrate is integrated with an induced charge detector, the implantation of a single donor can be detected by the electrons and holes that are induced in the substrate upon ion implantation.

The limits of spatial precision of the implanted ion are set by straggling, the aperture diameter of the nanostencil (< 10 nm is possible) and the relative positioning accuracy of the nanostencil to the sample stage (< 2 nm) [75]. Greater spatial precision can be achieved when implanting heavier donors to the same depth. However, the number of electron-hole pairs produced by a single ion implant is lower due to greater recombination in the plume of ionisation of increased density along the ion track that effectively shields the externally applied bias [76], leading to a lower detection fidelity. The number of electron-hole pairs generated, and hence the detection fidelity, can be enhanced by the use of molecular ions. For example, in PF_x molecules, the additional kinetic energy carried by the F bystander ions increases the induced ionisation, increasing the IBIC signal. Since F ions are fast diffusers in Si, post-implantation annealing is likely to remove F from the active region of the device, mitigating the degradation of the P donor quantum environment [75]. This is a topic of active research at present.

2.3.3 Annealing and Activation

The nuclear stopping component of energy dissipation during ion implantation creates damage to the crystal structure of the target material by the production of vacancies and interstitials if the incident ion imparts sufficient energy to overcome the atomic displacement energy of the Si lattice [77]. If the displaced ion has sufficient energy, it will become a secondary projectile which could create additional vacancy-interstitial defect pairs. In this manner, an implanted ion will produce a cascade of lattice damage around its track [78], as shown with the SRIM simulation in Fig. 2.10. These vacancy and interstitial point defects are mobile at room temperature and will migrate to recombine, cluster or interact with impurities or dopants to form a variety of extended defects that are stable up to various temperatures above room temperature [79].

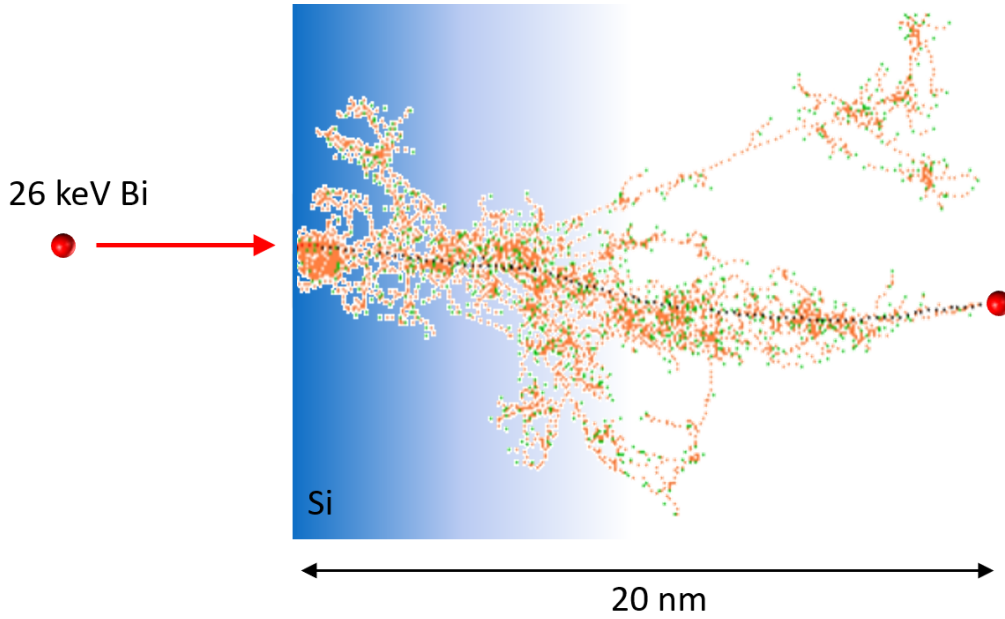


Figure 2.10: SRIM simulation of the damage cascade produced by the implantation of a single 26 keV Bi ion into Si [80]. The final resting positions of secondary Si projectiles are shown with green dots with their tracks shown with orange dots. The primary Bi ion final resting place is indicated in red, with its ion track marked with black dots.

After ion implantation, a large fraction of the implanted donors will not reside on crystal lattice sites and will be interstitial instead of substitutional. The donor electron may also not be bound to the donor nucleus and instead be found in charge trapping defects. The defects produced during ion irradiation can be paramagnetic which would increase the magnetic perturbations in the quantum environment of the donor and result in a decreased qubit coherence time. Post-implantation annealing is required to return the system back to its equilibrium low energy ordered state by repairing Si lattice damage and electrically activating implanted donors. The applied thermal budget can increase the substitutional fraction of the donors by providing the energy needed to overcome the barrier for them to reside on the crystal lattice sites. It can also repair damage to the surrounding Si lattice by the recombination of vacancies and self-interstitials and dissolution of dislocations. Importantly, it can increase the donor electrical activation yield by removing trapping defects and redistributing the donor electrons back onto donor nuclei. The annealing time is restricted to minimise the donor diffusion which would decrease spatial precision and could reduce electrical activation by the formation of electrically inactive complexes.

2.3.4 Donor Diffusion

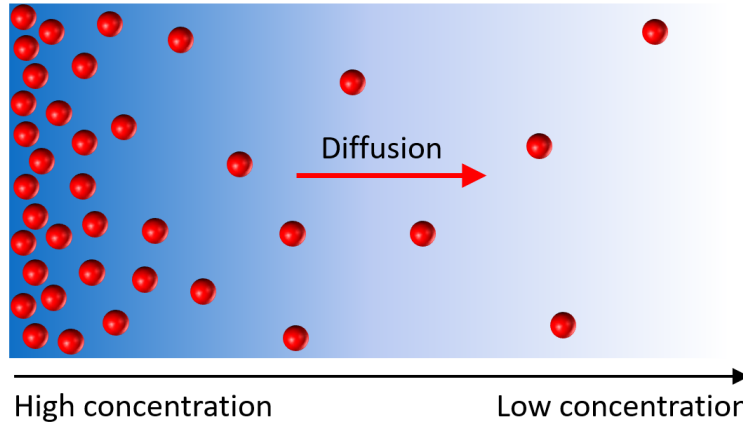


Figure 2.11: Diffusion is driven by a concentration gradient.

Diffusion of dopants through silicon can be an unwanted by-product of annealing, therefore, the thermal budget must be low enough such that dopants do not migrate away from the active region of a device. Diffusion is the process of mass transport of a particular species (atoms, ions or molecules, for example) that is driven by a concentration gradient, as illustrated in Fig. 2.11. Normal diffusion of a species from a region of higher concentration to a region of lower concentration can be described by Fick's laws. Fick's 2nd Law predicts how concentration changes with time due to diffusion. Dopant diffusion through silicon can be described with this partial differential equation:

$$\frac{\partial \phi}{\partial t} = D \nabla^2 \phi \quad (2.19)$$

where $\phi = \phi(t, x, y, z)$ is the concentration of dopant atoms, in units of cm^{-3} , that depends on time t and spatial location (x, y, z) and D is the dopant diffusivity, in units of cm^2s^{-1} , which depends on the temperature T through the following equation:

$$D = D_0 \exp(-E_A/k_B T) \text{ cm}^2/\text{s} \quad (2.20)$$

with a diffusion coefficient, D_0 , in units of cm^2s^{-1} , and an activation energy, E_A , typically given in units of eV [81].

In order to solve Fick's 2nd Law numerically for computationally efficient simulation and simplifying to one spatial dimension, the time and length domains are discretized into a mesh

of equally spaced points:

$$t_n = n\Delta t, n = 0, 1, \dots, N_t \quad (2.21)$$

$$x_i = i\Delta x, i = 0, 1, \dots, N_x \quad (2.22)$$

and the partial derivatives can be replaced using the finite difference approximation:

$$\frac{\phi(t_n + \Delta t, x_i) - \phi(t_n, x_i)}{\Delta t} = D \frac{\phi(t_n, x_i + \Delta x) - 2\phi(t_n, x_i) + \phi(t_n, x_i - \Delta x)}{\Delta x^2} \quad (2.23)$$

If we know the initial concentration profile, $\phi(t = 0, x)$, we can solve the concentration profile at any later time step, $n = 1, 2, \dots, N_t$, by applying the iterative equation for all internal spatial points:

$$\phi(t_n + \Delta t, x_i) = \phi(t_n, x_i) + \frac{D\Delta t}{\Delta x^2} (\phi(t_n, x_i + \Delta x) - 2\phi(t_n, x_i) + \phi(t_n, x_i - \Delta x)) \quad (2.24)$$

for $i = 1, 2, \dots, N_x - 1$ and applying the spatial boundary conditions:

$$\phi(t_n + \Delta t, x_i) = \phi(t_n, x_i) + \frac{D\Delta t}{\Delta x^2} (\phi(t_n, x_i + \Delta x) - \phi(t_n, x_i)) \text{ for } i = 0 \quad (2.25)$$

$$\phi(t_n + \Delta t, x_i) = \phi(t_n, x_i) \text{ for } i = N_x \quad (2.26)$$

by assuming that no dopants can diffuse in or out of the spatial boundary $x = 0$ and that the dopant concentration at $x = N_x\Delta x$ remains constant; applicable for when $N_x\Delta x$ is larger than the spatial extent of the diffusion. The time interval, Δt , must be sufficiently small in order to satisfy $\Delta t \leq \Delta x^2/2D$ for stability of the numerical solver.

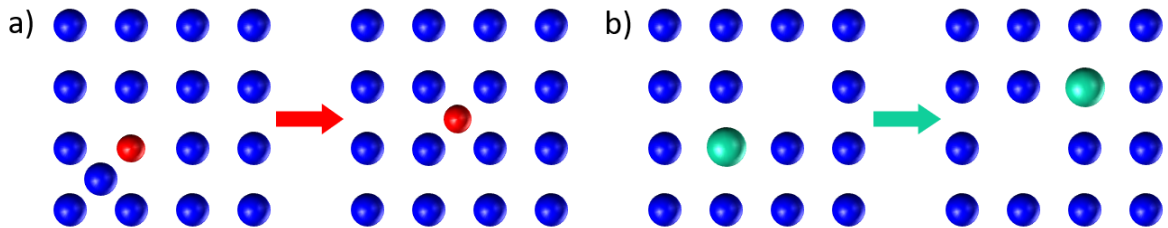


Figure 2.12: a) P donors (red) migrate through Si (blue) by interstitial-assisted diffusion. b) Bi donors (turquoise) migrate through Si by vacancy-assisted diffusion.

Dopant diffusion in Si can occur via two mechanisms; interstitial-assisted diffusion and vacancy-assisted diffusion [82], each having different microscopic descriptions as shown in Fig. 2.12a and Fig. 2.12b, respectively. Interstitial-assisted diffusion occurs when a Si interstitial pushes a substitutional dopant atom off its lattice site and into a neighbouring interstitial site, the interstitial dopant can then do the same to a neighbouring substitutional Si atom and migration occurs with the dopant alternating between substitutional and interstitial sites. Lighter group V donors diffuse in Si in this way, with interstitial-assisted diffusion being the primary mechanism for P and a component for As diffusion. With vacancy-assisted diffusion, a substitutional dopant atom can migrate by jumping into a Si vacancy at a nearest neighbour site. This mechanism is preferred for heavy group V donors in Si, with Bi and Sb diffusion in Si being predominantly vacancy-assisted and a component of As diffusion being vacancy-assisted. The group V donors have different activation energies, E_A , and diffusion coefficients, D_0 . For diffusion through the bulk of Si, at deep enough depths for surface effects to be negligible, the intrinsic diffusion constants for group V donors are summarised in the following table:

Donor	D_0 (cm ² s ⁻¹)	E_A (eV)
P	0.074	3.30
As	0.0655	3.44
Sb	0.214	3.65
Bi	1.080	3.85

Table 2.1: Intrinsic bulk diffusion constants for group V donors in Si; the diffusion coefficient, D_0 , and activation energy E_A [81]

The trend in activation energy, increasing from P through to Bi, can be explained by the increasing dopant covalent radius [83]. The larger the mismatch between covalent radii of Si and the donor atom, the greater the local strain energy in Si produced by replacing a host atom by a substitutional dopant atom. The diffusion constants reported above in table 2.1 serve as a useful reference to estimate the amount of donor diffusion during a given anneal, however, some caution must be taken when using these values. Diffusion of near-surface dopants in Si is likely to be higher than for intrinsic bulk diffusion due to the increased concentration of vacancies in-diffused from the free surface [83]. Damage introduced to the Si crystal during ion implantation can also significantly increase dopant diffusion during annealing; particularly for

interstitial-assisted diffusers that are susceptible to transient enhanced diffusion [84].

The extent of ion implanted donor diffusion during annealing is therefore important to quantify. In this work, the diffusion of near-surface implanted Bi in Si is measured after various anneals performed at different temperatures for different durations, as discussed in chapter 4. Additionally, the annealing steps performed during the fabrication of samples and devices in chapters 5 and 6 were chosen by considering the extent of donor diffusion that is required.

2.4 Probing the Donor Quantum Environment

The quantum environment of a donor spin is defined here as the interactions it makes with surrounding spins, such as P_{b0} centres at the Si/SiO₂ interface, the nuclear spins of ²⁹Si or impurity atoms and the electron and nuclear spins of nearby donors, and the magnetic and electric fields it experiences while residing in the Si lattice. This quantum environment determines the resonance frequency and coherence time of the donor electron and nucleus and so can be probed by measuring the electron spin resonance or nuclear magnetic resonance condition, respectively, and their coherence times.

2.4.1 Continuous-Wave Electron Spin Resonance and Nuclear Magnetic Resonance

The resonant frequency of donor electrons or nuclei can be found in continuous-wave electron spin resonance or nuclear magnetic resonance experiments in which the strength of an applied magnetic field is swept whilst irradiating the sample with microwaves to determine the magnetic fields at which an electron or nuclear spin resonance condition is met, respectively.

Electron spin resonance is a technique commonly used to study materials with unpaired electrons. Similarly, nuclear magnetic resonance is used to study materials containing nuclei with non-zero spin. The degeneracy of the electron and nuclear spin energy levels must first be removed by applying an external magnetic field B_0 to Zeeman-split the spin-up and spin-down

states. Electron and nuclear spin transitions can be induced by applying an oscillating magnetic field, B_1 , perpendicular to the static external magnetic field B_0 . The response of donor electron and nuclear spins in a static field B_0 aligned along the z-direction, and an alternating field B_1 aligned along the x-direction oscillating at frequency ν is described by the Hamiltonian (in frequency units):

$$\frac{\hat{H}}{h} = (\gamma_e \hat{S}_z - \gamma_n \hat{I}_z) B_0 + A \mathbf{S} \cdot \mathbf{I} + (\gamma_e \hat{S}_x - \gamma_n \hat{I}_x) B_1 \cos 2\pi \nu t \quad (2.27)$$

at a time t , where γ_e and γ_n are the electron and nuclear gyromagnetic ratios, respectively, in units of Hz/T. This Hamiltonian is the same as the donor spin Hamiltonian given in section 2.2.1 with the addition of the final term which accounts for the oscillating magnetic field B_1 . When the frequency ν of the applied magnetic field B_1 is such that the energy of this microwave field is equal to the electron or nuclear Zeeman splitting, electron or nuclear spin states will be on resonance and transitions will be excited. This is represented for an electron spin in Fig. 2.13.

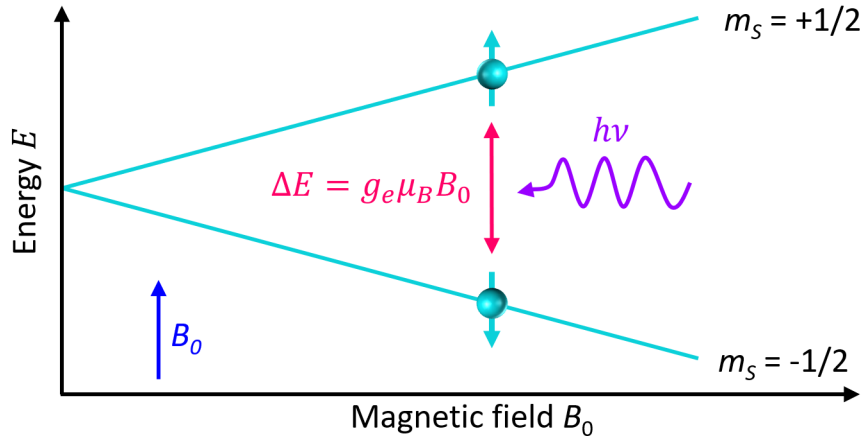


Figure 2.13: The energy of electron spin states are Zeeman-split by applying an external magnetic field B_0 . Spin transitions are driven at the resonance condition when the energy gap ΔE equals the energy $h\nu$ of incident photons.

Since the spin state of nearby nuclear spins affects the energy of the electron spin state via the hyperfine interaction, there will be multiple ESR transitions. In the high field regime, the allowed ESR transitions obey the selection rules:

$$\Delta m_S = \pm 1, \Delta m_I = 0 \quad (2.28)$$

For single electrons interacting with equivalent nuclei with spin I , there will be $2I + 1$ ESR transitions of equal intensity, separated by hyperfine splitting A . Additional forbidden transitions, outside the ESR selection rules, occur in the low field regime due to the intermixing of the flip-flop states (with opposite electron and nuclear spin), corresponding to a component of the state having an allowed transition. Nuclear spin transitions can be induced in a similar fashion using NMR, which obey the selection rules: $\Delta m_S = 0, \Delta m_I = \pm 1$. Since the Zeeman splitting is smaller for the spin of a nucleus than the spin of an electron, lower frequency microwaves are required to induce NMR transitions.

In this work, the electron spin resonance frequencies of near-surface implanted Bi donors were determined using continuous-wave ESR with a conventional ESR spectrometer (with a sensitivity of $\sim 10^{10}$ spins) containing a resonant cavity that measures a change in microwave absorption on resonance. This is discussed in chapter 4. Similarly, the electron spin resonance frequencies of P donors in Si were determined with an EDMR system (with a sensitivity of $\sim 10^5$ spins) that measures a change in substrate conductivity on resonance. This work and the theory of EDMR is discussed in more detail in chapter 6.

2.4.2 Pulsed Electron Spin Resonance and Nuclear Magnetic Resonance

The coherence time of donor electrons or nuclei can be found in pulsed electron spin resonance or nuclear magnetic resonance experiments in which resonant microwaves are applied in pulses, with the duration of the pulse corresponding to a rotation of the electron or nuclear spin by a certain angle, whilst the strength of the applied magnetic field is fixed. In this way, inversion recovery pulse sequences can be applied to determine T_1 and Hahn echo or dynamical decoupling pulse sequences can be applied to determine T_2 , as previously described in section 2.2.4.

In this work, the electron T_2 coherence time for P donors implanted in an isotopically enriched layer of ^{28}Si was measured using pulsed ESR with a Hahn-echo pulse sequence. This was achieved with an on-chip superconducting cavity (with a sensitivity of $\sim 10^8$ spins) and is discussed in chapter 5.

Chapter 3

Experimental Methods

The fabrication strategy used in this work to insert donors into silicon, with the aim of advancing donor qubit realisation, employs ion implantation. It is therefore essential to understand the operational principle and the ion implanter equipment used in this method. Thermal annealing is a necessary step that must be performed after ion implantation to repair the crystal lattice damage produced during ion implantation and to electrically activate the donors. The growth of a high quality oxide, with a low density of interface traps and fixed oxide charge, is required to achieve donors with long coherence times and can be used to electrically insulate the donors from surface electrodes. The composition, crystallinity and donor electrical activation and substitutional fraction of the sample must be determined after these processes to determine the suitability of the fabrication process flow to ultimately produce operational donor qubit devices. Finally, the donor quantum environment, defined as the spins that it couples with in its surroundings and the magnetic and electric fields that it experiences, must be probed to determine the donor resonance frequencies and coherence times with continuous-wave and pulsed ESR measurements, respectively.

This chapter will give an overview of the experimental techniques used in this work, including a brief history, principle of operation and where the technique is used in this work, and is split into three sections. The first section details the main sample fabrication techniques; ion implantation for the incorporation of donors into Si and the isotopic enrichment of Si, annealing to repair crystal lattice damage and electronically activate implanted donors and oxide growth

(the key methods for producing samples analysed in chapters 4, 5 and 6). The second section involves characterising the sample after ion implantation and annealing; predominantly to determine its electrical properties, composition and crystal quality (relevant for chapters 4 and 5). The final section gives the techniques used for determining the quantum environment of the implanted donors in Si by measuring donor electron spin resonance (the subject of chapter 6). More specific details on the experimental setup will be given in the relevant following chapters.

3.1 Sample Fabrication

Uniform high purity $^{\text{nat}}\text{Si}$ (UHPS), obtained from the manufacturer Topsil, was used as the substrate of choice for the implantation of Bi in chapter 4 and isotopic enrichment in chapter 5 due to its low level of background dopants and impurities. These single crystal $^{\text{nat}}\text{Si}$ wafers were grown using the float-zone method [85], where an RF heating coil is raised around a polycrystalline rod of ultrapure $^{\text{nat}}\text{Si}$ with a seed crystal at the bottom. During this process, the localised molten zone is raised up forming a solidified single crystal of Si below, held by surface tension. The process is carried out in an evacuated chamber or an inert gas and impurities are carried away in the molten zone resulting in low concentrations of impurities ($< 5 \times 10^{15} \text{ cm}^{-3}$ for both carbon and oxygen and $< 1 \times 10^{15} \text{ cm}^{-3}$ for nitrogen quoted by the supplier for UHPS Topsil). UHPS Topsil wafers are highly intrinsic, with a resistivity of $4 - 10 \text{ k}\Omega\cdot\text{cm}$ corresponding to a low background phosphorus concentration of $3.2 \times 10^{12} - 1.3 \times 10^{12} \text{ cm}^{-3}$. The float-zone method is a high-purity alternative to crystals grown by the Czochralski method [86], where a crucible is used to contain the molten Si which can introduce contamination with typical concentrations of around $4 \times 10^{17} - 2 \times 10^{18} \text{ cm}^{-3}$ for oxygen and $2 \times 10^{16} - 4 \times 10^{17} \text{ cm}^{-3}$ for carbon [87]. The Czochralski-grown Si impurity levels will be taken as the upper limit tolerable in a silicon device. However, carbon and oxygen concentrations on the order of $1 \times 10^{15} \text{ cm}^{-3}$ may be required in a silicon quantum computing device with exceptionally long coherence times [88].

Once these Si wafers were diced down to size using a laser cutter or diamond scribe and were cleaned (typically with acetone, isopropanol, deionized water, piranha (4:1 98% H_2SO_4 :

30% H_2O_2 , 90 °C), RCA-2 (5:1:1 H_2O : 30% H_2O_2 : 36% HCl , 70 °C) and, if the native oxide needs to be removed, HF), their composition, electrical properties and crystal structure were modified using ion implantation, thermal annealing and oxide growth.

3.1.1 Ion Implantation

Ion implantation is a material surface modification process whereby charged particles produced by a source are accelerated with an electric field and penetrate a solid target where they are slowed by nuclear and electronic energy losses. The origin of ion implantation can be traced back to 1911 when Ernest Rutherford constructed and operated a helium ion source for bombarding gold foil targets at the University of Manchester that lead to the discovery of the nucleus. However, this ion source was produced by the emission of alpha particles from radioactive radon gas and did not make use of an ion accelerator. The first commercially-viable use of ion implantation was given with a fundamental description for ion accelerator equipment in a patent filed by William Shockley in 1954 whilst working at Bell Labs entitled ‘Forming of Semiconductor Devices by Ionic Bombardment’ [89]. Since then, ion implantation has been crucial to the birth of the microelectronics industry, whereby the implantation of dopants can be used to finely tune the local conductivity of the semiconductor, essential for CMOS technology. Ion implantation is also important for metal finishing [90]. For example, in the production of tools, nitrogen or other ions are regularly implanted into steel to make the surface more resistant to crack propagation and corrosion. Additionally, ion implantation is used in the production of prosthetic joints to make the metal surface more resistant to chemical corrosion and friction.

The ion beam species can be selected using a mass spectrometer and determines the resulting elemental or isotopic composition of the surface of the target. The ion implantation energy determines the penetration depth into the target and the level of damage caused to the crystal structure of the target. Along with the ion species and energy, implantation fluence determines the extent of the compositional or structural surface modification. A schematic for the 150 keV ion implanter used in this work is shown in Fig. 3.1. It consists of an ion source, ion beam accelerator and target chamber, all under ultra-high vacuum conditions to minimise

contamination. A Source of Negative Ions by Caesium Sputtering (SNICS) source is used to produce negative ions which are extracted and electrostatically steered into the accelerator tube using an extractor and einzel lens. The energy of the ion beam is selected with the accelerator tube bias. A double focusing magnet with a bending radius of 0.381 m is used for mass analysis of the beam with a resolution of 1 amu for a transmitted ion mass of 190 amu and a lower transmitted mass range for lower mass ions. The strength of this electromagnet, set by the magnet current, is tuned such that only the ions with a desired mass to charge ratio will be deflected by 90° and transmitted through an aperture to enter the beamline downstream. An einzel lens is used to focus the mass-selected beam onto the target with a spot size of 3 mm and can be raster scanned across a maximum area of $40\text{ mm} \times 40\text{ mm}$.

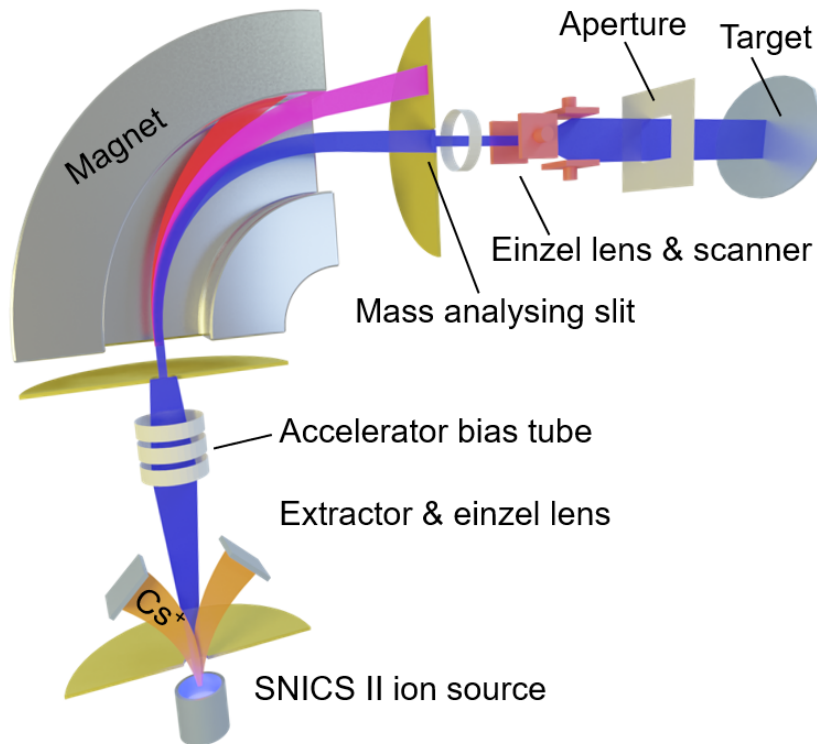


Figure 3.1: Schematic of the 150 keV ion implanter apparatus.

In this work, ion implantation with various ion species, energies and fluences was used to pre-amorphise Si and incorporate Bi donors in chapter 4 and to isotopically enrich a surface layer of natural Si and implant P donors in chapter 5. The majority of these ion implants were performed on a 150 keV implanter, shown in Fig. 3.2, at the Department of Electronic Materials Engineering at the Australian National University [91].

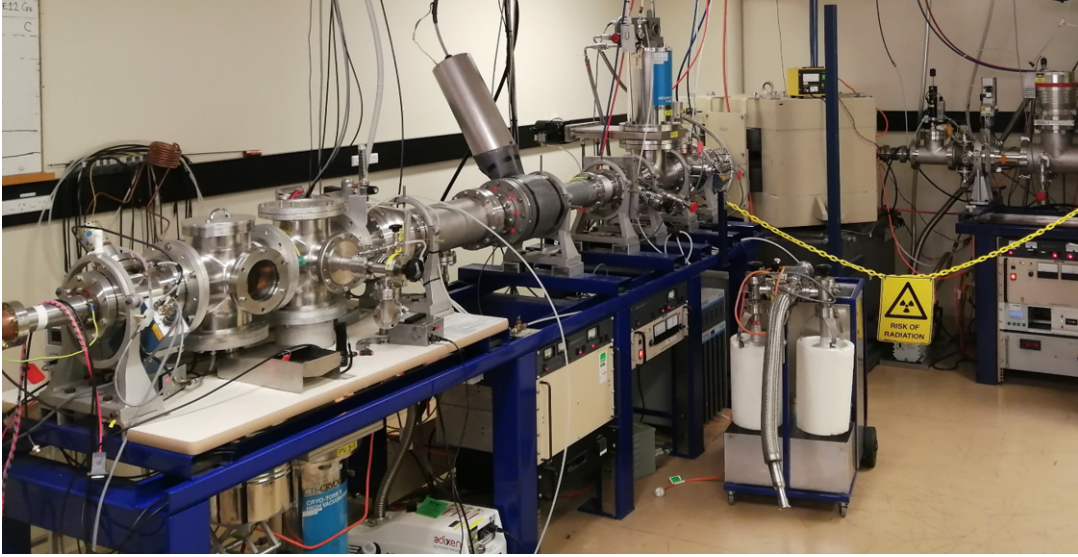


Figure 3.2: The 150 keV ion implanter used in this work with the target chamber on the left of the image.

3.1.2 Thermal annealing

Thermal annealing is a heat treatment that alters the microstructure of a material, changing its physical properties. Annealing is used to repair the crystal lattice after the damaging process of ion implantation [92]. Ion implantation results in primary crystalline damage, including the formation of Frenkel defects (pairs of vacancies and interstitials), higher order clusters of vacancies (voids) and interstitials (dislocation loops) and localised amorphous regions, and continuous amorphous layers. Primary crystalline damage annealing consists of the recombination of vacancies and self-interstitials, which can occur at room temperature up to $\sim 500^{\circ}\text{C}$, the formation of extended dislocations at around $500\text{-}600^{\circ}\text{C}$ which can capture impurity atoms and the dissolution of dislocations at around 1000°C . The annealing of continuous amorphous layers can occur by Solid Phase Epitaxy (SPE) where the atoms in the amorphous phase rearrange at the amorphous-crystalline interface using the crystalline substrate as a template at temperatures between $500\text{-}600^{\circ}\text{C}$. The electrical activation of implanted donors is also achieved by annealing where the donors have sufficient activation energy to become substitutional in the lattice and charge trapping defects are removed, releasing carriers into the conduction and valence bands of Si.

In chapter 4, post-implantation annealing was used to repair the Si crystal structure and

electrically activate the implanted Bi donors. Studies were carried out to optimise the annealing strategy to maximise the electrical activation of Bi without substantial Bi diffusion. In chapter 5, annealing was used to transform the amorphous enriched layer of ^{28}Si into a single crystal by SPE regrowth. Various anneals were used throughout the fabrication process flow for EDMR devices to in-diffuse As donors to form ohmic contact regions and to improve the ohmic nature of the source and drain contacts after metallisation. Annealing was either performed in a silicon furnace or a rapid thermal annealer (RTA), both located in the School of Physics at the University of Melbourne. In the silicon furnace, samples were placed in a quartz boat on a clean piece of Si which could be pulled into the furnace with an external magnet to ensure a short ramp time up to the processing temperature. Samples were annealed in a forming gas (ArH) ambient. The RTA (RTP-600xp) is capable of heating samples to high temperatures (up to over 1000 °C) on a timescale of several seconds. The temperature of samples placed on a Si wafer is controlled by the intensity of a lamp, with feedback from a pyrometer, and the flow rate of ambient Ar gas is controlled.

3.1.3 Silicon Oxide Growth

The oxide of silicon, commonly known as silica with a chemical formula of SiO_2 , is found in nature in its crystalline form as quartz and is a major constituent of sand. In its high-purity form, it is commonly used in the microelectronics industry as an electrical insulator to create a barrier to current flow between metal electrodes and the semiconductor substrate. The formation of an oxide layer will change the chemistry of the silicon surface and allow for surface passivation, whereby the semiconductor surface is rendered inert. This is important to ensure the electrical properties of the semiconductor do not deteriorate as a result of exposure to the gaseous ambient environment or contact with other materials. In fact, the excellent properties of silicon oxide, such as chemical stability and electrical insulation, are a major reason why silicon has dominated over germanium in transistor technology. Silicon oxide layers can also be used as a mask during drive-in diffusion of dopants. The growth of silicon oxide is routinely used in the manufacture of metal-oxide-semiconductor field-effect transistors (MOSFETs) and silicon integrated circuit chips. An example of a MOSFET with a Si nanowire channel, insulated from

a top gate with a thin layer of SiO_2 , is shown in the Transmission Electron Microscopy (TEM) images in Fig. 3.3 [93].

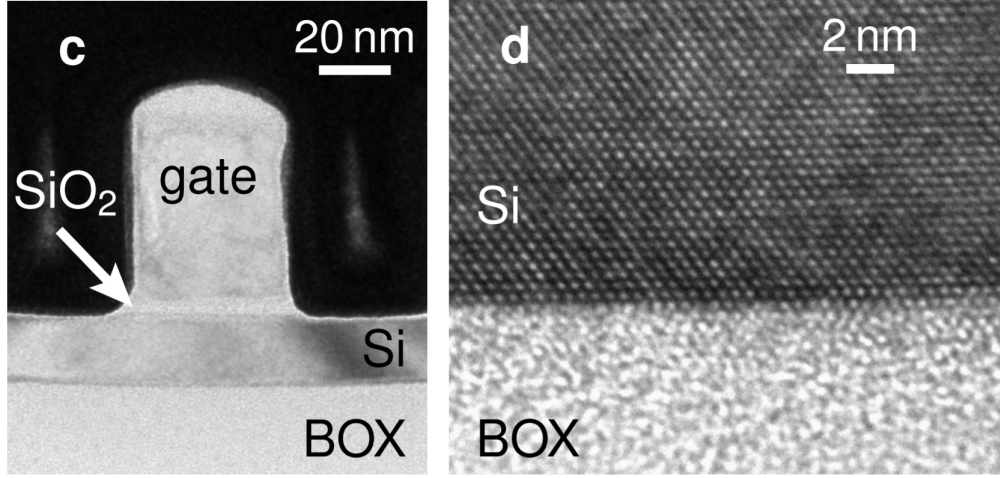


Figure 3.3: TEM images of the cross section of a gated Si nanowire [93]. c) The nanowire (Si) is separated from the poly-Si gate with a 4 nm thick oxide layer (SiO_2). d) High-resolution image showing the atomic lattice of the Si nanowire and its interface with the buried oxide (BOX) of SiO_2 .

The surface of silicon will spontaneously oxidise in ambient conditions, forming a native SiO_2 layer with a self-limiting thickness of around 2 nm [94]. The growth of thicker layers of silicon oxide can be achieved using thermal oxide growth where the thickness and quality (e.g. density of interface traps and fixed oxide charge) of the oxide is controlled by the ambient conditions, oxidation temperature and time. The formation of a thermally grown SiO_2 layer greatly reduces the concentration of electronic states at the silicon surface compared to a native oxide layer which improves the performance of microelectronic devices by reducing the leakage current. Thermal growth of silicon oxide can be achieved by a dry oxidation process with an oxygen ambient:



or a wet oxidation process with a water ambient:



In both cases, a layer of Si at the surface is consumed during the oxidation process.

Thermal oxidation of Si was used in the fabrication of EDMR devices in chapter 6. The layer

of SiO₂ was used to electrically insulate the semiconductor bulk from the microwave stripline and extended source and drain electrodes. Thermally grown silicon oxide was chosen instead of a native oxide to provide a high quality interface with a lower concentration of dangling bonds (P_{b0} centres), which is suggested to optimize the EDMR signal produced by spin-dependent recombination [95]. All oxidation processes were performed in a Si furnace in the School of Physics at the University of Melbourne with an ultra high purity oxygen ambient ($\geq 99.999\%$ O₂).

3.2 Ion Implantation Characterisation

The following techniques were used to characterise the composition, crystallisation kinetics, donor electrical activation yield, substitutional fraction, diffusion and crystal quality after ion implantation into Si.

3.2.1 Secondary Ion Mass Spectrometry

Secondary Ion Mass Spectrometry (SIMS) is an ion beam analysis technique used to characterise the near-surface composition of a solid. In 1910, J. J. Thomson observed the emission of positive ions and neutral atoms from a solid surface upon ion bombardment in the Cavendish Laboratory at the University of Cambridge [96]. However, it wasn't until 1949 that the first prototype SIMS experiments were carried out by Herzog and Viehböck at the University of Vienna [97], after the improvement of vacuum pump technology. These days, SIMS is commonly used in the semiconductor industry to determine the levels of doping and impurities for quality control. It is also used to characterise the composition of natural samples from this planet and others, with the COSIMA SIMS instrument used onboard the Rosetta space probe to determine the minerals contained in cometary dust [98].

During the operation of SIMS, the concentration of various elements or isotopes is measured by sputtering surface layers with a focused primary ion beam and the ejected secondary ions are analysed using a mass spectrometer. Static SIMS uses low energy and current primary ion

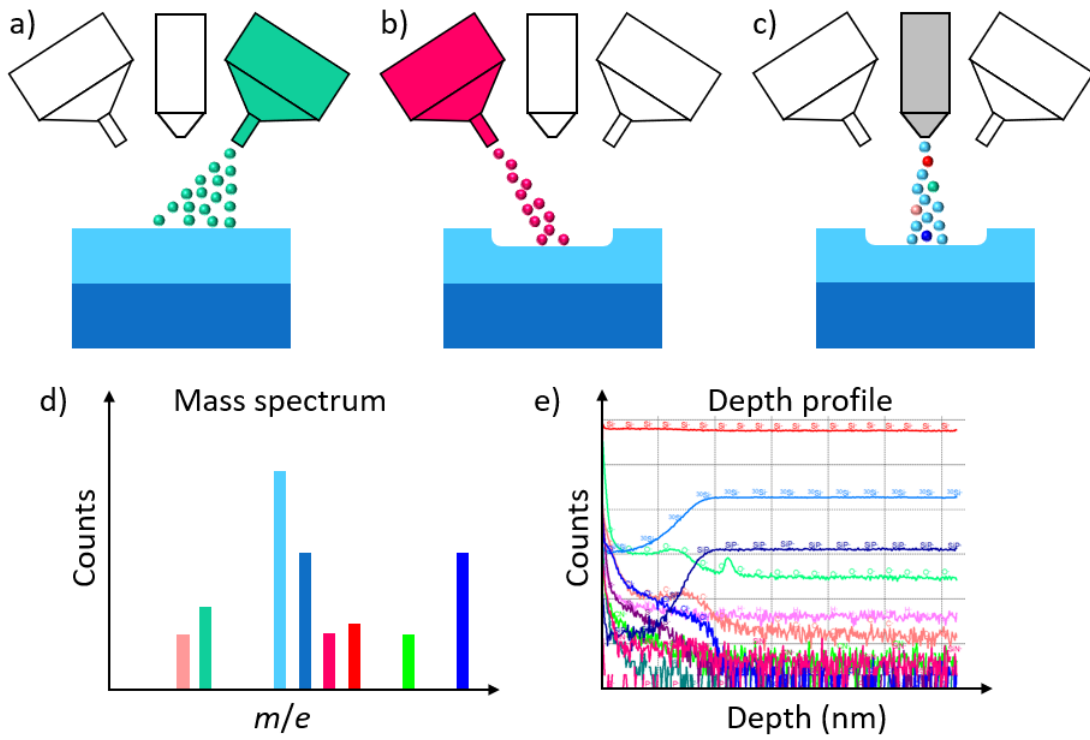


Figure 3.4: The operation principle of dynamic SIMS in dual beam mode: a) Sputter ion gun pulse erodes a crater. b) Primary ion gun pulse for analysis. c) Secondary ions sputtered from the surface are collected by a flight tube that determines their mass. d) A mass spectrum of counts against mass m / charge e is collected at each time interval. e) Counts for various ion species are collected as a function of sputter time and a depth profile is produced by calibrating the sputter time with crater depth. An example SIMS depth profile from an isotopically enriched layer of ^{28}Si , produced in chapter 5, is shown here.

beams which only sputter a few surface monolayers and so analyses only the surface of the sample. Dynamic SIMS uses higher energy and current primary ion beams which erode deeper into the sample over time, allowing a depth profile of the sample composition to be measured up to a few μms below the surface.

In this work, SIMS was used to measure the concentration of silicon isotopes and impurities with depth to determine the effectiveness of isotopic enrichment of natural Si by ^{28}Si ion implantation in chapter 5. The instrument used (TOF.SIMS 5 from IONTOF) was a Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) in dual beam mode which allows for high mass resolution depth profiling. In standard TOF-SIMS, the primary ion beam is pulsed to remove atomic monolayers from the surface. The secondary ions are accelerated into a ‘flight tube’ and their mass is determined by measuring the exact time at which they reach the detector. Since the primary ion beam is pulsed, the current density and resulting erosion rate is low. Therefore,

TOF-SIMS is usually performed in static mode and can only analyse the surface. Dual beam mode allows for depth profiling by alternately using a high current beam of Cs^+ or O_2^+ ions to sputter a crater and a low current beam of Bi^+ or Ga^+ primary ions to analyse the composition of the bottom of the crater. The operation principle of dynamic SIMS in dual beam mode is shown in Fig. 3.4. SIMS measurements were performed at the University of New South Wales, the IOM, Leipzig and the University of Western Sydney. The former two used the TOF.SIMS 5 instrument from IONTOF, whereas the later used the Cameca IMS 5fE7.

3.2.2 Time Resolved Reflectivity

Time-Resolved Reflectivity (TRR) offers a practical method for measuring the progression of the amorphous/crystalline interface in real-time during solid phase epitaxy [99]. Before the development of TRR in the 1980s [100], the velocity of the a/c interface during SPE was determined by measuring the thickness of an amorphous layer after annealing for a certain time at a certain temperature using Rutherford Backscattering Spectrometry (RBS)-channeling techniques [101]. The increased practicality that TRR offers, with the real-time measurement avoiding the need for multiple anneals and RBS measurements, combined with its greater reliability and accuracy, with the measurable regrowth rate of a -Si being extended by over 5 orders of magnitude to $> 10^6 \text{ \AA/s}$ [102], mean that TRR has all but replaced RBS in the study of crystallisation kinetics.

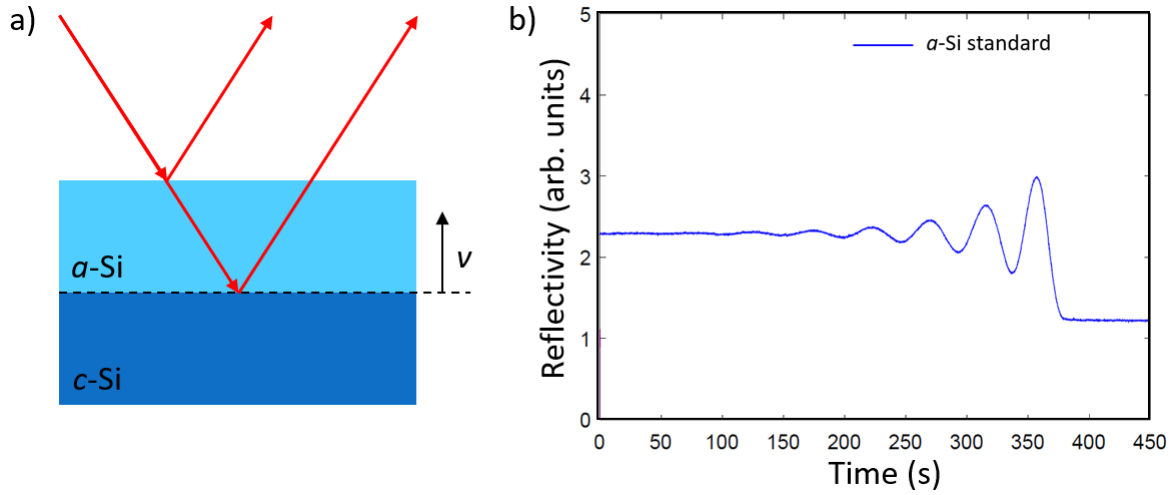


Figure 3.5: Schematic of the TRR setup showing a laser beam reflected off the surface and the a/c interface progressing at a rate v during SPE regrowth. b) The corresponding TRR curve measured in this work showing the oscillating reflectivity during the annealing of an α -Si standard sample at a temperature of 609°C.

The principle of TRR relies on the difference in refractive index of crystalline and amorphous Si. Laser light shone on a crystalline Si sample with a surface amorphous layer will be reflected both from the surface and from the buried crystal-amorphous interface, as shown in Fig. 3.5a. During illumination, the sample is mounted on a resistively heated nickel vacuum chuck to perform annealing. The reflected laser signals will interfere with each other, resulting in interference fringes in the intensity of reflected light collected by a photodiode detector over time as the a/c interface moves towards the surface during SPE regrowth, as shown in Fig. 3.5b. A reference and signal detector are used in combination to minimise the change in reflectivity due to fluctuations in laser intensity. The amplitude of the oscillation in reflectivity increases as the thickness of the amorphous surface layer decreases due to the amount of laser light absorbed in the amorphous layer decreasing. Once the sample is completely recrystallised, the reflectivity will remain a constant with time. The total number of oscillations in reflectivity is proportional to the initial thickness of the amorphous layer, whereas the velocity of the a/c interface can be extracted from the frequency of oscillation.

In this work, TRR was used to determine the regrowth rate of an isotopically enriched surface layer of amorphous ^{28}Si produced by high fluence implantation of $^{28}\text{Si}^-$ ions. This enrichment process and the important reason behind the choice of negative ions is discussed in detail in chapter 5. For TRR, a 632.8 nm red laser was used, which is sensitive only to the

surface 300 nm due to its attenuation in amorphous Si; suitable for the ~ 100 nm thick ^{28}Si amorphous layers produced. The crystallisation kinetics were compared with an $a\text{-Si}$ standard sample with a $2.2\ \mu\text{m}$ -thick amorphous layer produced by the implantation of $^{28}\text{Si}^-$ ions at a higher energy and a lower fluence. The regrowth rate was found to be impeded by the introduction of impurities during the high fluence enrichment process, as discussed in chapter 5.

3.2.3 The Hall Effect

The Hall effect was discovered in 1879 when Edwin Hall observed that a potential difference is generated across an electrical conductor upon the application of a magnetic field perpendicular to the direction of current flow [103]. This Hall voltage is mutually perpendicular to both the direction of current flow and the magnetic field and is generated by the Lorentz force acting on the charge carriers which causes opposite charge to accumulate on opposite faces of the conductor. This charge separation establishes an electric field which counteracts the effect of the magnetic field and prevents further charge migration. A schematic showing the Hall effect for electrons flowing in a conductor is given in Fig. 3.6.

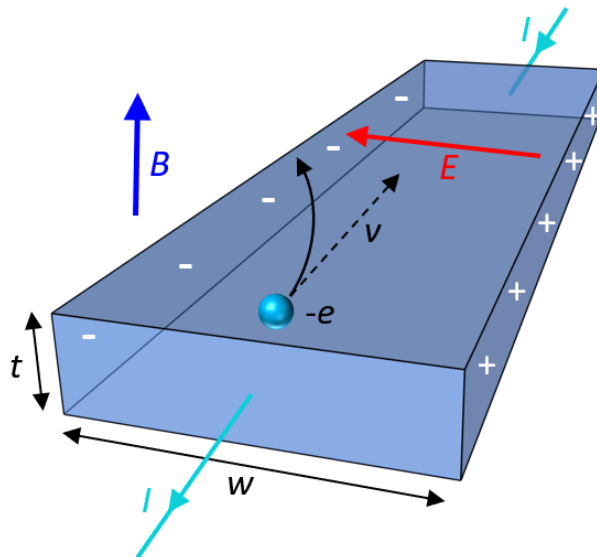


Figure 3.6: In the Hall effect, an applied magnetic field B perpendicular to the current I causes charge carriers to be deflected by the Lorentz force. This induces an electric field E across the conductor which maintains a steady state separation of charge on opposite faces of the conductor. In this case, the charge carrier is an electron.

The flowing charge carriers experience a Lorentz force:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (3.3)$$

where q is the charge of the charge carrier (e for holes and $-e$ for electrons), $\mathbf{E}$ is the electric field pointing in the direction from the positive to the negatively charged face, $\mathbf{v}$ is the drift velocity of the charge carriers pointing in the direction of their motion and $\mathbf{B}$ is the applied magnetic field. In the steady state case, $F = 0$ and so the strength of the Hall electric field is given by $E_H = vB$. Since the electric field is defined as $\mathbf{E} = -d\mathbf{V}/dx$, the Hall voltage is given by:

$$V_H = vBw \quad (3.4)$$

where w is the width of the conductor. This can be expressed in terms of the electrical current:

$$V_H = \frac{IB}{nte} = \frac{IB}{n_s e} \quad (3.5)$$

where n is the charge carrier density, t is the thickness of the conductor and n_s is the sheet carrier density. The Hall coefficient R_H is defined as the ratio of the Hall electric field to the product of the current density J and the applied magnetic field. It can be expressed as:

$$R_H = \frac{E_H}{JB} = \frac{V_H t}{IB} = \frac{1}{ne} \quad (3.6)$$

The Hall coefficient is therefore a characteristic of the conductor material from which the charge carrier density n can be extracted.

The van der Pauw method is a technique commonly used to measure the resistivity and Hall coefficient of a substrate. Van der Pauw devices have 4 ohmic contacts around the perimeter of the sample that allow for the measurement of sample properties of an arbitrary shape [104]. In order for this measurement technique to work, the sample must; be a lamella of uniform thickness, have no isolated holes, be homogeneous and isotropic, have contacts located at its edges, have an area at least 10 times larger than the area of any of its individual contacts [105]. From measurements of the potential difference between two opposing contacts when a current is applied between the other two contacts, whilst a perpendicular magnetic field is applied,

with various contact configurations, the Hall voltage V_H can be determined. The sign of V_H determines the polarity of the charge carriers; if $V_H > 0$, the material is p-type and if $V_H < 0$, the material is n-type. Using Eq. 3.5, the sheet resistivity n_s can be extracted in units of cm^{-2} . Dividing this sheet resistivity by the implanted fluence gives the electrical activation yield. Van der Pauw devices were fabricated and the Hall probe in the School of Physics, University of Melbourne was used to determine the electrical activation yield of Bi implanted in Si after various anneals in chapter 4.

3.2.4 Rutherford Backscattering Spectrometry and Ion Channeling

In a series of Geiger-Marsden experiments performed at the University of Manchester between 1909-1914 in which alpha particles (He^{2+} ions) were fired at gold foil [106], Ernest Rutherford discovered that every atom comprises a tiny, dense nucleus, containing all of its positive charge and most of its mass, and electrons, containing all of its negative charge, orbiting the nucleus. He theorised that the charged alpha particles undergo elastic scattering by Coulomb interactions with the gold nuclei to explain the observation that a fraction of alpha particles were backscattered (deflected by an angle of greater than 90°) from the gold foil. This revolutionised the understanding of atomic structure by replacing the contemporary theory proposed by J. J. Thomson, the ‘plum pudding model’, in which electrons are distributed through a sphere of positive charge [107]. The Thomson and Rutherford models of the structure of the atom, along with their predicted results of the Geiger-Marsden experiments, are depicted in Fig. 3.7. Since these pioneering alpha particle bombardment experiments, ion beam analysis has become a popular tool for characterising the nature of solids.

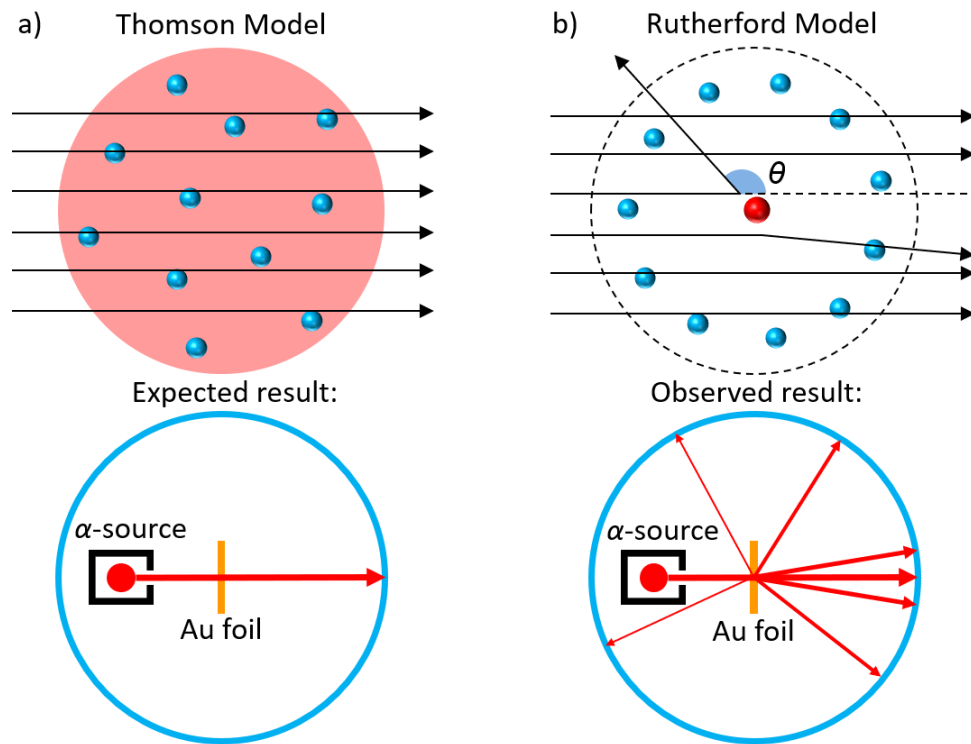


Figure 3.7: a) J. J. Thomson's 'plum pudding model' of the atom [107], with electrons distributed through a diffuse cloud of positive charge, predicts that alpha particles will pass undeflected through gold foil. b) Ernest Rutherford's model of the atom, with the positive charge localised in a dense central nucleus, explains the observed results from the Geiger-Marsden experiments in which a fraction of alpha particles are backscattered from the gold foil [106].

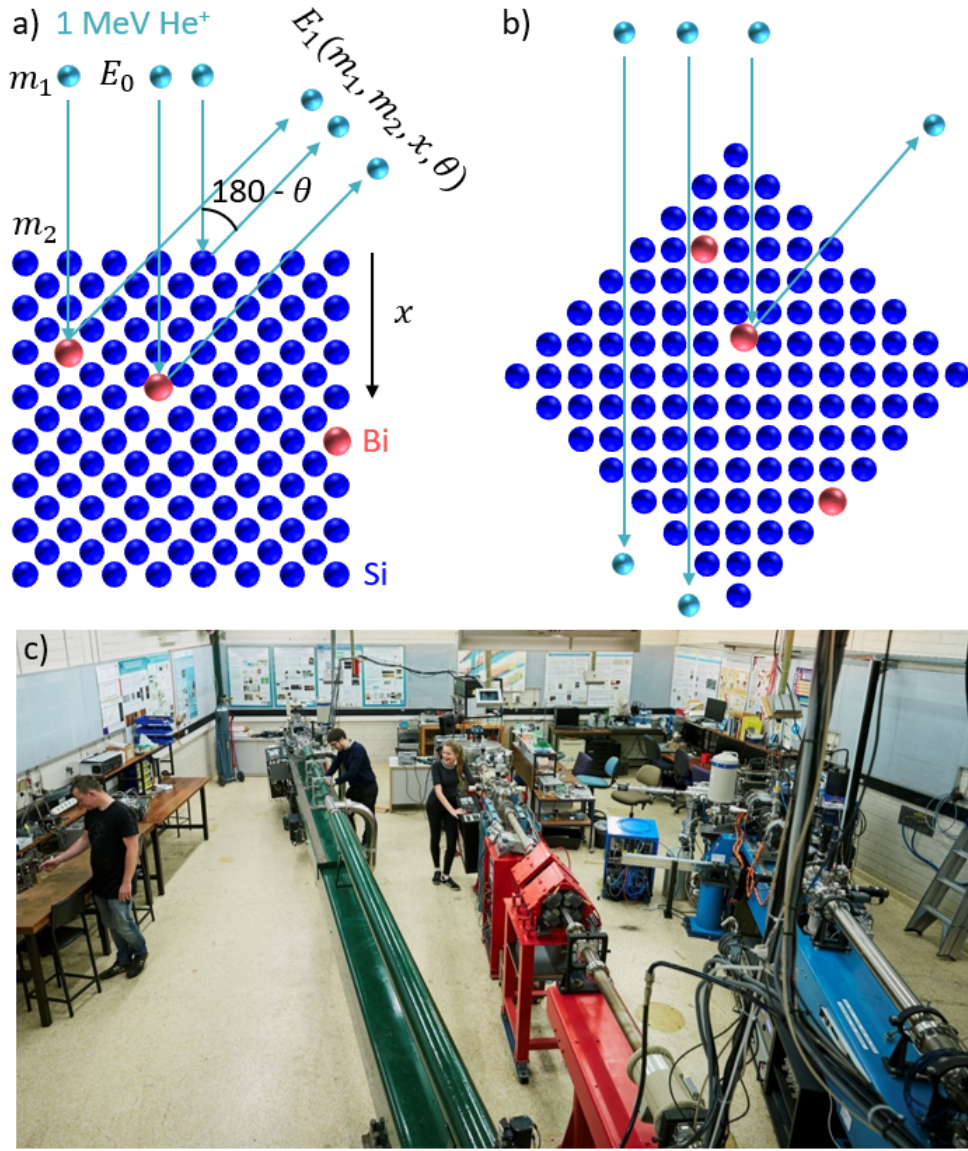


Figure 3.8: a) RBS measurements are performed by accelerating ions (in this case 1 MeV He^+) onto a Si target and measuring the number and energy of He^+ ions backscattered at an angle θ . Elemental composition and distribution of the target can be determined from a histogram of backscattered energies. b) The crystallinity of the target can be determined by orienting the sample such that incident ions are channelled down crystal lattice directions. By comparing the number of backscattered ions with the sample in the channelled and random orientations, the substitutional fraction of various elements can be obtained. c) The red line of the Pelletron 5U accelerator at the University of Melbourne was used for RBS in this work.

RBS is an analytical technique used to measure the structure and composition of a target material by measuring the intensity and energy of backscattered ions at a particular angle θ from an incident high energy ion beam (typically consisting of protons or alpha particles). Considering the kinematics of Rutherford backscattering (an elastic, hard-sphere collision between a high kinetic energy incident projectile and a stationary target particle), as shown in Fig. 3.8a,

the energy E_1 of the scattered projectile is reduced from the initial energy E_0 by a kinematic factor k :

$$E_1 = kE_0 \quad (3.7)$$

where the kinematic factor k can be expressed in terms of the masses of the projectile (m_1) and target nucleus (m_2) and the angle θ through which the projectile is scattered in the laboratory reference frame:

$$k = \left(\frac{m_1 \cos \theta \pm \sqrt{m_2^2 - m_1^2 (\sin \theta)^2}}{m_1 + m_2} \right)^2 \quad (3.8)$$

where the plus sign is taken when the mass of the projectile is less than that of the target (as is typically the case) and the minus sign is taken otherwise [108]. This shows that a projectile will have a higher energy E_1 when it is backscattered off a target nucleus with a larger mass m_2 due to the greater kinematic factor k .

The kinetic energy of incident ions gradually decreases as they penetrate deeper into the target substrate due to inelastic small-angle scattering off electrons, lowering the effective incident energy of the projectile when it eventually collides with a target nucleus. Similarly, backscattered projectiles lose kinetic energy to electronic losses as they exit the target substrate. The amount by which the projectile loses energy after penetrating to a certain depth in the substrate is given by the stopping power S :

$$S(E, x) = - \left. \frac{dE}{dx} \right|_x \quad (3.9)$$

where E is the projectile energy and x is the distance travelled through the substrate [108].

From this, we can see that the energy of the backscattered projectile depends on the mass of the target nucleus that participated in the elastic collision and the depth below the surface where the collision took place. Thus, information about the depth distribution of various elements in the sample can be deduced from an RBS spectrum of backscattered projectile energies. The heavier the impurity elements in a target and the closer they are to the surface, the higher the energy of the peaks that will appear in the RBS spectrum. This method was used in chapter 4 to determine the depth profile of implanted Bi donors in Si and to monitor diffusion after annealing. High-resolution RBS was also used to measure the ratio of Si isotopes in the surface

layer of enriched ^{28}Si samples produced in chapter 5.

In channeling measurements, the incident beam of He^+ ions is aligned down a crystal axis of the target sample, as shown in Fig. 3.8b, where they are steered through small-angle collisions, resulting in a minimum in the backscattered yield [109]. Target atoms which are not substitutional in the crystal lattice will increase the yield of backscattered ions, thus allowing the Si crystal quality and the fraction of substitutional implanted Bi donors to be determined, as in chapter 4.

In this work, all RBS measurements were performed on a 5U Pelletron accelerator in the School of Physics, University of Melbourne, as shown in Fig. 3.8c. An incident beam of 1 MeV $^4\text{He}^+$ ions was used, with detectors positioned at 110° and 170° scattering angles to determine the yield of backscattered $^4\text{He}^+$ ions.

3.2.5 Transmission Electron Microscopy

TEM forms high resolution images by transmitting a beam of electrons through a thin sample, typically less than 100 nm thick, which interact with the sample through Coulomb forces. The image is then magnified and focused using electromagnetic lenses onto an imaging device, such as a fluorescent screen, photographic film or scintillation sensors. TEM was first demonstrated in 1931 by Max Knoll and Ernst Ruska [110], with the 1986 Nobel Prize in physics awarded to Ruska for the development of TEM. These microscopes are capable of imaging at significantly higher resolution than optical microscopes due to the smaller de Broglie wavelength of electrons. This allows for imaging down to the atomic scale, thousands of times smaller than the resolution limit of an optical microscope. TEM is a popular imaging technique widespread across many different scientific fields, including the study of cells, bacteria and viruses in biology and the study of crystal structures in materials science. As an example, a TEM image of human coronavirus particles are shown in Fig. 3.9.

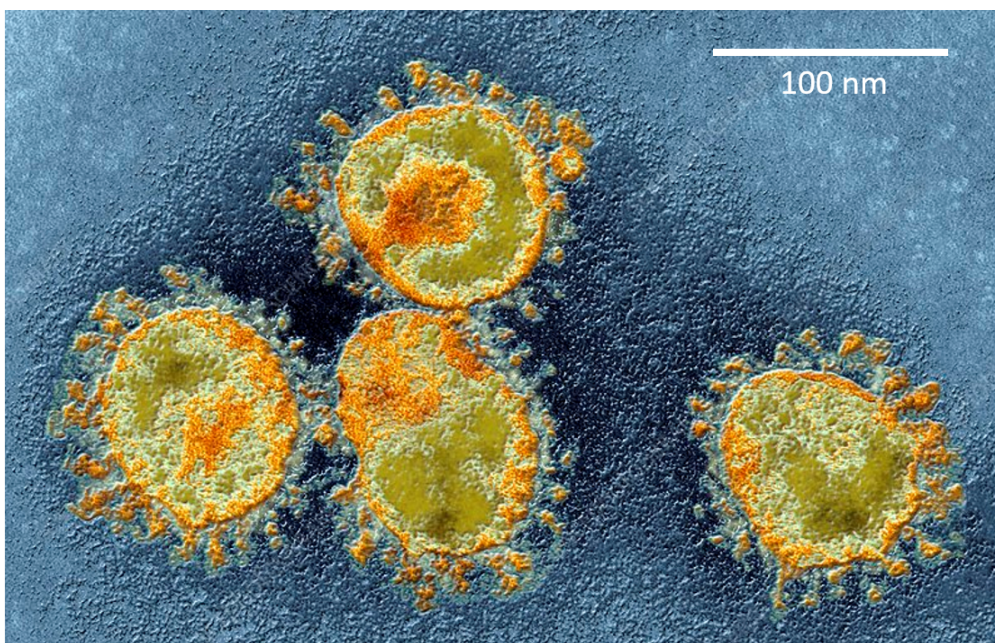


Figure 3.9: False-colour TEM image of human coronavirus particles (virions). They are named after the corona (crown) of surface proteins that are used to penetrate a host cell. Image credit: Ami Images / Science Photo Library.

Electrons from an electron gun are typically accelerated up to energies of 30 keV and then focused onto the sample, held on a specimen stage, with condenser lenses and apertures. The electron beam interacts with the sample and electrons are either scattered or undeflected and form a real image using a focusing objective lens. This image is magnified using a projector lens onto the image plane. The entire system is kept under vacuum to minimise interactions of the electron beam with molecules. The two basic TEM operation modes are imaging and diffraction, with a schematic for both modes shown in Fig. 3.10. In imaging mode, the objective aperture is inserted in the back focal plane of the objective lens. A bright field (BF) image is obtained if the objective aperture allows only the central undeflected beam to pass through whilst blocking the scattered electrons. A dark field (DF) image is obtained if only the scattered electrons are allowed to pass through the aperture. In diffraction mode, a selected area aperture is inserted in the image plane of the objective lens and is used to determine the specimen area that is imaged. The strength of an intermediate lens is adjusted such that the diffraction pattern (the back focal plane of the objective lens) will be projected onto the image screen [111].

In this work, cross-sectional TEM images were taken of isotopically enriched layers of ^{28}Si produced in chapter 5. In order to prepare a thin specimen for imaging, a ~ 100 nm-thick

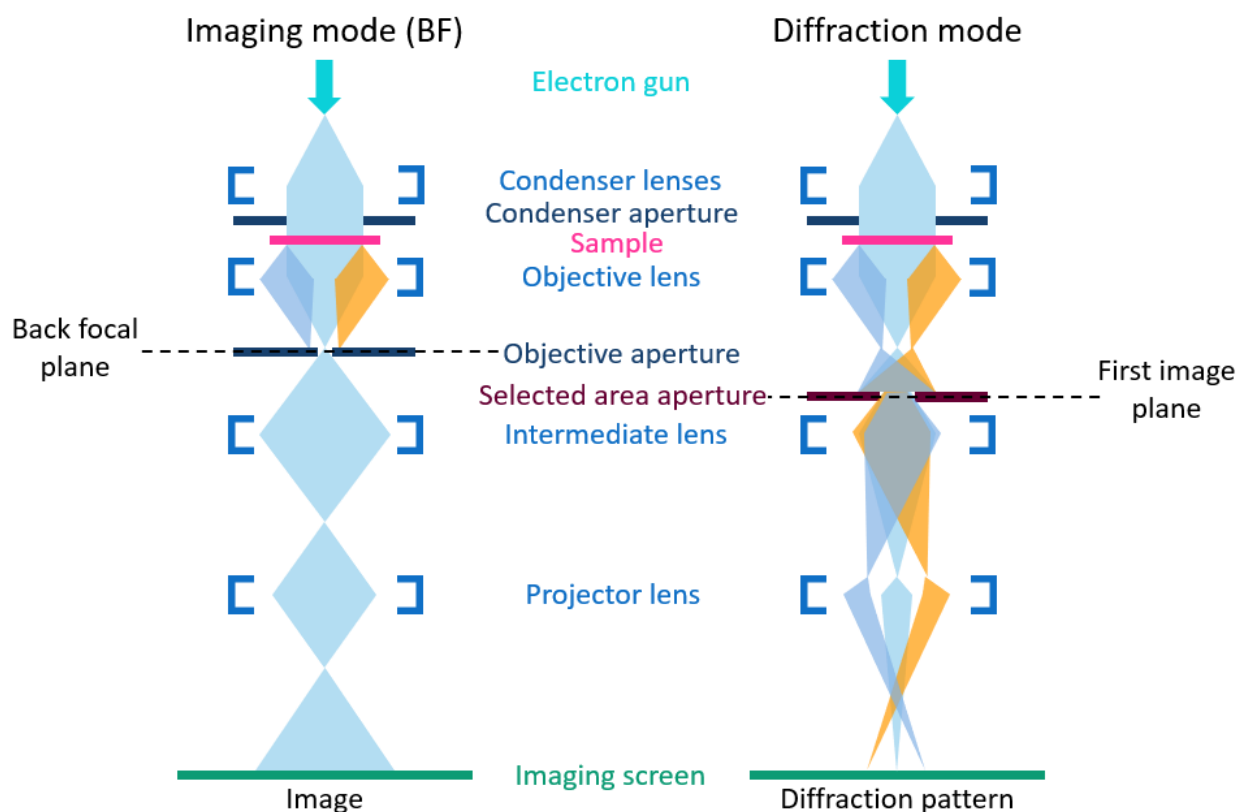


Figure 3.10: Electron beam ray diagrams for the Bright Field (BF) imaging and diffraction modes of TEM. In imaging mode, an objective aperture is inserted in the back focal plane of the objective aperture to select the undeflected (BF) or scattered (DF) electrons and the strength of the intermediate lens is such that the image of the objective lens is projected on the imaging screen. In diffraction mode, a selected area aperture is inserted in the first image plane of the objective lens and the strength of the intermediate lens is such that the diffraction pattern is projected onto the imaging screen.

lamella was cut out from the Si sample using a Focussed Ion Beam (FIB) and mounted on a specimen grid for imaging. Atomic structure was directly imaged with High-Resolution Transmission Electron Microscopy (HRTEM), allowing the crystal quality and end of range defects to be revealed. Taking a Fast Fourier Transform (FFT) of the HRTEM image produces a frequency distribution of the intensity of the image in reciprocal space. The FFT is equivalent to taking a diffraction image of the sample where an array of dots (or a set of diffuse rings) is produced as a result of Bragg scattering as the electron beam passes through a crystalline (or polycrystalline) sample. Information about the crystal structure, for example the lattice constant, can be extracted from this diffraction image. In this work, two different transmission electron microscopes were used; the FEI, Tecnai TF20 at Bio21, University of Melbourne and the JEOL, 2100F at RMMF, RMIT.

3.3 Donor Quantum Measurement

The following experimental techniques were used to observe spin resonance of electrons bound to donors in Si. Continuous-wave ESR was used to confirm the electrical activation of implanted donors and to determine the resonance frequencies of the donor spins. Pulsed ESR was used to obtain the coherence time T_2 of donors implanted in an isotopically enriched layer of ^{28}Si . Combined, these measurements can probe the quantum environment of the donor in the silicon lattice.

3.3.1 Electron Spin Resonance

The phenomenon of ESR absorption was first observed with manganese (Mn) and copper (Cu) salts in 1945 by Yevgeny Zavoisky in Kazan University, Russia [112]. ESR is a non-destructive technique that gives information about the magnetic environment surrounding the unpaired electrons in a material [113] and is important in the fields of quantum chemistry, materials science and pharmaceuticals.

The spin of an electron will align either parallel or antiparallel to an externally applied magnetic field, B_0 . The energy gap, ΔE , between these two spin states is given by the Zeeman splitting. When the electron spins are not excited by a resonant microwave field, most will occupy the lower energy spin state, according to Maxwell-Boltzmann statistics. Electron transitions can be excited by applying an oscillating magnetic field, $B_1(t)$, with a particular microwave frequency, ν , given by the resonance condition, as shown in Fig. 3.11a. Continuous-wave ESR involves applying an oscillating magnetic field, $B_1(t)$, with a fixed microwave frequency whilst sweeping the external magnetic field, B_0 , and measuring the microwave absorbance, which will increase when unpaired electrons in the material are on resonance. The ESR spectrum is typically plotted as the first derivative of the absorption, which can be measured directly using field modulation and lock-in amplification, as shown in Fig. 3.11b. A small additional oscillating magnetic field is applied to modulate the external field strength B_0 , typically at a frequency of ~ 100 kHz. The field oscillates between B_{lo} and B_{hi} , causing the microwave absorption to oscillate between I_{lo} and I_{hi} . By detecting the peak to peak amplitude I_{pp} of this microwave

absorption oscillation, the first derivative of the absorption will be measured. By using phase sensitive detection, only the signals with the same modulation frequency are detected, resulting in a higher signal to noise ratio.

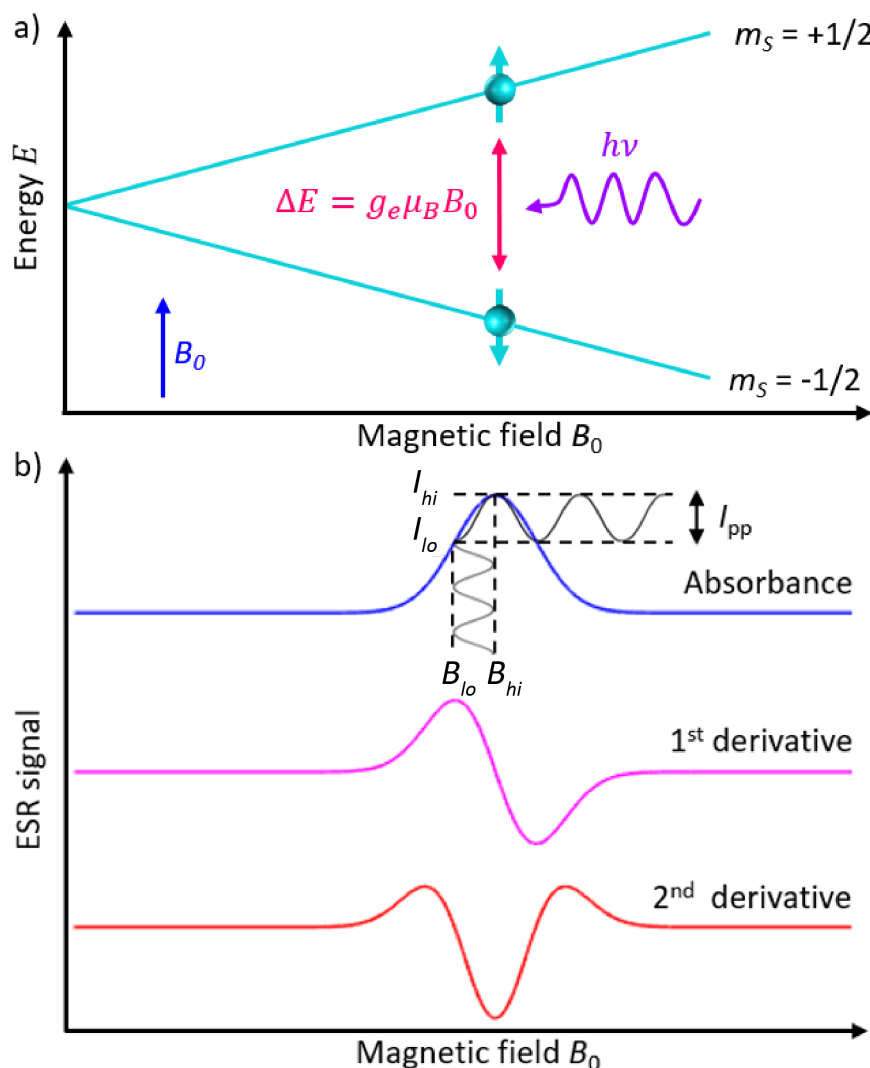


Figure 3.11: ESR measurement principle. a) Spin transitions are driven between Zeeman-split electron states upon the application of microwaves with a frequency given by the resonance condition. b) This corresponds to a peak in the microwave absorbance. By modulating the magnetic field and measuring the peak to peak amplitude I_{pp} of the component of the signal oscillating at the modulation frequency, the first derivative ESR signal can be measured directly.

Fig. 3.12a shows the components of a typical ESR spectrometer. A microwave bridge contains the microwave radiation source (klystron) which emits monochromatic radiation and a microwave detector. A directional coupler sends half of the microwave power to the cavity and half to the reference arm. The reference arm contains a phase shifter that sets a defined phase relationship between the reference and reflected signal. The sample is placed in a cavity, which

enhances the weak microwave absorption signals from the sample, between an electromagnet which splits the electronic energy levels and allows for field modulation. The microwave absorption signal is detected at this field modulation frequency. A typical ESR spectrometer operates at a fixed microwave frequency while scanning the applied magnetic field.

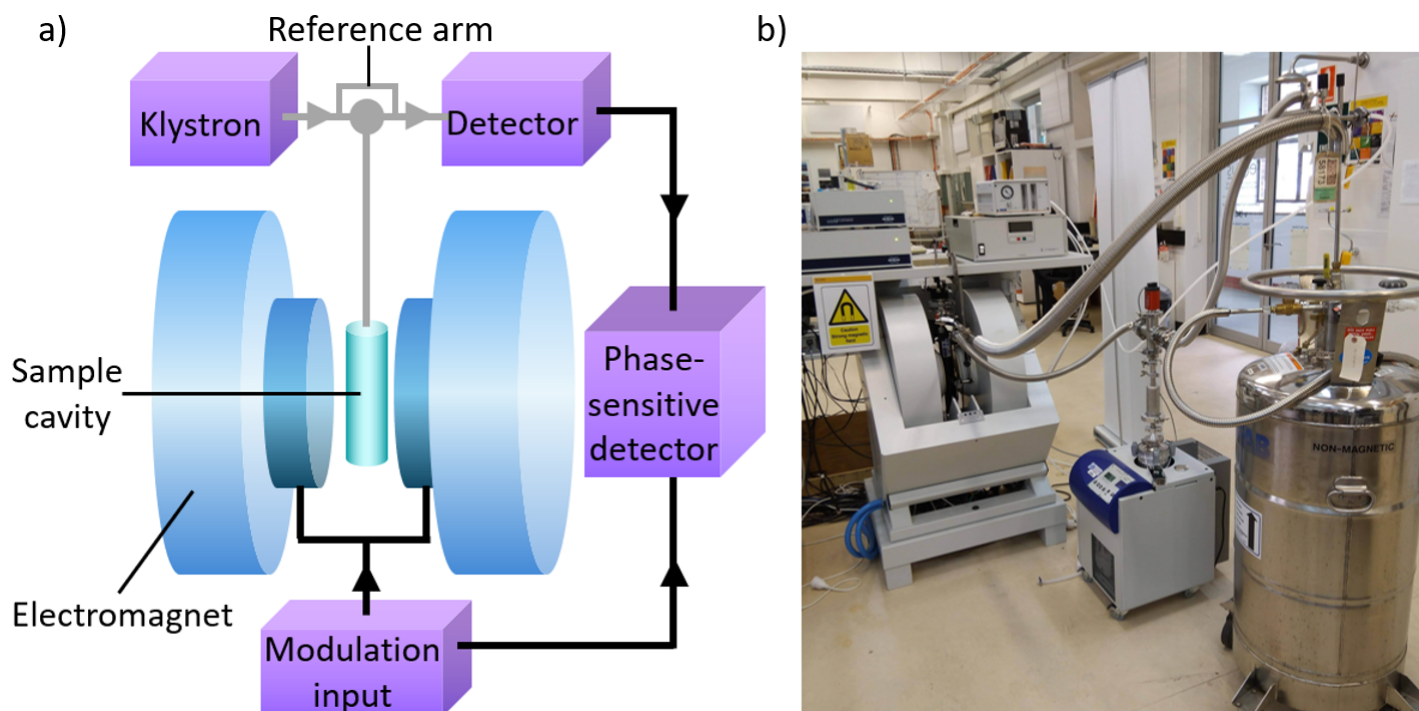


Figure 3.12: a) A schematic showing the components of a typical ESR spectrometer. b) A Bruker Elexsys II ESR spectrometer was used in this work to detect spin resonance from implanted Bi donor electrons. The setup is shown here with a tank of liquid helium for low temperature measurements.

ESR was a key technique used in chapter 4 to identify the presence of electrically activated near-surface implanted Bi donors. A continuous-wave ESR spectrum containing all 10 of the hyperfine-split transition lines was collected using a Bruker Elexsys II ESR spectrometer at UNSW, as shown in Fig. 3.12b. This conventional ESR spectrometer is sensitive to resonance of down to 10^{10} spins. Pulsed ESR measurements with a Hahn echo pulse sequence were also performed with an increased sensitivity, capable of measuring on the order of 10^8 spins, using an on-chip superconducting cavity to measure the coherence time T_2 of P donor electrons implanted in an isotopically enriched layer of ^{28}Si in chapter 5. The relevant ESR experimental parameters are given in chapters 4 and 5.

3.3.2 Electrically Detected Magnetic Resonance

A change in sample electrical conductivity upon spin resonance was first observed with Si:P by Schmidt and Solomon in 1966 [114]. This EDMR achieves greater sensitivity than conventional ESR that measures a change in microwave absorption, with an EDMR signal measured from less than 100 implanted donors detected[115]. This is achieved in Si by measuring the spin resonance of unpaired donor electrons via a change in electrical conductivity of the substrate caused by spin dependent recombination, mediated by paramagnetic defects in the band gap, in this case P_{b0} centres (dangling bonds at the interface of Si and its oxide). The principle of EDMR is much the same as ESR, with the resonance conditions measured by sweeping the applied magnetic field B_0 whilst irradiating the sample with an oscillating magnetic field B_1 at a fixed microwave frequency and modulating either the magnetic field strength B_0 or the microwave frequency for phase-sensitive detection.

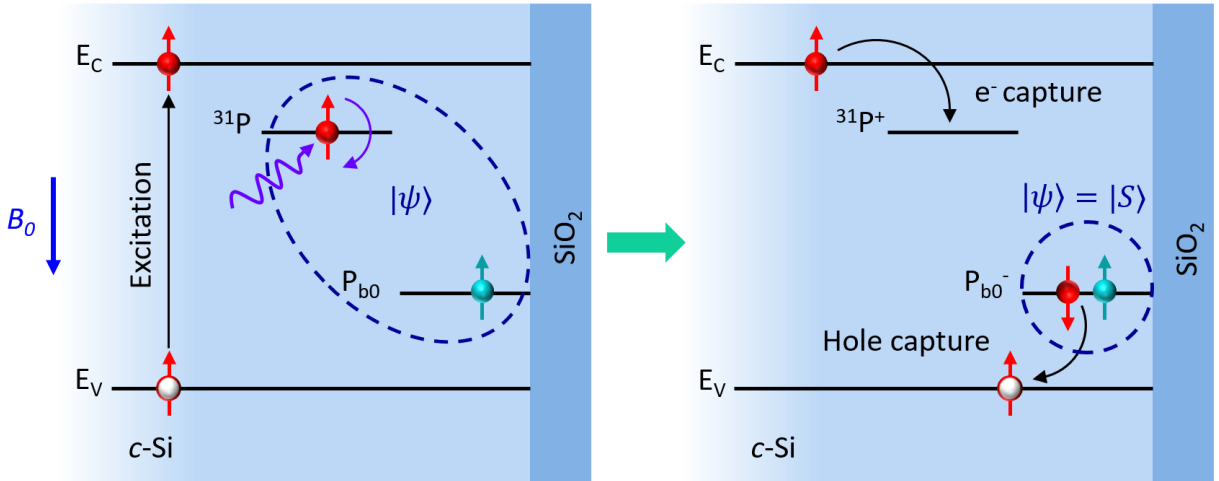


Figure 3.13: Band diagram of the Si/SiO₂ interface showing the spin-dependent recombination mechanism in Si:P EDMR in which the P donor is on resonance with the applied microwave field (purple). Similarly, the P_{b0} electron can be flipped by microwaves resonant with its Zeeman-splitting which also lifts the Pauli spin blockade.

The spin dependent recombination mechanism in Si:P EDMR is shown in Fig. 3.13 and is briefly described as follows. Electrons and holes are generated in the conduction and valence bands of Si by illuminating with above-band gap light. An external magnetic field B_0 aligns the spins of paramagnetic defects in the ground state, creating a spin pair that cannot combine into the same energy level due to Pauli's exclusion principle. When resonant microwaves are

applied to flip either spin of the paramagnetic defects, the Pauli spin blockade is lifted and the electron and hole can recombine via the energy levels of the defects in the band gap. The carrier recombination rate is therefore modulated when the resonance condition is met, leading to a change in substrate conductivity indicating spin resonance. In the case of Si:P, the ^{31}P donor electron and the P_{b0} centre are the paramagnetic defects with energy levels in between the Si band gap involved in the spin dependent recombination. The theory of EDMR is expanded upon in chapter 6.

Unlike conventional ESR measurements on bulk-doped Si samples, EDMR only probes the near-surface layer of donor spins that lie within the range of the P_{b0} centres at the oxide interface. EDMR therefore provides a more realistic measurement of donor spin coherence times in a real qubit device as it is only sensitive to donor spins up to ~ 20 nm below the interface and it can determine the degrading effect of the oxide proximity and surface metallisation. Its high sensitivity is required for the measurement of a low concentration of donor spins, necessary to limit donor-donor interactions that contribute to decoherence, which, when implanted in a ~ 100 nm thick surface layer of ^{28}Si , would not be measurable with conventional ESR.

An EDMR setup was designed and implemented in the School of Physics, University of Melbourne in chapter 6 with the future aim of measuring spin resonance from a small number of donors implanted into an isotopically enriched layer of ^{28}Si . EDMR devices were fabricated on background doped Si:P to test the experimental set up and to optimise the sensitivity for future measurements.

Chapter 4

Activation and ESR of Near-Surface Implanted Bi in Si

4.1 Introduction

Group V donor qubits in silicon (Si) have attracted considerable interest in the field of quantum computing since the Kane architecture was first proposed in 1998 [40]. The ‘semiconductor vacuum’ of the spin-free single crystal of the ^{28}Si isotope offers long electron and nuclear spin coherence times [24] desirable for high fidelity qubit operation. Donor qubits have been realized for phosphorus in Si using surface electrodes for readout and control of the electron and nuclear spin states [16, 17, 116], leading to various quantum computing architectures [62, 117, 64] to be proposed. Of interest is the bismuth (Bi) donor which offers technological advantages including its potential for use as a quantum memory due to the large nuclear spin ($I = 9/2$) providing a 20-dimensional Hilbert space [20]. Bi donors exhibit clock transitions [21] where the transition frequency to first-order is insensitive to magnetic field variations offering increased coherence times. The large zero field splitting of 7.4 GHz also could allow Bi spin qubits to be coupled to superconducting flux qubits [36, 118, 119] due to their closely matched energy splitting to form a hybrid qubit architecture.

For the realisation of quantum computing devices, donors are placed ~ 20 nm below the

Si-oxide interface [64] to enable readout and control of spin qubits by surface nanocircuitry, as illustrated in Fig. 4.1. The density of donors is chosen such that they have a spacing of ~ 20 nm in the exchange-coupled Kane architecture [40] or $\sim 100 - 500$ nm in the electric dipole-coupled flip-flop qubit architecture [64]. A promising solution for fabricating such donor devices in Si is low energy, low fluence ion implantation. With this method, Bi offers increased qubit placement precision over other group V donors owing to its reduced longitudinal straggle of 4.1 nm compared to 9.5 nm for phosphorus when implanted to a mean projected range of 20 nm in Si, based on Monte-Carlo simulations using the Stopping and Range of Ions in Matter (SRIM) [80] software package. Deterministic ion implantation technology [120, 72, 73, 18] provides a possible pathway for creating a scalable array of single donors required for quantum computing architectures.

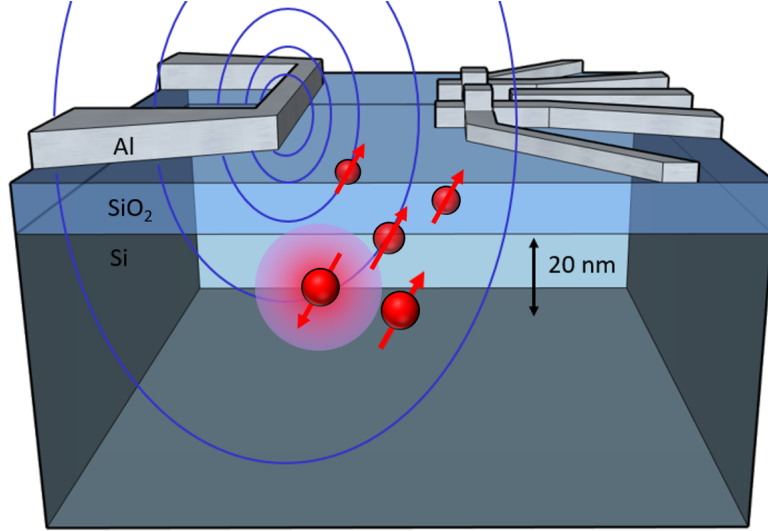


Figure 4.1: An example of a proposed donor qubit device (not to scale) with implanted donors (red). Donors are located ~ 20 nm below the Si-oxide interface enabling spin manipulation by an on-chip microwave antenna and readout by coupling to a SET. Control and readout of a single Bi donor could be achieved by tuning the potential of surface gates [24].

The high atomic mass of Bi, however, results in a dense damage profile upon implantation. Bi also has a low equilibrium solid solubility limit of $8 \times 10^{17} \text{ cm}^{-3}$ at 1320°C [121], which poses a challenge in obtaining a workable active Bi concentration in Si. Achieving operational Bi donor qubits requires an annealing scheme that results in a high electrical activation yield (i.e. a high fraction of donors that have one electron available to donate to the conduction band of Si), a high fraction of substitutional donors in the Si lattice and a measurable ESR spectrum. Diffusion

during annealing must be limited as this causes an increase in donor placement uncertainty and may decrease the donor density in the active region of a device. Channeling of implanted ions down crystallographic directions can also increase donor placement uncertainty. This can be avoided by amorphizing the Si with a sufficiently high fluence implant of ^{28}Si ions, selected using a mass spectrometer, before the implantation of Bi, here termed ‘pre-amorphization’. The ^{28}Si isotope was chosen due to its high abundance and zero nuclear spin.

This work considers the effect of a Pre-Amorphisation Implant (PAI) and annealing on the activation of Bi donors implanted to a depth of 20 nm at fluences above and below the Si amorphization threshold. Optimal activation strategies are proposed by determining the dependence of Bi electrical activation yield, calculated using resistivity and Hall effect measurements, and substitutional fraction and diffusion, measured using RBS, on implant and anneal parameters. The full hyperfine spectrum of implanted Bi donors, solely residing near the Si surface, was obtained using ESR to confirm successful activation.

4.2 Theory

A donor spin qubit in Si can be produced from any one of the group V elements excluding nitrogen, each with their unique characteristics which can offer potential advantages and disadvantages. Relevant parameters for group V donors in Si are summarised in Table 4.1, which can inform the choice of a particular donor over the rest. The advantages that the Bi donor offers owing to its spin Hamiltonian and ion implantation properties are highlighted in the following sections 1.2.1 and 1.2.2, respectively.

Donor	I	1s binding energy (meV)	A (MHz)	γ_n (MHz/T)	Implant energy (keV)	Straggle (nm)
^{31}P	1/2	45.59	117.53	17.26	12	9.5
^{75}As	3/2	53.76	198.35	7.31	20	7.2
^{123}Sb	7/2	42.74	101.52	5.55	22	5.6
^{209}Bi	9/2	70.98	1475.4	6.96	26	4.1

Table 4.1: Parameters for group V donors in Si, including; ground state 1s binding energies [47], hyperfine interaction A [122], nuclear gyromagnetic ratio γ_n [123], implantation energy required for a donor depth of 20 nm below the surface of Si and the longitudinal straggle from SRIM simulations [80].

4.2.1 The Bi Donor Spin Hamiltonian

The spin Hamiltonian of the Bi donor system in an external magnetic field, B_0 , is given in frequency units as:

$$\frac{\hat{H}}{h} = \gamma_e B_0 \hat{S}_z - \gamma_n B_0 \hat{I}_z + A \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \quad (4.1)$$

where $\gamma_e \approx 28$ GHz/T is the electron gyromagnetic ratio and $\gamma_n = 6.96$ MHz/T is the Bi nuclear gyromagnetic ratio [123]. The eigenenergies of this Hamiltonian are plotted using the Breit-Rabi formula, previously derived in Eq. 2.16, in Fig. 4.2.

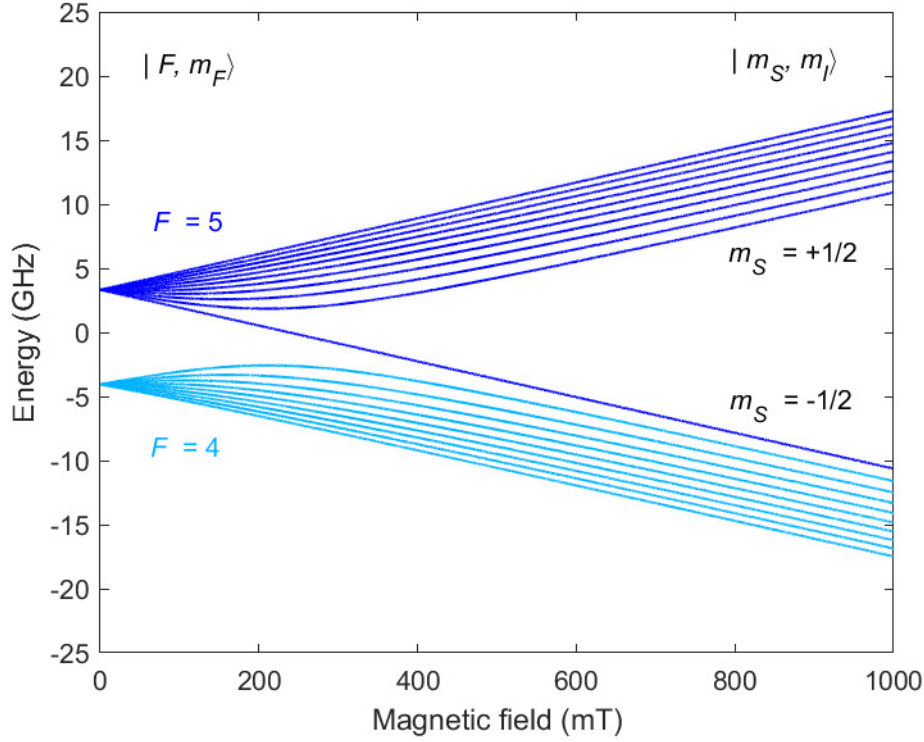


Figure 4.2: The $(2I+1)(2S+1) = 20$ energy levels, in frequency units, of a Bi donor in Si as a function of applied magnetic field. In the low field regime, the hyperfine interaction dominates the Zeeman interaction and the eigenstates are classified by $|F, m_F\rangle$; the total angular momentum and its projection. In the high field regime, the Zeeman interaction dominates the hyperfine interaction and the eigenstates are classified by $|m_S, m_I\rangle$; the electron and nuclear angular momentum projections.

Bi has the highest nuclear spin of the stable group V donors, with $I = 9/2$ resulting in 10 nuclear energy levels. Combined with the donor electron spin, $S = 1/2$, this yields $(2I+1)(2S+1) = 20$ distinct energy levels of the donor system. The Bi donor system therefore represents a qudit, where its state vector lives in a d-dimensional Hilbert space and encodes $\log_2 d$ bits of information, as opposed to a qubit with a 2-dimensional Hilbert space capable of encoding 1 bit of information. The increased Hilbert space of Bi has the potential to store an increased amount of quantum information in a solid-state quantum memory [20] and opens up the possibility of error correction on a single qudit [124].

The spin Hamiltonian of the Bi donor system can be exploited to result in increased spin coherence times in a working qubit device. The 20 energy levels of Bi, with 10 ESR-type transitions, are shown in Fig. 4.3a. The intermediate-field regime ($B \approx 50 - 500$ mT [125]), in which eigenstates are superpositions of the $|F, m_F\rangle$ and $|m_s, m_I\rangle$ basis states (as discussed

previously in section 2.2.2), is of interest here. However, the eigenstates will be labelled by their electron and nuclear angular momentum projections, m_S and m_I , (good quantum numbers in the high-field regime) in the following for convenience. Certain Bi donor spin states exhibit clock transitions, where the transition frequency, f , is insensitive to magnetic field, B , variations, at least to first order (i.e. the derivative $df/dB = 0$). Bi has four ESR-type clock transitions (indicated with black circles in Fig. 4.3b and Fig. 4.3c) corresponding to m_I values of $-1/2, -3/2, -5/2$ and $-7/2$, all occurring at non-zero magnetic fields in the regime of < 200 mT. At these optimal working points, the resonant frequency of the qubit is more robust to magnetic field perturbations arising, for example, from fluctuating ^{29}Si nuclear spins in natural Si [126] and from fluctuating dangling bond spins at the Si/SiO₂ interface [57]. A reduction in ESR linewidth by a factor of 24 and an increase in the electron spin coherence time T_{2e} by over two orders of magnitude has been demonstrated in a Bi-doped natural Si substrate by tuning to a Bi clock transition [21]. Operating Bi donor qubits at clock transitions could therefore relax the constraints on the environment surrounding the donor when engineering a near-surface donor qubit in Si or allow for quantum error correction methods which require fewer physical qubits to create a single logical qubit robust to errors.

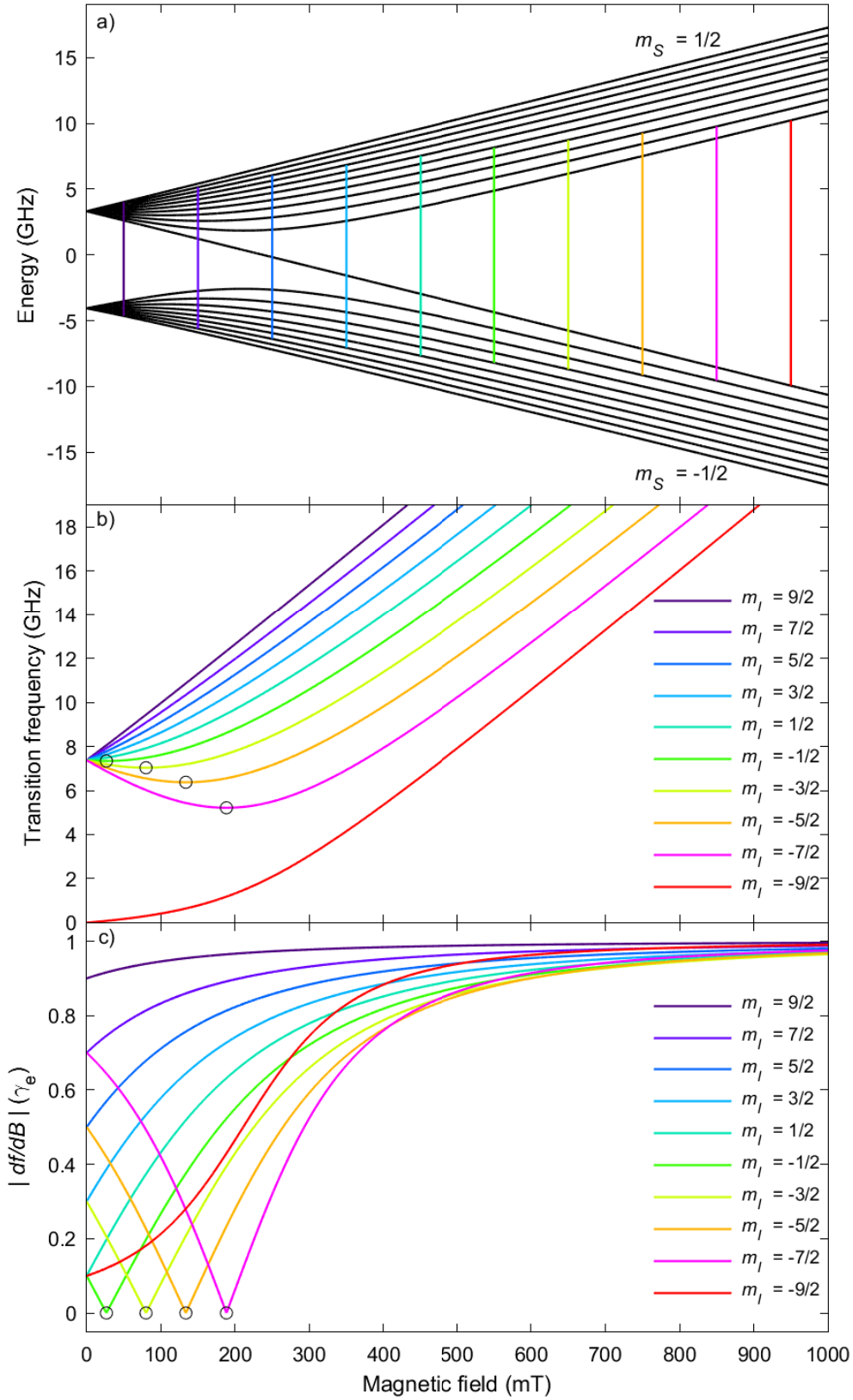


Figure 4.3: The Bi donor system exhibits 4 ESR-type clock transitions, as indicated by black circles. a) Bi donor in Si energy levels, in frequency units, as a function of applied magnetic field. The ESR-type transitions ($\Delta m_S = \pm 1, \Delta m_I = 0$) are indicated as vertical lines coloured according to their corresponding m_I values. b) The transition frequency required to excite the 10 ESR-type transitions as a function of magnetic field. c) The absolute value of the gradient of the transition frequency as a function of magnetic field for each of the ESR-type transitions.

The large zero-field splitting, given in frequency units by $\Delta W = A(I + 1/2) \approx 7.4$ GHz, is similar to the transition frequency of superconducting flux qubits [127]. This could allow Bi donors to be coupled to the strong magnetic dipole of superconducting flux qubits- giving potential for hybrid qubit devices in which superconducting qubits are used for fast processing [128] and donor electron spins are used for quantum memories due to their long coherence times. Coupling of on-chip superconducting resonators to electron spin ensembles has been demonstrated with both Cr^{3+} spins in ruby and N substitution (P1) centres in diamond [129] and nitrogen-vacancy centres in diamond [130].

Donor electrons are most tightly bound to Bi nuclei out of the group V donors, as shown in Table 4.1. The correspondingly small Bohr radius of Bi minimises the effect of spectral diffusion caused by the presence of naturally occurring ^{29}Si spins within the donor electron wavefunction. The electron spin coherence time of Bi donors has been found to be 30% longer than that for P donors in natural Si [119]. Additionally, the correspondingly large ionisation energy of Bi donors limits the amount of thermal excitations and results in a longer T_1 time at a given temperature [20]. This could allow for increased operation temperatures, important for power consumption at cryogenic temperatures.

Bi donors could also be used to demonstrate quantum chaos [123]. Although neglected from the spin Hamiltonian in eq. 6.5, the Bi nucleus has a non-zero quadrupole moment, resulting from a non-spherical nuclear charge distribution, which adds an additional interaction term to the Hamiltonian. The strength of the quadrupole interaction increases with increasing electric field gradient and becomes non-negligible if the electron Zeeman and hyperfine interactions are removed by ionising the donor and the nuclear Zeeman term is decreased by reducing the applied magnetic field B_0 . This nuclear quadrupole term scales quadratically with the nuclear spin operators, and so adding this term to the Hamiltonian, along with a periodic drive, produces a chaotic system. This would open up the exciting possibility of studying the unexplored dynamics of a quantum chaotic system. The incorporation of chaotic quantum spins into existing quantum architectures could also offer speedup for solution convergence by rapidly exploring the available Hilbert space.

4.2.2 Bi Ion Implantation

Bi is the heaviest stable group V donor, with an atomic mass of 209 u . This results in reduced straggling when implanted to a certain depth in silicon [80]. The comparative straggle of the group V donors when implanted to a depth of 20 nm is shown in the SRIM simulation in Fig. 4.4. Bi therefore has the highest placement precision possible of the group V donors for fabricating qubit devices using ion implantation, important for the creation of consistent coupling strengths between implanted donors and surface electrodes.

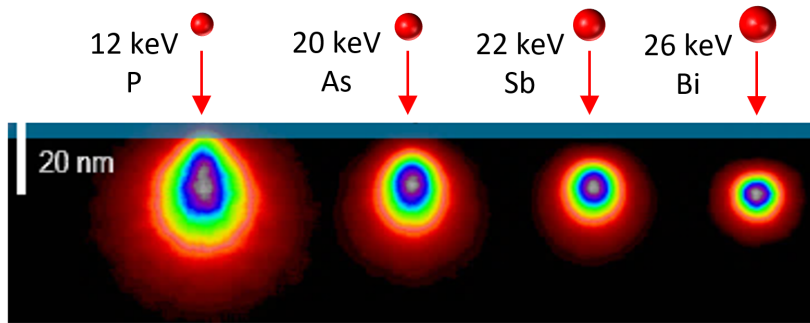


Figure 4.4: The comparative straggle of group V donors implanted in Si to a depth of 20 nm is demonstrated with a SRIM simulation showing the spatial distribution of implanted ions. Heavier ions result in less straggling.

However, a disadvantage of implanting Bi donors is the large amount of damage it generates in the Si crystal. The heavier mass of Bi requires a higher implantation energy to reach the same depth as the lighter P ions. Additionally, a larger fraction of this kinetic energy is dissipated in nuclear stopping processes (generating vacancies and phonons), with a 26 keV Bi ion losing 69.3% of its energy to nuclear stopping processes when implanted in Si, compared to 66.3% for 12 keV P (simulated using SRIM [80]), resulting in increased crystal damage. The large mismatch between Bi and Si covalent radii also causes the most significant lattice distortion at the donor site [131] and thus makes it the least soluble of the group V elements in Si [121]. If the amount of interstitial or substitutional defects (including vacancies) or the local lattice strain around the Bi donor is too high after ion implantation, the coherence of the Bi spin qubit will be destroyed due to the additional decoherence pathways.

It is also important to note that the number of electron-hole pairs resulting from the implantation of a single Bi ion is lower than that for lighter elements. This is due to the Funsten

correction which describes the increased electron-hole recombination in the dense plume of ionisation produced along the ion track [76]. For example, 14 keV P, implanted with a mean range of 23 nm into Si, produces ~ 950 electron-hole pairs, whereas 33 keV Bi, implanted to the same depth, produces only ~ 760 electron-hole pairs [75]. For Bi, this leads to a reduced ion beam induced charge signal and hence would reduce detection fidelity [73]. The noise floor of the IBIC detector would have to be suitably low to allow for the reliable placement of Bi donors using this method of deterministic ion implantation.

4.2.3 Activation and diffusion of Bi

Since Bi is the least soluble of the group V donors in Si [121], an increased fraction of the implanted donors will be pushed off substitutional lattice sites and onto energetically-favourable interstitial sites during the repair of the Si crystal. A carefully chosen annealing strategy is therefore required to maximise the Bi substitutional fraction and electrical activation yield.

If the substrate is annealed at a high enough temperature, Bi undergoes vacancy-assisted diffusion in Si [81]. Diffusion of a SRIM-simulated Bi profile, implanted to a depth of 20 nm at an energy of 26 keV and a fluence of $6 \times 10^{12} \text{ cm}^{-2}$, modelled by Fickian diffusion in one dimension previously derived in Eq. 2.24, Eq. 2.25 and Eq. 2.26, is shown for various temperature anneals for 300 s in Fig. 4.5. A Bi diffusion activation energy of $E_A = 3.85 \text{ eV}$ [81] and a diffusion coefficient of $D_0 = 4 \text{ cm}^2\text{s}^{-1}$, found for Bi implanted into crystalline Si in the following experimental results, was used. This gives an approximate estimate of the amount of Bi diffusion and the shape of the implantation profile in the z-direction that can be expected after thermal annealing. Negligible broadening of the implanted Bi depth profile due to diffusion is observed below 900°C , suggesting that prolonged annealing ($\sim 5 \text{ min}$ or longer) should be performed at less than 900°C .

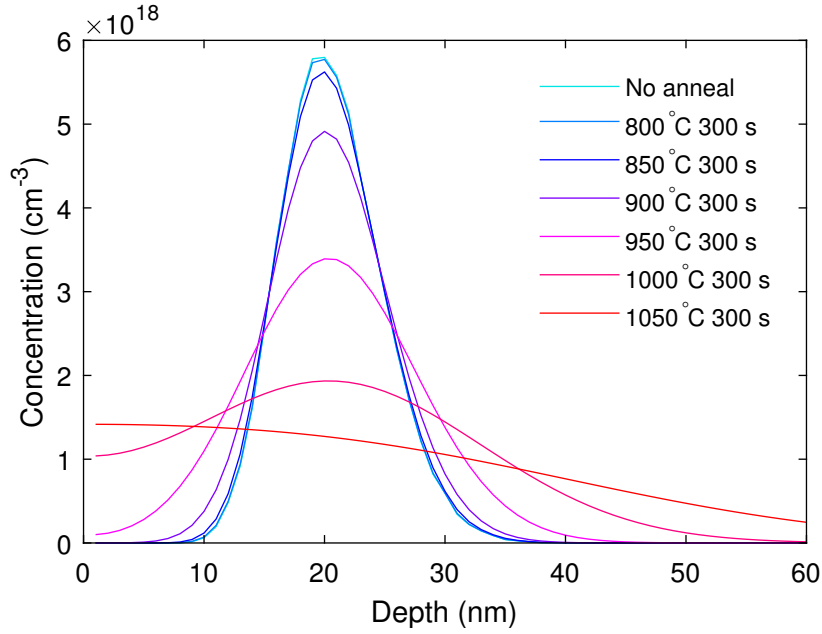


Figure 4.5: Calculated Fickian diffusion of Bi in Si during annealing for 300 s at various temperatures.

Once the thermal energy is great enough for the dopants to overcome the activation energy barrier, significant diffusion will occur during annealing; the amount of which depends on the annealing time, as shown in Fig. 4.6 for a 1000°C anneal. This suggests that, depending on the tolerance of diffusion for a given qubit device, annealing at a temperature of 1000°C should be restricted to a duration of ~ 10 s or less.

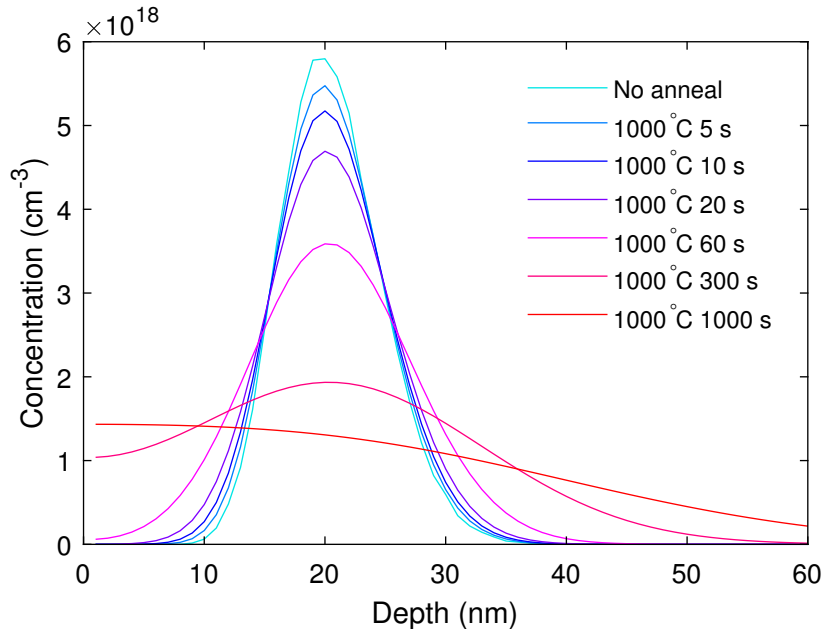


Figure 4.6: Calculated Fickian diffusion of Bi in Si during annealing at 1000°C for various times. The depth profiles look similar to those in Fig. 4.5, however, note the different annealing temperature and durations.

4.3 Experimental Review

4.3.1 Implantation and Annealing of Bi in Si

Previous annealing studies on the substitutional fraction of Bi implanted Si have been carried out [132, 133, 134, 135, 136]. The implantation and annealing parameters and the resulting substitutional fraction, are summarised in Table 4.2. Typically, a high substitutional fraction of Bi donors of around 80–100% is achieved with a low temperature anneal of around 600°C. These studies only probe the high fluence regime as a large Bi concentration is required in order to measure the substitutional fraction via the method of Rutherford backscattering spectrometry. Therefore, the Bi fluences used for substitutional fraction studies are typically above the Si amorphisation threshold. Since the annealing temperature of 600°C is well suited to the repair of the amorphised Si by solid phase epitaxy, this temperature therefore also corresponds to maximising the Bi substitutional fraction.

Energy (keV)	Fluence (cm ⁻²)	Anneal	Substitutional fraction	Electrical activation yield	Ref.
150	$2-4 \times 10^{18}$	650°C 30 min	85%	-	[132]
150	5×10^{14}	600°C 1 min	95%	90%	[133]
15 – 80	1×10^{15}	650°C or 750°C 30 min	97%	-	[134]
40	2×10^{14}	600°C	80%	16%	[135]
240	3×10^{14} 1×10^{15}	600°C 30 min	-	60% 65%	[137]
100	$3 \times 10^{12-13}$	Various	-	Unchanged with continued annealing	[138]
100	$3 \times 10^{14-15}$	Various	-	Decreases with continued annealing	
5	7×10^{14}	Various	Decreases for > 700°C	Decreases for > 700°C	[136]
500-2000	$1-6 \times 10^{12}$	700°C; 800°C; 900°C 5 min	-	41%; 53%; 59%	[139]
40-360	1.1×10^{12}	900°C 15 min	-	67%	[126]

Table 4.2: A summary of previous annealing studies on the substitutional fraction and electrical activation of Bi implanted Si. In these studies, highly intrinsic or p-type (with resistivities as low as 1 Ω .cm) Si substrates were used in order to determine the electrical activation yield of Bi by electrically isolating the implanted layer required for Hall effect measurements. The exception is in reference [138], which used 1000 Ω .cm n-type Si and measures the Bi electrical activation yield by spreading resistance profiling.

Previous annealing studies on the electrical activation of implanted Bi in Si have also been carried out [133, 137, 135, 139, 136, 138, 126]. The implantation and annealing parameters and resulting electrical activation yield are summarised in Table 4.2. The electrical activation yield of Bi is typically measured using the Hall effect; a method which has a higher sensitivity than RBS and so allows the measurement of a lower concentration of implanted Bi. Implantation fluences below the amorphisation threshold of Si can therefore be investigated in electrical activation studies. The fraction of Bi donors that are electrically active is consistently measured

to be significantly lower than the fraction of those that are substitutional in the Si lattice. The majority of the studies are conducted with high energy (> 100 keV) implanted Bi that typically achieve a higher electrical activation yield than those which use a lower implantation energy. This is likely due to the proximity of the surface deactivating a larger proportion of Bi donors due to the increased concentration of charge traps and defects at the interface. The electrical activation yield of Bi implanted in the low fluence regime has been found to not depend strongly on the annealing temperature in the range of 600°C - 1100°C [138], whereas that of Bi implanted at a higher fluence has been found to decrease with increasing annealing temperature. This can be explained by the increased thermal energy accelerating the precipitation of Bi into electrically-inactive clusters at increased temperatures when the Bi concentration lies above the solubility limit.

Finally, many annealing studies on the diffusion of implanted Bi in Si have been carried out; a few of which are mentioned here [136, 126, 71]. These studies show that significant diffusion of Bi only occurs above around 950°C . In particular, Bi donors implanted at 5 keV to a fluence of $5 \times 10^{14} \text{ cm}^{-2}$ showed negligible diffusion at $600 - 700^{\circ}\text{C}$ but significant diffusion when annealed at 950°C for 10 s [136]. Bi donors implanted at various energies between 40 – 360 keV to a total fluence of $1.1 \times 10^{12} \text{ cm}^{-2}$ showed only limited diffusion when annealed at 800°C for 20 min [126]. In comparison, Bi donors implanted at 80 keV to a fluence of $3 \times 10^{11} \text{ cm}^{-2}$ showed significant diffusion after annealing at 1000°C for 10 s [71].

In this thesis, a comprehensive annealing study was undertaken on the electrical activation, substitutional fraction and diffusion of Bi implanted to a depth of 20 nm, technologically useful for qubit devices, implanted at fluences above and below the Si amorphisation threshold into crystalline and pre-amorphised Si. Such an annealing study is important for the future fabrication of Bi qubit devices to maximise the operational yield.

4.3.2 Probing the Bi Donor Quantum Environment

The quantum environment of a donor qubit can be described as the local magnetic and electric fields that it experiences, which determine its resonance frequency and can be measured by

continuous-wave ESR, and the decoherence mechanisms it experiences (such as those caused by fluctuating fields in its local environment), which determine its coherence time and can be measured by pulsed ESR. The 10 ESR transitions corresponding to the Bi nuclear spin, $I = 9/2$, have previously been obtained on electrically activated Bi donors in natural Si [119, 140] and ^{28}Si [126], with spin dependent recombination based magnetic resonance spectroscopy [141] and bound exciton photoluminescence [142]. Yet these experiments were performed on Bi donors implanted to depths between 35 nm to 150 nm [126, 141] or incorporated into the bulk of Si using the pedestal technique [143] during float zone growth [119, 142, 140]. Electron spin resonance of implanted Bi donors in Si solely residing in the near-surface region 20 nm deep, demonstrated in this thesis, is therefore important to confirm the successful electrical activation and to show promise for the fabrication of single Bi donor qubits using ion implantation.

4.3.3 Bi Donor Qubits

The initialisation and manipulation of quantum information stored in both ensembles of electron and nuclear Bi spins incorporated in natural Si via bulk doping has been demonstrated [20]. This shows the feasibility of Si:Bi as a qubit system, as T_1 and T_2 coherence times were found to be at least as long as for Si:P in natural Si. However, a single Bi donor spin qubit is yet to be fabricated and controlled or coupled to a superconducting flux qubit, leaving the door open to many exciting demonstrations with the Bi donor system in the near-future.

4.4 Experimental Methods

After covering the background theory on the advantages and challenges of Bi donor qubits and reviewing previous experimental work performed on Bi donors in Si, we are now primed to discuss the experimental work carried out in this thesis. From the previous experimental review, it is clear that an investigation into the implantation, activation and ESR measurement of Bi donors implanted solely into the near-surface region 20 nm deep, suitable for the operation of a donor qubit with surface nanocircuitry, is necessary. This section describes the fabrication of Bi implanted Si substrates and the techniques used to measure the electrical activation yield,

substitutional fraction, diffusion and ESR of Bi donors after various implantation and annealing conditions, with the aim of optimising the operational yield of future Bi donor qubit devices.

4.4.1 Sample Fabrication

Highly intrinsic (4 - 10 k Ω .cm), float zone natural Si (Uniform High Purity Silicon (UHPS) Topsil) was implanted at room temperature with 26 keV Bi with a tilt angle of 7° with respect to the incident beam axis to suppress channeling. A SRIM (v2013) [80] simulation with Bi implanted into Si at this energy and angle of incidence gave a mean projected range of 20 nm. The pre-amorphization parameters and Bi fluences investigated in this work are specified in Table I. The fluences of $6 \times 10^{12} \text{ cm}^{-2}$ and $1 \times 10^{14} \text{ cm}^{-2}$ were chosen to straddle the Si amorphization threshold [137]. The SRIM-simulated depth profiles for both fluences are shown in Fig. 4.7, from which the maximum concentration and corresponding minimum Bi spacing at the peak of the depth profile were extracted for each fluence and given in Table 4.3. After implantation and a piranha (4:1 98% H_2SO_4 : 30% H_2O_2 , 90 °C) and RCA-2 (5:1:1 H_2O : 30% H_2O_2 : 36% HCl , 70 °C) clean, samples A-D were given a Rapid Thermal Anneal (RTA) in Ar atmosphere at a range of temperatures, 600 - 1000 °C, and durations, 5 - 300 s.

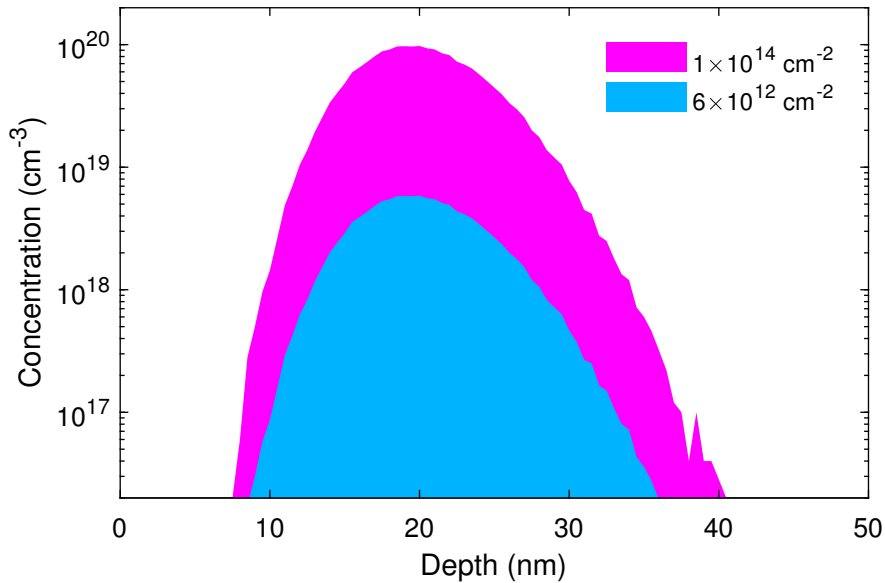


Figure 4.7: Depth profiles of 26 keV Bi donors implanted into Si at a tilt angle of 7° at fluences of $6 \times 10^{12} \text{ cm}^{-2}$ and $1 \times 10^{14} \text{ cm}^{-2}$, simulated using SRIM.

Implantation step	Sample			
	A	B	C	D
^{28}Si PAI (keV, cm^{-2})	None	None	20, 1×10^{15}	20, 1×10^{15}
Bi implant (keV, cm^{-2})	26, 6×10^{12}	26, 1×10^{14}	26, 6×10^{12}	26, 1.0×10^{14}
Max. Bi conc. (cm^{-3})	6.3×10^{18}	1.0×10^{20}	6.3×10^{18}	1.0×10^{20}
Min. Bi spacing (nm)	5.4	2.1	5.4	2.1

Table 4.3: Implant parameters investigated for samples A-D.

4.4.2 Electrical Activation Yield

Samples A-D then underwent a HF etch to remove the native oxide and 200 nm of Al was deposited by electron-beam evaporation onto the corners exposed by a hard shadow mask. A forming gas (Ar:H) anneal at 400 °C for 30 min was used to ensure good ohmic contacts. Resistivity and Hall effect measurements were taken at room temperature using Van der Pauw devices with a magnetic field sweep between -0.7 and 0.7 T at currents of 5 μA . The Bi electrical activation yield was calculated by dividing the measured effective carrier sheet density, determined from Hall measurements, by the total implanted fluence. The measured carrier sheet density of the intrinsic UHPS substrate was negligible and so the Hall measurements can be assumed to be probing solely the electrons provided by the Bi donors.

4.4.3 Substitutional Fraction and Diffusion

RBS measurements were performed on a 5U Pelletron accelerator with 1 MeV $^4\text{He}^+$ ions using detectors positioned at 110° and 170° scattering angles with solid angles of 3.36 msr and 4.23 msr, respectively. For the high fluence Bi samples B and D, the substitutional fraction, f , of Bi donors on lattice sites to the total number of donors present was measured using [144]:

$$f = \frac{1 - \chi_I}{1 - \chi_R} \quad (4.2)$$

where χ_I and χ_R are the proportions of the integrated area of the Bi peak and the Si edge height in the RBS spectra for the sample aligned in the channeled orientation (with the $^4\text{He}^+$ beam aligned along a $\langle 100 \rangle$ crystal direction) to the random orientation (where the beam is not aligned with any low-index crystal directions or planes), respectively.

$$\chi_I = \frac{A(\text{Bi,C})}{A(\text{Bi,R})} \quad (4.3)$$

$$\chi_R = \frac{H(\text{Si,C})}{H(\text{Si,R})} \quad (4.4)$$

Here, $A(\text{Bi,C})$ and $A(\text{Bi,R})$ are the areas of the Bi peaks in the channeled and random orientations, respectively, and $H(\text{Si,C})$ and $H(\text{Si,R})$ are the heights of the Si edge in the channeled and random orientations, respectively. These parameters are labelled in the channeled and random RBS spectra in Fig. 4.8b. The substitutional fraction of Bi will be high if the area of the Bi peak in the channeled orientation is small with respect to the area of the Bi peak in the random orientation, i.e. when the amount of He^+ ions backscattered from Bi atoms that are not substitutional in the Si lattice is low. Bi depth profiles were fitted with Gaussian curves and the Full Width at Half Maximum (FWHM) was extracted, enabling a quantitative measure of Bi diffusion coefficients.

4.4.4 Continuous-Wave Electron Spin Resonance

To independently confirm the presence of near-surface implanted and successfully annealed Bi in Si, Continuous-Wave Electron Spin Resonance (CW-ESR) measurements were carried out on a $6 \times 10^{12} \text{ cm}^{-2}$ Bi implanted sample using a Bruker Elexsys II ESR Spectrometer in an X-Band cavity at 9.7209 GHz. This sample was selected to ensure the Bi concentration was below the metal-insulator transition (around $2 \times 10^{19} \text{ cm}^{-3}$ for Bi in Si [145]) to avoid the non-resonant absorption of the microwave energy due to dissipative currents that appear in the sample [146]. The magnetic field was swept between 0 and 600 mT to ensure the collection of all 10 Bi donor ESR transitions and measurements were performed at 25 K, below the Bi donor freeze out temperature. The microwave power was set to 0.4743 mW and the magnetic

field was modulated at a frequency of 100 kHz and an amplitude of 0.1 mT to ensure a suitable ESR signal to noise ratio.

4.5 Results and Discussion

Now that the experimental methods and parameters have been given, the results collected from the Hall effect, RBS and ESR measurements are displayed and discussed.

4.5.1 Implantation Damage Characterisation

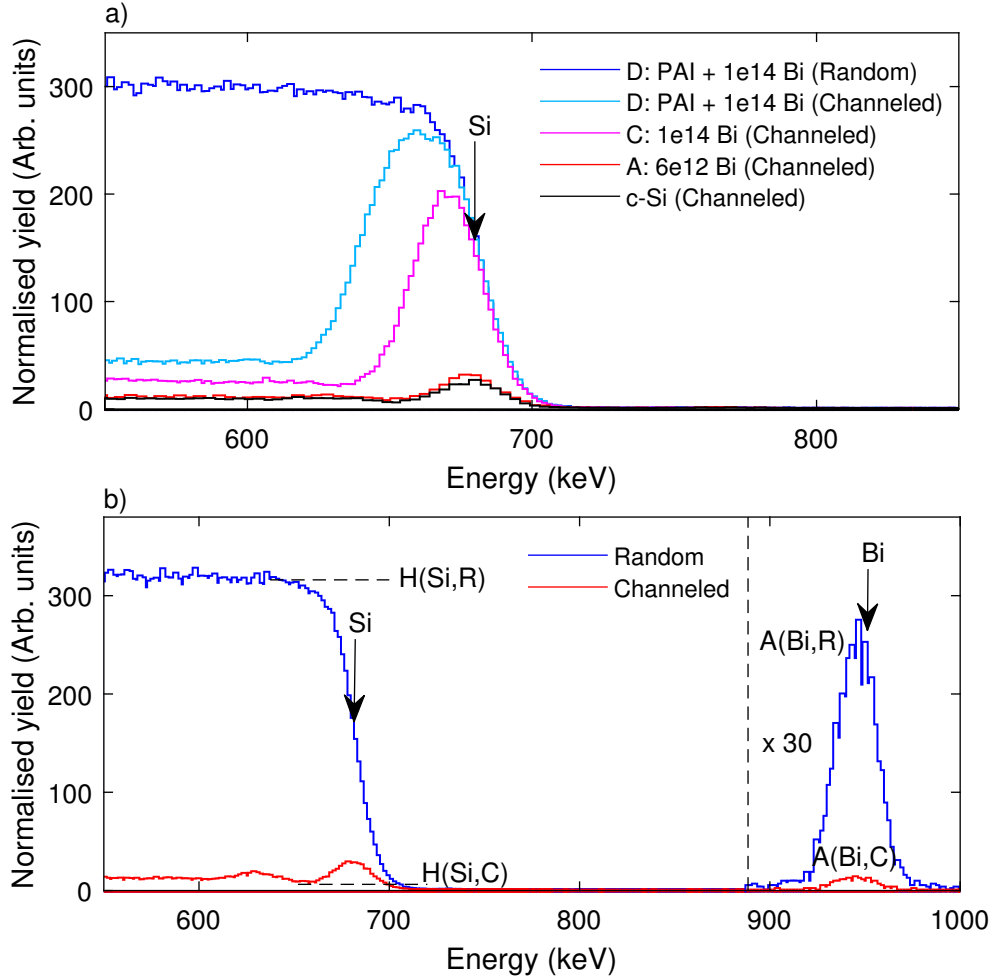


Figure 4.8: 1 MeV He⁺ RBS spectra collected at a scattering angle of 110°. The labelled arrows indicate the expected energy of a He⁺ ion backscattered off a particular element based on their kinematic factor. The slope of the edges are due to the energy resolution of the detector. a) The damage to the Si crystal caused by the various implants in Table 4.3 before annealing can be seen in the Si edge height in the channelled orientation. (Legend in order of decreasing Si edge height.) b) Sample D annealed at 700 °C for 5 min. With the sample aligned in the channelled orientation, the Si surface peak and lower energy peak corresponding to channeling oscillations [109] are visible. The reduced area of the Bi peak for the channelled sample orientation compared with the random orientation is due to the high substitutional fraction.

Bi implantation fluences in this work were chosen to straddle the Si amorphization threshold, where a continuous amorphous layer is formed at $\gtrsim 1 \times 10^{14} \text{ cm}^{-2}$ for keV Bi ions [147]. This was confirmed by Raman spectroscopy (not shown) and from the height of the Si edge in the RBS spectra for samples in the channelled orientation, shown in Fig. 4.8a. A Bi fluence of $6 \times 10^{12} \text{ cm}^{-2}$ was shown to not result in a continuous amorphous layer as the channelled RBS

spectrum from sample A closely matches that produced by a crystalline Si (c-Si) sample without implantation. Comparisons with simulations using the RBS software RUMP [148] suggest a continuous amorphous Si layer is present after implanting 1×10^{14} Bi cm $^{-2}$ (sample C). The RBS spectrum for sample D with a PAI has a wider Si edge that is consistent with a thicker amorphous layer. The height of the channeled edge does not reach that of the random edge due to the thickness of the amorphous layer and a detector energy resolution FWHM of 25 keV, as calculated by matching the shape of the Si edge with RUMP simulations [148]. Both the Si surface peak and a lower energy peak are visible in the RBS spectrum collected in the channeled direction in Fig. 4.8b due to channeling oscillations [109]. When charged projectiles are steered down a particular crystallographic direction, they experience a continuum potential from the surrounding atoms in the lattice which results in oscillations that are transverse to their direction of motion. Charged projectiles that approach the atomic planes are more likely to be dechanneled, resulting in an increase in backscattering at a characteristic depth that corresponds to the wavelength of the channeling oscillations.

4.5.2 Electrical Activation Yield

Sections of samples A-D underwent an RTA at temperatures between 600 and 1000 °C for 5 min. Bi electrical activation yield data is shown in Fig. 4.9a. A significant decrease in Bi activation is observed at temperatures above 800 °C for high fluence samples B and D. This is in agreement with previous studies of Bi implanted at fluences above the Si amorphization threshold, where a maximum electrical activation yield, up to $\sim 90\%$ [133], is achieved for temperatures around 600 – 700 °C for a few minutes [133, 137, 135, 136]. The high fluence implant exceeds the Si amorphization threshold and so crystallization proceeds via SPE [149] in which Bi donors are incorporated onto substitutional sites (a metastable state), often above the solid solubility limit. The decrease in Bi activation observed above 800 °C may be a result of an increased thermal budget allowing the Bi to move off lattice sites into interstitial sites (an equilibrium configuration) where they form electrically inactive Bi clusters due to the Bi concentration being well above the solid solubility limit. Bi diffusion at these high temperatures was also observed using RBS, as described below, which supports this theory. A PAI produces a thicker,

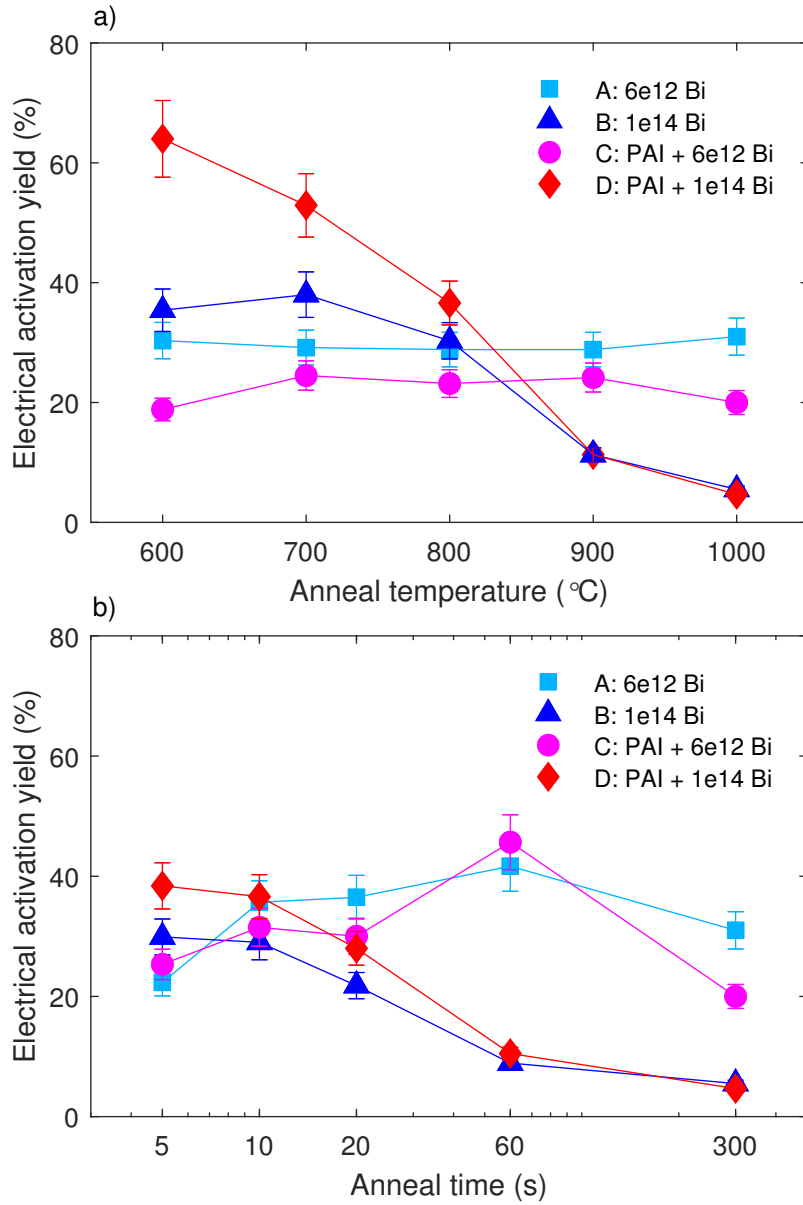


Figure 4.9: Electrical activation yield of Bi implanted Si given a) a 5 min RTA at various temperatures and b) a 1000 °C RTA for various times. Errors are dominated by the uncertainty in the implant fluence.

and likely more homogeneous amorphous layer, than $1 \times 10^{14} \text{ Bi cm}^{-2}$ alone which therefore increases Bi activation for low temperature anneals by aiding the SPE regrowth mechanism. For implant fluences below the Si amorphization threshold, higher temperature anneals of around 900 °C have been shown to maximize Bi activation [139, 126, 138]. However, for the implant parameters considered in this work, no significant dependence on anneal temperature is observed. The PAI in this case results in a slightly lower electrical activation yield of 22% on average, whereas without the PAI, the yield is closer to 30%.

Sections of samples A-D underwent an RTA at 1000 °C for durations between 5 and 300 s.

The Bi electrical activation yield data for these samples is shown in Fig. 4.9b. For high fluence samples B and D, a shorter anneal time of 5 s maximizes Bi activation for high temperature annealing but does not come close to the higher level of activation achieved at 600 °C. For low fluence samples A and C, Bi activation increases with anneal time from 5 s to 60 s but then drops when further increased to 300 s. During a 1000 °C anneal, the decrease in electrical activation for the high fluence case occurs at shorter times than the low fluence case. This could be explained due to the higher fraction of Bi above the equilibrium solubility limit which can be deactivated in the high fluence case.

Optimal Bi electrical activation yields in the low and high fluence regimes were found to be 46% and 64%, corresponding to active concentrations of around $2.0 \times 10^{18} \text{ cm}^{-3}$ and $6.6 \times 10^{19} \text{ cm}^{-3}$ at the implant profile peak estimated using SRIM and taking into account diffusion as measured by RBS, respectively. These active concentrations are well above the equilibrium solid solubility limit for Bi in Si of $8 \times 10^{17} \text{ cm}^{-3}$ [121]. This agrees with previous studies of ion implanted Si, where SPE can produce a metastable substitutional solid solution, where the Bi solubility limit can be as high as $9 \times 10^{19} \text{ cm}^{-2}$ [150].

4.5.3 Substitutional Fraction and Diffusion

For the high fluence samples B and D, the Bi substitutional fraction as a function of anneal temperature and time is shown on the left axes in Fig. 4.10. In general, almost all of the implanted Bi is substitutional in the Si lattice after 5 min anneals between 600 and 800 °C and for 1000 °C anneals between 5 and 20 s. The substitutional fraction drops above 800 °C for 5 min anneals and above 20 s for 1000 °C anneals, in agreement with previous studies [133, 135, 136]. With increasing applied thermal budget, more of the Bi donors are displaced from metastable lattice site locations and become stable interstitial defects. This aids the understanding of the observed trends in electrical activation yield for the high fluence Bi samples.

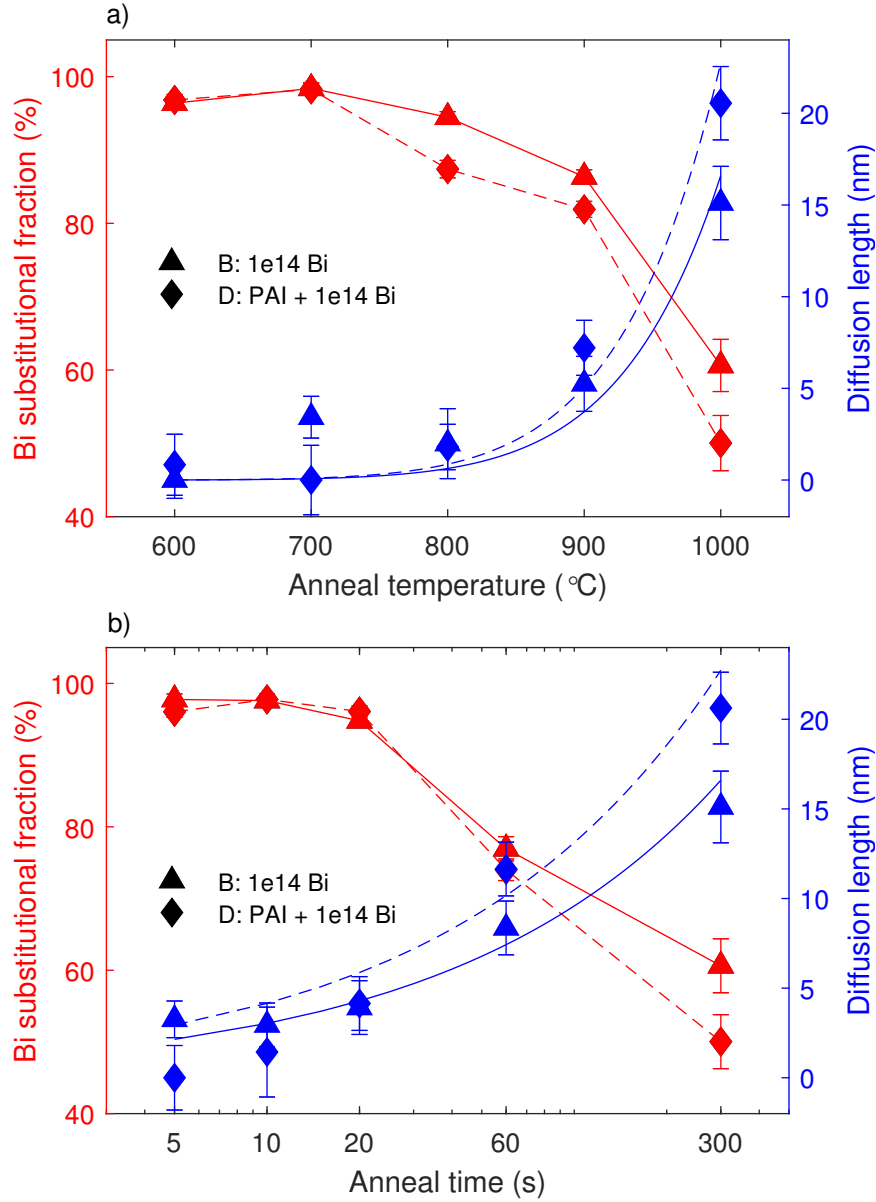


Figure 4.10: a) The substitutional fraction of Bi measured using RBS at a scattering angle of 170° (red) and the diffusion length of Bi measured from the FWHM of the Bi peak in RBS spectra collected at a scattering angle of 110° (blue) as a function of anneal temperature for a 5 min RTA. b) The same as a function of anneal time for a 1000 °C RTA. The diffusion length data was fit with Eq. 4.8 and Eq. 4.6 with a fixed activation energy $E_A = 3.85$ eV [81], resulting in diffusion coefficients of $D_0 = 4.0 \pm 0.5$ cm²s⁻¹ and 7.5 ± 0.5 cm²s⁻¹ in samples without and with pre-amorphization, respectively. Error bars are estimated from the RBS spectra (red) and the standard deviation of Gaussian fitting to the depth profiles (blue).

The maximum electrical activation yields measured are significantly lower than the near 100% substitutional fraction of high fluence samples B and D as measured by RBS. This discrepancy could partially be due to the fact that the effective number of electrically active charge carriers as measured by the Hall effect is less than the true value of electrically active

charge carriers as determined by integrating layer stripping results [151] due to the non-uniform distribution of charge carrier density and mobility. Indeed, previous work [152] suggests that the Bi electrical activation yield may be as much as 1.5 times larger than the measured values reported here. Additionally, since the present RBS measurements were performed with channeling along only the $\langle 100 \rangle$ axis, the actual substitutional fraction could be lower than measured if Bi is displaced from lattice sites but hidden from the He^+ ion beam. This was found in a previous study, with a similar implant fluence and annealing conditions, in which RBS measurements were taken using an angular scan across the $\langle 100 \rangle$ axis. From this, it was determined that a fraction of the Bi atoms that are apparently substitutional when measured in the $\langle 100 \rangle$ direction are in fact slightly displaced from crystal rows [133] and are therefore electrically inactive. However, a significant fraction of the substitutional Bi donors are likely to be electrically inactive due to a number of possible causes including; an abundance of interface traps, oxide charge due to low quality native oxides or strain fields due to lattice mismatch between Si and its oxide and due to the large covalent radius mismatch between Bi and Si.

Bi depth profiles in randomly oriented RBS spectra were fit with Gaussian curves to extract the FWHM to determine the extent of diffusion during annealing. Broadening of a Gaussian dopant profile [153] can be described by Fickian diffusion where the donor concentration, n , at a depth below the surface, x , is given by:

$$n(x) \propto \exp(-(x - R_p)^2 / 2(\sigma^2 + 2Dt)) \text{ cm}^{-3} \quad (4.5)$$

with a projected range, R_p , a standard deviation of the Gaussian profile before annealing, σ , and anneal time, t . The dopant diffusivity, D , at a temperature T is given by:

$$D = D_0 \exp(-E_A / k_B T) \text{ cm}^2/\text{s} \quad (4.6)$$

with a diffusion coefficient, D_0 , and an activation energy, E_A [81]. The measured FWHM of the Bi peak can be expressed as:

$$\text{FWHM} = 2.355 \sqrt{\sigma^2 + 2Dt + \sigma_E^2} \quad (4.7)$$

where the detector energy resolution was modelled as a Gaussian with standard deviation σ_E which convolves with the Gaussian Bi doping profile. This was used to calculate the diffusion length:

$$l = 2\sqrt{Dt} \quad (4.8)$$

which is plotted as a function of anneal temperature and time on the right axes in Fig. 4.10. Bi diffusion in Si only becomes significant to within the precision of our measurement for anneal temperatures at and above 900 °C for 5 minutes and for anneal times at and above 60 s for 1000 °C. If the diffusion length is comparable to the mean donor spacing, Bi clustering into undesirable electrically-inactive complexes can occur [154]. Since high fluence samples B and D have a smaller mean donor spacing, this can also explain why their Bi activation is significantly decreased at lower thermal budgets compared to low fluence samples A and C. Fickian diffusion curves, described by Eq. 4.6 and Eq. 4.8, with an activation energy, E_A , taken to be 3.85 eV [81] were fitted to the data to give diffusion coefficients $D_0 = 4.0 \pm 0.5 \text{ cm}^2\text{s}^{-1}$ and $7.5 \pm 0.5 \text{ cm}^2\text{s}^{-1}$ without and with a PAI respectively. These values are higher than that found for Bi diffusion into crystalline Si from an epitaxially deposited layer of $D_0 = 1.08 \text{ cm}^2\text{s}^{-1}$ [81]. Bi diffusion is vacancy mediated [155], therefore the Si lattice damage created during ion implantation could enhance diffusion.

So in conclusion, for the high fluence Bi implanted Si samples B and D, the Bi substitutional fraction was found to decrease while the diffusion length increased for increasing applied thermal budgets. This supports the observation for high fluence Bi implanted Si that a decreasing fraction of Bi is electrically active for increasing applied thermal budgets as the donors move off lattice sites or cluster into electrically-inactive complexes.

4.5.4 Continuous-Wave Electron Spin Resonance

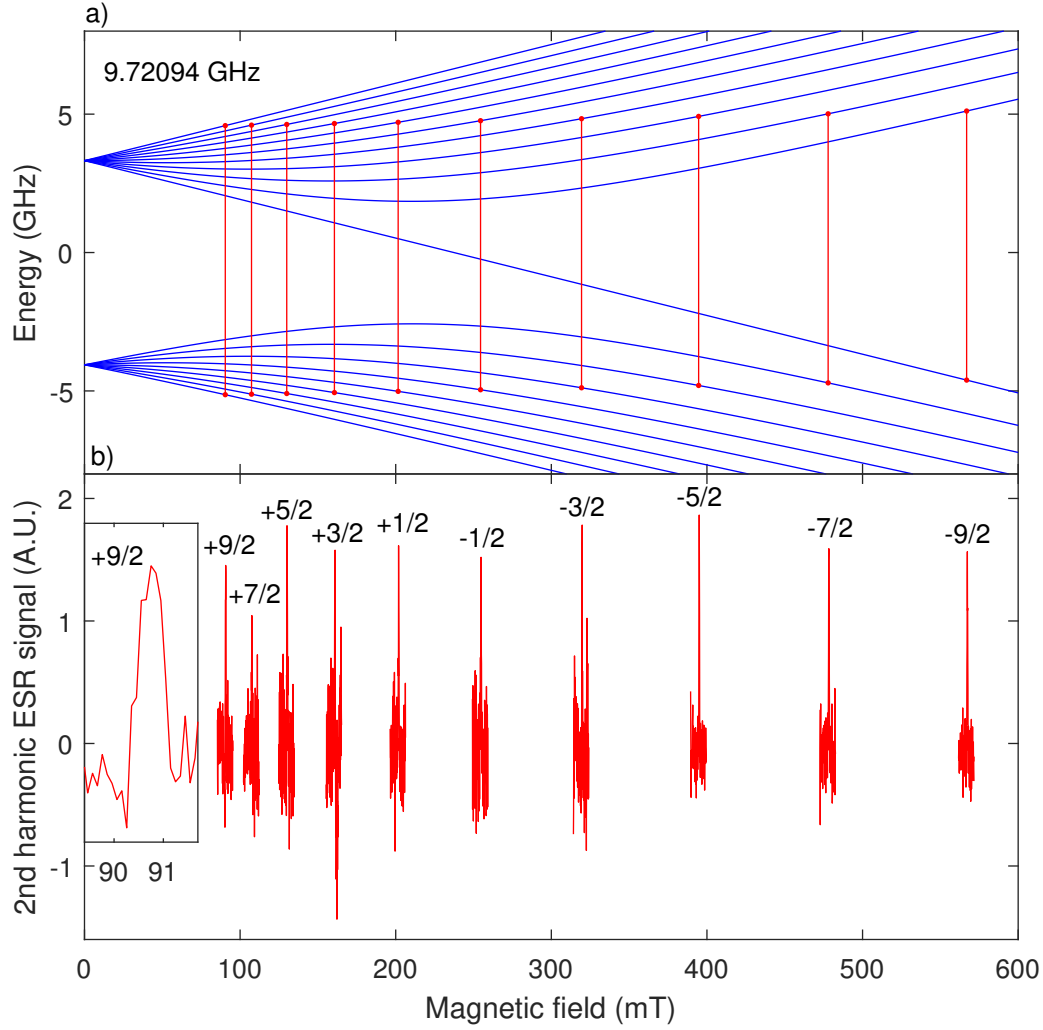


Figure 4.11: a) The energy levels of Bi in Si as a function of magnetic field, simulated using EasySpin [156]. The red lines show the magnetic field at which microwaves with frequency 9.7209 GHz are on resonance with an ESR transition. b) The hyperfine spectrum of near-surface implanted Bi in Si measured using CW-ESR at $T = 25$ K with a microwave frequency of 9.7209 GHz at 0.4743 mW. All 10 ESR transitions were measured and are labelled with their projected nuclear spin, m_I . The inset shows an expanded view of the $m_I = +9/2$ transition.

The presence of active implanted Bi donors in Si was confirmed using ESR. At X-band, a large magnetic field range of 0 to 600 mT is required to collect the complete Bi hyperfine spectrum due to the large nuclear spin ($I = 9/2$) and hyperfine interaction ($A = 1475.4$ MHz) of Bi [157]. The Bi hyperfine energy levels, here simulated using EasySpin [156], and the CW-ESR data are shown in Fig. 4.11. Samples are required to be non-metallic for ESR, therefore a low fluence Bi implant of $6 \times 10^{12} \text{ cm}^{-2}$, with a maximum Bi concentration below the metal-insulator transition

($N_C = 1.8 \times 10^{19} \text{ cm}^{-3}$ [145]) was chosen. This sample did not have a PAI and donors were activated with an RTA at 1000 °C for 5 s, resulting in an estimated electrical activation yield of 22.4%, as measured with the Van der Pauw devices. A sample area of 0.65 cm², resulting in a total of 3.9×10^{12} implanted Bi donors contained within the sample, was laser cut and stacked to fit inside the sapphire cavity of the ESR machine. Assuming an electrical activation yield of 22.4%, this corresponds to a total of 8.7×10^{11} active Bi spins contained within the sample which produced a measureable signal above the experimental sensitivity limit. The experimental data was collected in 10 subsets, each spanning 10 mT and centered on the expected magnetic field. Each subset was scanned 1000 times to increase the signal to noise ratio. The magnetic field between the 10 peaks was not scanned to reduce the data collection time. The background signal due to resonances and defects in the sapphire cavity was fitted and subtracted from the data. The strongest ESR transition signal was found in the second harmonic and is shown here. This can be explained by the saturation of the second harmonic ESR signal with increasing microwave power being much less than that of the first harmonic [158]. The inset of Fig. 4.11b shows the shape of the second harmonic ESR signal for the $m_I = +9/2$ transition from which the ESR peak-to-peak linewidth can be extracted to be $l_{pp} = 7.5 \pm 0.5 \text{ G}$. The linewidth for Bi incorporated in the bulk of natural Si has previously been measured to be $\sim 4 \text{ G}$ [119]. In this experiment, the magnetic field B_0 was modulated at an amplitude of 0.1 mT with a frequency of 100 kHz. This modulation amplitude is significantly smaller than the expected linewidth of Bi in natural Si and so does not contribute to the linewidth broadening. The increased linewidth observed in this experiment could be explained due to a combination of the close proximity of the native oxide interface increasing the variation in the local magnetic environment of the Bi donors, strain fields within the crystal, microwave power broadening or magnetic field inhomogeneities within the electromagnet. In future, these factors would have to be overcome to be able to see clearly the effect of the removal of ²⁹Si nuclear spins on the ESR signal linewidth.

The collection of the complete Bi hyperfine spectrum verifies a successful implantation and annealing strategy for near-surface Bi in Si. As shown in Fig. 4.11, each of the 10 measured ESR peaks occur at the expected magnetic field for the given microwave frequency, as predicted with the EasySpin simulation. This confirms that the local magnetic and electric field of the near-

surface implanted Bi donors result in resonance frequencies that closely match those predicted for bulk-doped Bi donors in Si. To fully probe the quantum environment of the Bi donors, the coherence time could be measured using pulsed ESR measurements.

4.6 Summary

In conclusion, optimal implant and annealing strategies for near-surface implanted Bi donors at fluences of $1 \times 10^{14} \text{ cm}^{-2}$ and $6 \times 10^{12} \text{ cm}^{-2}$ were found to be; solid phase epitaxy at 600°C for 5 min and a RTA at 1000°C for 60 s, both following pre-amorphisation of the Si substrate, resulting in electrical activation yields of 64% and 46% respectively. The substitutional fraction and diffusion of Bi were measured to aid the explanation of the trends found. The full Bi hyperfine spectrum containing all 10 transitions was obtained for Bi donors implanted to a depth of $\sim 20 \text{ nm}$ below the native oxide interface and subsequently annealed. This confirms the successful annealing of the damaged Si lattice caused by heavy ion implantation and the electrical activation of a significant fraction of the Bi donors. These results show promise for Bi donor implantation as a method for fabricating near-surface spin qubits that could be coupled to surface control and readout circuitry for integration into a large-scale device that exploits the unique properties of Bi. With a Bi donor environment of isotopically pure ^{28}Si , the removal of ^{29}Si nuclear spins would prolong coherence times which are desirable attributes for an engineered device.

4.7 Acknowledgements

I would like to acknowledge the following people for work performed in this chapter: Will Lawrie for his previous studies on Bi activation at the University of Melbourne (not shown in this work), Dr Amir Asadpoordarvish and Prof Dane McCamey for the CW-ESR measurement in this work performed at UNSW.

Chapter 5

Isotopic Enrichment of Silicon by $^{28}\text{Si}^-$ Ion Implantation

5.1 Introduction

Donor and quantum dot spin qubits in silicon (Si) are attractive candidates for high-fidelity scalable quantum computing architectures [40, 39, 159]. Si provides a desirable matrix for hosting spin qubits due to its important role in the microelectronics industry, weak spin-orbit coupling and the existence of isotopes with zero nuclear spin. Natural Si consists of three isotopes: ^{28}Si (92.23%), ^{29}Si (4.67%) and ^{30}Si (3.1%) [160]. The dominant source of qubit decoherence in $^{\text{nat}}\text{Si}$ is due to coupling with the surrounding ^{29}Si nuclei, which possess a nuclear spin of $I = 1/2$, in a process called spectral diffusion. In the semi-classical description of spectral diffusion, dipolar fluctuations of ^{29}Si spins cause perturbations in the local magnetic field, resulting in a time-varying qubit resonance frequency [161]. In the quantum mechanical description, the coupling between the central spin and the nuclear spin bath produces entanglement and results in the irreversible leakage of the quantum information from the central spin to the environment [162]. This spectral diffusion limits the spin coherence time to around 200 μs for electrons [16] and 60 ms for ionised donor nuclei [17], as measured for a single phosphorus (P) donor at low temperature using the Hahn-echo pulse sequence. The presence of ^{30}Si nuclei in the substrate is not detrimental to qubit coherence as they have zero spin, however, they can cause a variation

in lattice bond length (an isotope-dependent property), making the qubit environment non-identical. Fortunately, the most abundant isotope, ^{28}Si , has no nuclear spin and can therefore provide an ideal low-noise environment for spin qubits. Minimising the number of ^{29}Si nuclei within the Bohr radius of the donor electron (~ 2 nm for ^{31}P in Si [163]) reduces the coupling of the donor electron to the dynamics of the ^{29}Si spin-bath through the contact hyperfine interaction [23]. Long coherence times for donor spin qubits in a ^{28}Si epilayer with 800 ppm residual ^{29}Si [164] have been demonstrated, with Hahn-echo decay times of around 1 ms for electrons and 1.75 s for ionised donor nuclei measured for a single P donor at low temperature, which can be further extended with dynamical decoupling [24]. Isotope engineering of semiconductor materials also has applications for increased thermal conductivity [165, 166, 167], capable of improving heat dissipation in Si integrated circuits [168].

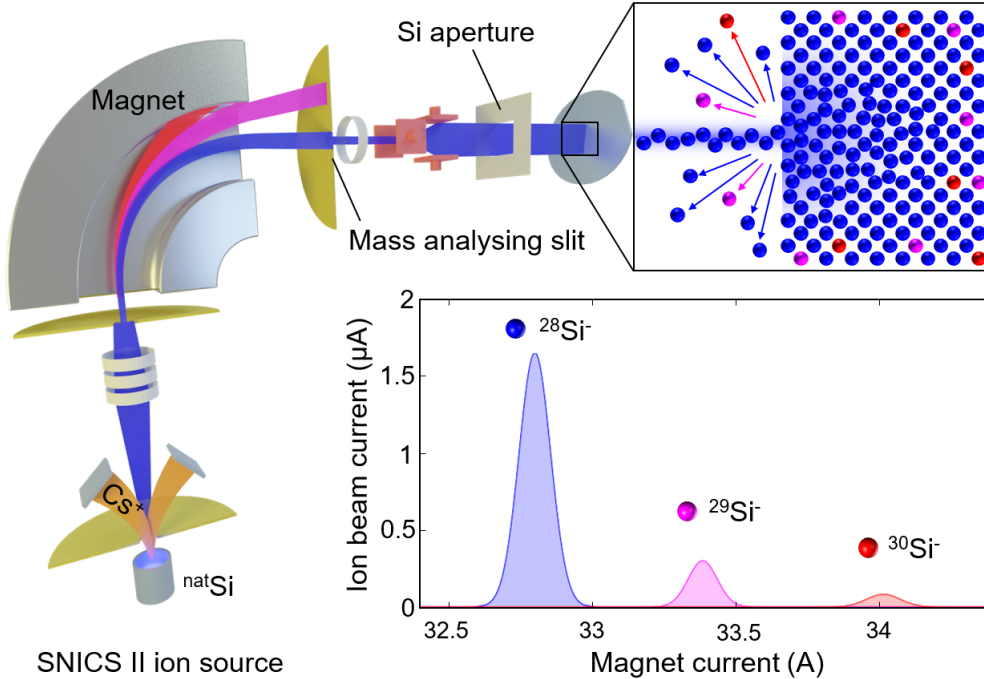


Figure 5.1: A $^{28}\text{Si}^-$ ion beam, filtered by a mass-selecting magnet from a solid-state $^{\text{nat}}\text{Si}$ source, is used to isotopically enrich a $^{\text{nat}}\text{Si}$ substrate surface layer by sputtering. The mass spectrum of the ion implanter shows isotopic resolution of Si.

In this work, we achieve isotopic enrichment by implanting a high fluence of $^{28}\text{Si}^-$ ions, mass-separated from an accelerated ion beam produced from a solid-state $^{\text{nat}}\text{Si}$ source, into a $^{\text{nat}}\text{Si}$ substrate, as shown in Fig. 5.1. Each implanted ^{28}Si ion imparts energy onto the target $^{\text{nat}}\text{Si}$ atoms during nuclear stopping processes. If the imparted energy is sufficient, a target atom can leave the substrate in a process known as sputtering. The sputter yield is defined as the average number of atoms removed from the target surface per incident ion. Since any isotope in the

substrate can be sputtered from the surface, but only ^{28}Si ions are implanted, the levels of ^{29}Si and ^{30}Si are depleted with increasing fluence. An enriched surface layer of ^{28}Si can be produced with sufficient volume for donor qubits; typically implanted to a depth of around 20 nm below the Si surface for effective control and readout by surface nanocircuitry [64]. This method has the advantage of using standard ion beam laboratory equipment, enabling the integration of *in-situ* enrichment with existing ion-implanted donor qubit fabrication [73]. Additionally, the creation of an amorphous ^{28}Si layer increases the placement precision of implanted donors by suppressing ion channeling [169] and can increase the donor electrical activation yield [22]. Solid phase epitaxy (SPE) of an amorphous Si (*a*-Si) surface layer formed by Si implantation can produce near-perfect single-crystal Si (*c*-Si) [170] with a smooth surface [171], in which no long-range atomic displacement occurs [172]. A one-for-one replacement regime, in which the sputter yield is one, results in a planar Si surface suitable for post-fabrication of nanocircuitry. This sputtering regime could allow for local enrichment of regions using a focused ^{28}Si ion beam into which donors are implanted.

The concentration of impurities introduced to the enriched layer during high fluence ^{28}Si implantation must be minimised, with particular care taken to avoid co-implantation of the molecular isobars CO and N_2 . The presence of C, N and O in the *a*-Si layer at levels of around 0.5 at. % cause retardation of the SPE regrowth rate [173] and can lead to polycrystalline nucleation during annealing at increased implant concentrations [174]. Impurity nuclei, such as the spin- $1/2$ ^{13}C , could also negatively impact the quantum environment of the qubit leading to reduced coherence times [175]. The key innovation here is to employ a negative ^{28}Si ion beam to ensure a negligible component of the isobars CO and N_2 , since these negatively charged molecular ions are electronically unstable.

In the present work, 45 keV $^{28}\text{Si}^-$ ions were implanted at a high fluence into $^{\text{nat}}\text{Si}$. The extent of ^{29}Si depletion and impurity levels introduced were measured using secondary ion mass spectrometry (SIMS). The concentration of impurities introduced by the high fluence implantation was lower than the typical values found in Czochralski-grown Si [87], used here as the standard for comparison, allowing for crystallisation to take place via SPE, resulting in a single crystal layer of ^{28}Si , as shown by transmission electron microscopy (TEM). The recrystallisa-

tion kinetics were determined using time resolved reflectivity (TRR) and the coherence time of P donors implanted into the enriched ^{28}Si layer was measured using pulsed electron spin resonance (ESR).

5.2 Experimental Review

5.2.1 Methods of Isotopic Enrichment

Isotopically enriched ^{28}Si can be produced by various methods, many of which involve the centrifugation of silicon tetrafluoride gas to produce high purity $^{28}\text{SiF}_4$, as shown in Fig. 5.2 [176, 177, 178, 179, 180, 181, 182]. In the Avogadro Project [180], where spheres of pure ^{28}Si were produced in order to define the kg, $^{28}\text{SiF}_4$ is reduced into isotopically pure silane gas, $^{28}\text{SiH}_4$, which is used to grow polycrystalline ^{28}Si by chemical vapour deposition (CVD). Float-zone growth is then used to produce ^{28}Si single crystal rods. An isotopic purity of < 10 ppm ^{29}Si and the highest chemical purity to date ($< 4 \times 10^{15} \text{ cm}^{-3}$ for C and $< 4 \times 10^{14} \text{ cm}^{-3}$ for O) was achieved [182]. However, the growth of this bulk-enriched Avogadro ^{28}Si is an intensive process taking weeks to complete. Epilayers of ^{28}Si can be grown on $^{\text{nat}}\text{Si}$ substrates by CVD [88, 183] (a method employed by the Isonics Corporation [164]) or molecular beam epitaxy [184, 185, 186] (suitable for encapsulation of scanning tunneling microscopy-placed donors in ^{28}Si [187, 188]). These methods rely on isotopically enriched sources of silane gas or solid-state ^{28}Si .

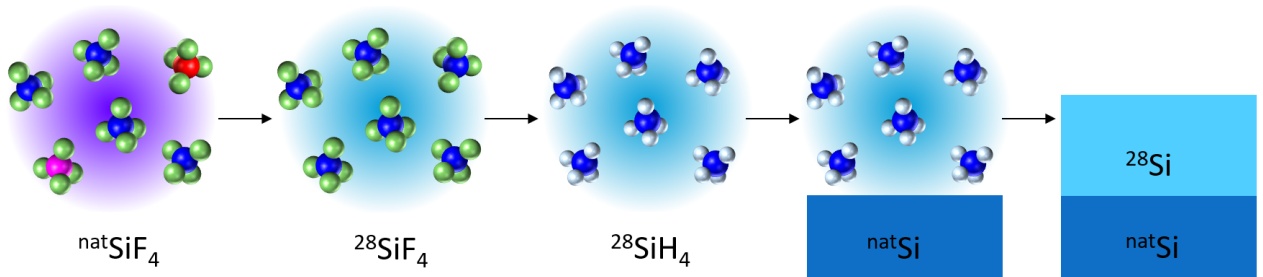


Figure 5.2: Process flow for the enrichment of ^{28}Si . SiF_4 gas is isotopically enriched by centrifugation. This is reduced into isotopically enriched silane gas, which can be deposited onto a $^{\text{nat}}\text{Si}$ substrate to form an epilayer of ^{28}Si .

Mass spectrometry, on the other hand, can be used to separate ^{28}Si ions from a natural

silane gas source. This has been used in conjunction with hyperthermal energy ion beam deposition to achieve a residual ^{29}Si fraction of < 1 ppm in a layer of ^{28}Si [189, 190]. However, the concentration of C and O was greater than $1 \times 10^{19} \text{ cm}^{-3}$ [189] and the level of ^{13}C nuclear spins was 300 times greater than residual ^{29}Si spins, which would limit qubit coherence times [189]. The epitaxial growth of ^{28}Si thin films by ion beam deposition with a solid $^{\text{nat}}\text{Si}$ source has also been achieved by depositing low energy (~ 40 eV) $^{28}\text{Si}^-$ ions [191].

Deposition of low energy ^{28}Si requires an Ultra High Vacuum (UHV) implanter end-station to minimise oxidation and the incorporation of contaminants present as residual gas into the deposited layer and is thus unsuited to a conventional implanter. The implantation of higher energy 20 keV ^{28}Si into $^{\text{nat}}\text{Si}$ with a conventional implanter was investigated in unpublished work (referenced in [192]). However, RBS measurements showed that the isotopic enrichment was limited to 95% ^{28}Si after the implantation of $2 \times 10^{17} \text{ ions cm}^{-3}$ due to the self-sputtering of Si with a sputter yield of ~ 1.3 atoms ion^{-1} at an energy of 20 keV. Attempts have been made to limit the oxidation (associated with low energy ^{28}Si deposition) and self-sputtering (associated with ~ 20 keV ^{28}Si implantation) in a conventional implanter by using an implanted layer exchange method in which 30 keV ^{28}Si was implanted into a layer of aluminium deposited on $^{\text{nat}}\text{Si}$ and subsequently annealed [192]. However, the epitaxial regrowth of a single crystal layer of ^{28}Si was not successful; perhaps due to the native oxide below the deposited Al layer. Al contaminants introduced using this method would also strongly perturb the quantum environment of donor qubits due to their electronic spin with an effect ~ 2000 times stronger than ^{29}Si nuclear spins.

The method of isotopic enrichment used in this work relies on the high fluence implantation of 45 keV $^{28}\text{Si}^-$ ions, mass-selected in an ion implanter, into $^{\text{nat}}\text{Si}$. The energy of the ion beam is chosen to result in a sputter yield of 1. This method does not require isotopically enriched source materials or a specialised UHV implanter, opening up the possibilities for more accessible ^{28}Si production. The choice of a negative ^{28}Si ion beam implanted at the particular energy of 45 keV avoids the issues of contamination or limited isotopic enrichment encountered with previous enrichment attempts with conventional ion implanters.

5.3 Theory

5.3.1 Decoherence Mechanisms

Increasing qubit coherence time significantly reduces the resources required for quantum error correction with reduced qubit error rates allowing for robust architectures with fewer ancilla qubits. It is therefore important to understand the mechanisms that limit the coherence of donors in silicon. As we saw in section 2.2.4, the coherence time at low temperatures is limited by the transverse phase coherence time T_2 as the longitudinal spin relaxation time T_1 is very long due to the suppression of phonon-assisted inelastic decay processes (spin-lattice relaxation) at low temperature. The coherence time T_2 of the electron-nucleus donor spin system is dominated by that of the donor electron, since its magnetic moment, $\mu_e = -g_e \frac{e\hbar}{2m_e} S$, is much larger than that of the nucleus, $\mu_n = g_n \frac{e\hbar}{2m_p} I$, making it more sensitive to magnetic field fluctuations. Hence the relatively short coherence time of the donor electron (0.95 ms), intermediate coherence time of the neutral donor nucleus (20.4 ms) and long coherence time of the ionised donor nucleus (1.75 s), with the values of T_2 quoted for Hahn echo measurements of a ^{31}P donor implanted in isotopically enriched ^{28}Si with 800 ppm residual ^{29}Si [24]. By applying a large magnetic field ($\gtrsim 100$ mT), we can assume only flip-flop dynamics between near-identical spins which conserve the Zeeman energy dominate the decoherence mechanisms [23].

In $^{\text{nat}}\text{Si}$, the dominant decoherence mechanism of the donor electron is the spectral diffusion of its resonance frequency caused by magnetic perturbations from spin-1/2 ^{29}Si nuclei. The polarisation of the ^{29}Si spin bath fluctuates temporally due to dipole interaction-induced flip-flops of nearby ^{29}Si nuclei, as shown in Fig. 5.3a. The donor electron is coupled to surrounding nuclear spins by the hyperfine interaction. When the nuclear spins in question lie within the Bohr radius of the donor electron, this is dominated by the contact hyperfine interaction ($\propto |\psi(r)|^2$, where $\psi(r)$ is the electron wavefunction at the location of the nuclear spin, r). When the nuclear spins are far outside the donor electron wavefunction radius, this may be approximated as the dipolar hyperfine interaction ($\propto 1/r^3$) [23]. The contact hyperfine and dipolar regimes dominate T_2 at high and low concentrations of ^{29}Si , respectively, as shown in Fig. 5.4.

The P donor electron wavefunction contains around 78 ^{29}Si nuclei within its volume in $^{\text{nat}}\text{Si}$, assuming a Bohr radius of 2 nm. In $^{\text{nat}}\text{Si}$, the donor electron Hahn echo signal contains a non-exponential decay due to the ^{29}Si -induced spectral diffusion:

$$V(\tau) = V_0 \exp \left(-\frac{2\tau}{T_{2e}} - \left(\frac{2\tau}{T_{SD}} \right)^n \right) \quad (5.1)$$

where τ is the time between the two pulses of a Hahn echo experiment, T_{SD} is the characteristic time of spectral diffusion, n is an exponent stretching factor which may vary between 2 and 3 for different regimes of spectral diffusion ($n = 3$ was observed with $^{\text{nat}}\text{Si}$ in [193]) and T_{2e} is the characteristic time accounting for other relaxation processes, including the spin-lattice T_{1e} relaxation processes and instantaneous diffusion (discussed in the following section), both of which are described by a simple exponential decay.

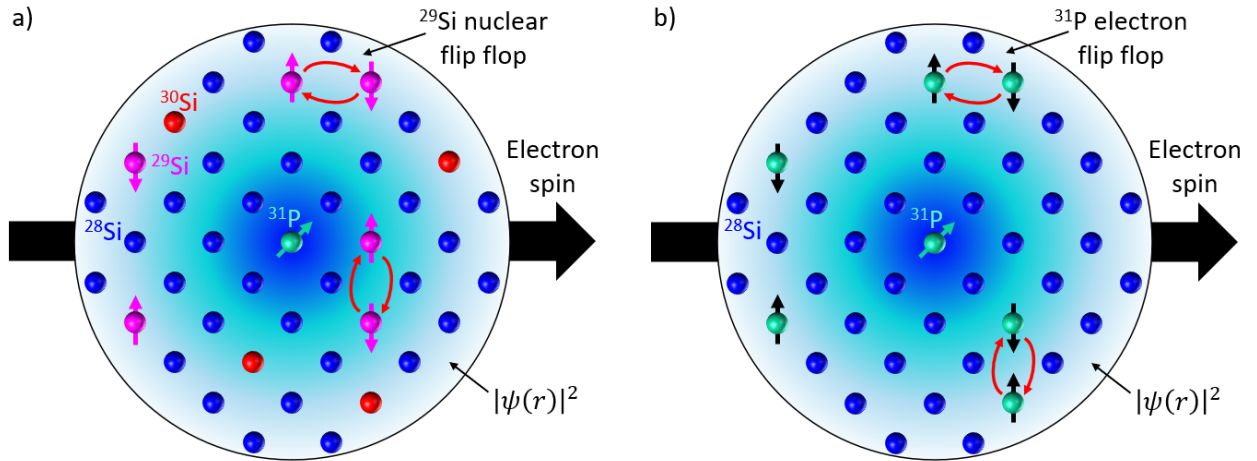


Figure 5.3: The electron of a P donor in Si experiences spectral diffusion due to the dynamics of the spin bath encompassed by its wavefunction $\psi(r)$. a) In $^{\text{nat}}\text{Si}$, decoherence is dominated by spectral diffusion caused by dipole-induced ^{29}Si nuclear flip flops. b) In ^{28}Si , the intrinsic coherence time is limited by spectral diffusion caused by dipole-induced ^{31}P donor electron flip flops. This decoherence mechanism is reduced by ensuring the P concentration is sufficiently low in a qubit device.

In isotopically enriched ^{28}Si , the effect of ^{29}Si -induced spectral diffusion is reduced, resulting in a simple exponential decay of the donor electron Hahn echo signal:

$$V(\tau) = V_0 \exp \left(-\frac{2\tau}{T_{2e}} \right) \quad (5.2)$$

The Hahn echo measurement adds a dephasing mechanism known as instantaneous diffusion,

which can dominate once ^{29}Si -induced spectral diffusion is reduced. Instantaneous diffusion is due to the π -pulse in the Hahn echo pulse sequence simultaneously flipping all resonant donor electrons, creating a change in the local magnetic field experienced by each spin. Instantaneous diffusion is purely a measurement artifact and can be removed by shortening the π -pulse to a smaller rotation angle (therefore resulting in a smaller change in the local magnetic field at the expense of a smaller Hahn echo signal) and extrapolating to an angle of zero to find the intrinsic T_2 [54]. At low temperatures and ^{29}Si concentrations, this intrinsic T_2 of the donor electron is dominated by the spectral diffusion of its resonance frequency caused by magnetic perturbations from donor electrons. The polarisation of the donor electron spin bath fluctuates temporally due to dipole interaction-induced flip-flops of nearby donor electrons, as shown in Fig. 5.3b. Below 4 K, the intrinsic T_2 of P donor electrons in ^{28}Si (50 ppm ^{29}Si) is inversely proportional to the donor density, with the electron spin sensitive to other donor electron spins separated by ~ 200 nm through the dipole interaction [55]. These surrounding donor nuclei are present as either intentionally-placed donor qubits or as trace impurities contained within even the highest purity Si wafers with a background concentration of $\sim 10^{12} - 10^{14} \text{ cm}^{-3}$ dopant impurities, typically phosphorus. The flip flop dynamics of the donor nuclei can be suppressed if the difference in resonance frequencies of the two spins involved is greater than the dipole interaction strength. This can be achieved by inhomogeneous broadening by either an external magnetic field gradient or ^{29}Si hyperfine broadening. Therefore the presence of some ^{29}Si can actually increase T_2 in a concentration regime where spectral diffusion from ^{29}Si is not the dominant decoherence mechanism.

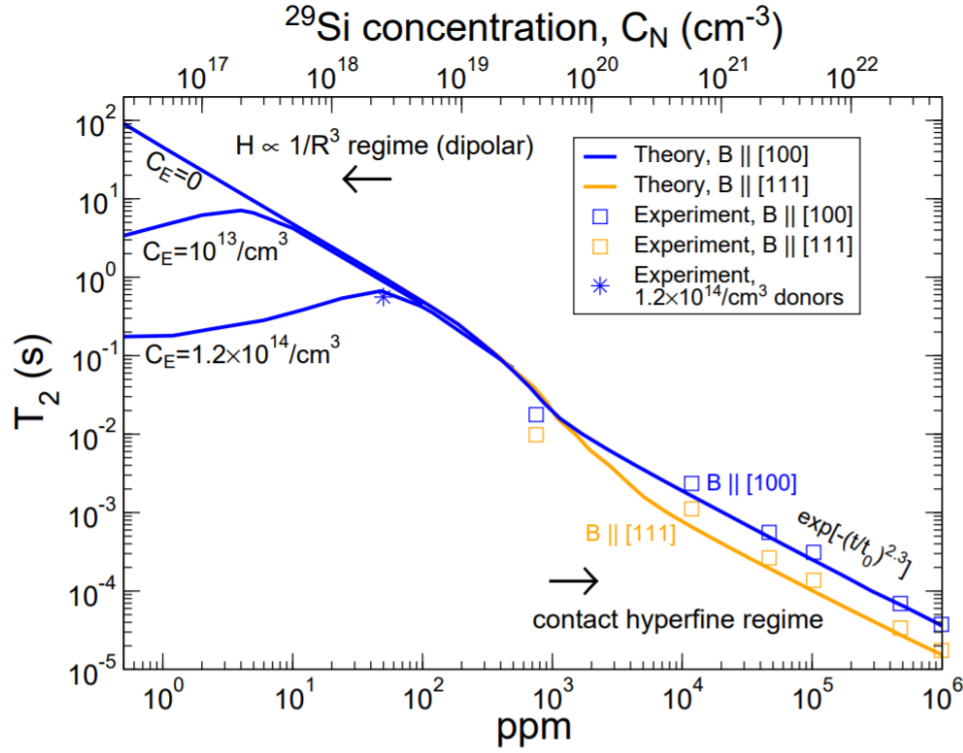


Figure 5.4: Hahn echo coherence time T_2 of Si:P donor electron spins as a function of ^{29}Si concentration, C_N . At high C_N , contact hyperfine interactions dominate and T_2 is dependent upon the magnetic field direction relative to the lattice orientation. At low C_N , T_2 is dependent upon the concentration of P donor electrons, C_E , and is eventually dominated only by dipolar interactions. Figure reprinted from reference [23].

5.3.2 Solid Phase Epitaxy

The high fluence implantation of ^{28}Si ions utilised in this work to isotopically enrich the surface layer of $^{\text{nat}}\text{Si}$ by sputtering result in a completely amorphised surface layer. The crystallinity of this metastable amorphous layer, in direct contact with the still-crystalline natural Si substrate below, can be regrown by a low temperature ($\sim 600^\circ\text{C}$) annealing process known as SPE [101]. When heated, atoms in the amorphous phase reorder by local bond rearrangements at the crystalline-amorphous interface, resulting in regrowth of the crystalline surface layer. The SPE rate, v , is the propagation velocity of the crystalline-amorphous interface through the amorphous layer and is described by the Arrhenius relation:

$$v = v_0 e^{-E_a/k_B T} \quad (5.3)$$

where $E_A = 2.70$ eV is the activation energy and $v_0 = 4.64 \times 10^{16}$ Å/s is the velocity prefactor for intrinsic Si [194]. The concentration of impurities [173] and open-volume defects [195] in the amorphous layer can affect the SPE rate. As we saw in Chapter 4, electrically active dopant concentrations well in excess of the dopant solid solubility limit can be achieved with SPE.

5.3.3 Diffusion

Care must be taken during annealing to avoid unwanted diffusion of the ^{29}Si and ^{30}Si isotopes from the high concentration region of natural Si to the low concentration region in the enriched layer. This diffusion would broaden the transition between the isotopically purified layer and the underlying natural substrate and increase the concentration of ^{29}Si in the active region of a device where donors are implanted; thus reducing coherence times. The self-diffusion of Si has previously been measured using SIMS after annealing Si isotope heterostructures. The self-diffusion of Si was found to be described by an activation energy of $E_A = 4.75$ eV and a diffusion coefficient of $D_0 = 530$ cm²s⁻¹, over a temperature range of 855 - 1388°C [196].

5.4 TRIDYN Simulations

The dynamic changes to the composition of the target substrate due to atomic relocation in the bulk and sputter erosion at the surface during the high fluence implantation process can be simulated using the TRIDYN software package, a Monte Carlo simulation which uses the binary collision approximation [197]. The initial target is defined as a multi-layered structure formed of equisized depth intervals. The local composition of each depth interval is defined in terms of the partial atomic areal density for each atomic species present. The dynamic simulation of the transport of moving atoms (projectiles or recoil atoms) employs pseudo atoms which represent a certain areal density of real atoms. During the dynamic simulation, the areal density of atoms in the depth intervals may be modified due to the deposition of projectiles or the relocation of recoil atoms. In this section, the sputter yield as a function of energy and angle, the level of isotopic enrichment as a function of fluence for various energies and the effects of ion beam mixing and sources of contamination are explored.

An initial interval spacing of 5 - 10 Å was chosen to be longer than the mean free path, $\lambda = n^{-1/3}$, (around 3 Å for Si with atomic density $n = 5 \times 10^{22} \text{ cm}^{-3}$) but small enough to avoid artifacts from a coarse grid, where local composition changes are distributed over too large intervals. The target was simulated as a semi infinite body with a thickness greater than the maximum range of implanted ions. A high statistical quality was achieved by simulating a large number of pseudo projectiles (determined by the precision value) to keep the maximum relative change of layer areal density per projectile to less than 1% [197]. Due to the large number of pseudo projectiles required to simulate high fluence implantation, these TRIDYN simulations were run on the cloud partition of Spartan, the High Performance Computer (HPC) at the University of Melbourne [198]. The simulation was performed across 4 compute nodes with 8 central processing units (CPUs) per node with 32 GB of memory allocated to the entire job. The time taken to simulate an implantation of $5 \times 10^{18} \text{ ions cm}^{-2}$ on the HPC ranged from 22 hours to 5 days for an implantation energy ranging from 10 keV to 60 keV.

5.4.1 Sputter Yield Dependence on Implantation Energy

The average number of ions sputtered from the target surface per implanted ion, given by the sputter yield, is dependent on the energy of the implanted ion. TRIDYN was used to simulate the implantation of $1 \times 10^{17} \text{ cm}^{-2}$ ^{28}Si ions at normal incidence at various energies into $^{\text{nat}}\text{Si}$. A total target thickness of 200 nm and depth interval thickness of 5 Å was input into the simulation. A precision value of 0.1 was used, which kept the maximum relative change of layer areal density per projectile to less than 0.68%.

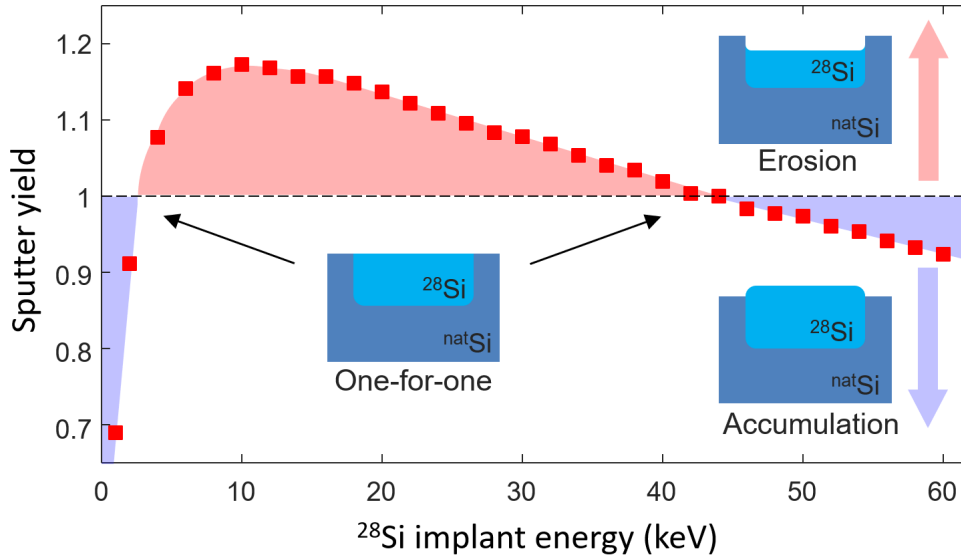


Figure 5.5: TRIDYN simulation showing sputter yield as a function of energy for the implantation of ^{28}Si at normal incidence at a fluence of $1 \times 10^{17} \text{ cm}^{-2}$ into natSi . Schematics of the post-implantation surface are shown in the erosion, one-for-one replacement and accumulation regimes.

The sputter yield dependence on implantation energy, shown in Fig. 5.5, is in agreement with previous experimental Si sputter yields [199, 200] and theoretical fits [201]. This validates the use of TRIDYN for our high fluence implant simulations.

For a ^{28}Si implant energy of $< 3 \text{ keV}$, most projectiles do not have sufficient energy to be implanted or to bounce off the target surface and so the majority end up stuck to the surface where they accumulate. This results in the deposition of ^{28}Si onto the Si surface. At around 3 keV, the ^{28}Si projectile energy is such that it will bounce off the surface of the target substrate like a trampoline, resulting in a sputter yield of one and a negligible production of isotopically enriched material. Between an implant energy of 3 keV and 45 keV, the ion will either bounce off the target or be implanted while imparting sufficient energy onto the surface target atoms causing them to be sputtered. The sputter yield is greater than one and the surface will be eroded. The self-sputtering of ^{28}Si atoms limits the level of isotopic enrichment possible in this energy regime and reduces the thickness of the enriched layer. At 45 keV, the projectile is implanted and imparts energy such that it sputters one atom on average. ^{28}Si ions with energies $> 45 \text{ keV}$ have a greater implantation depth such that sputtering from the surface is suppressed, resulting in a sputter yield of less than one. In this energy regime, the isotopic enrichment level is not limited by self-sputtering and a thick layer of ^{28}Si is formed as the

surface height is pushed up from below. This is desirable for producing a thick layer of ^{28}Si with a high level of enrichment, however, the surface will not be planar.

A sputter yield of 1 is achieved at implant energies of around 3 keV and 45 keV, both of which result in a planar surface; desirable for surface nanocircuitry fabrication. 45 keV was selected in order to produce a ^{28}Si surface layer thicker than the qubit target depth of ~ 20 nm in the one-for-one replacement regime and to optimize the transmission of the ion beam through the implanter.

5.4.2 Sputter Yield Dependence on Implantation Angle

The implantation angle of incidence has a large effect on the sputter yield. The sputter yield will increase with increasing angle up to a certain angle which depends on the masses of the projectile and target nuclei. TRIDYN was used to simulate the implantation of $1 \times 10^{17} \text{ cm}^{-2}$ 45 keV ^{28}Si into 200 nm of $^{\text{nat}}\text{Si}$ at various angles. A depth interval thickness of 5 Å and a precision value of 0.1 was input into the simulation, which kept the maximum relative change of layer areal density per projectile to less than 0.69%.

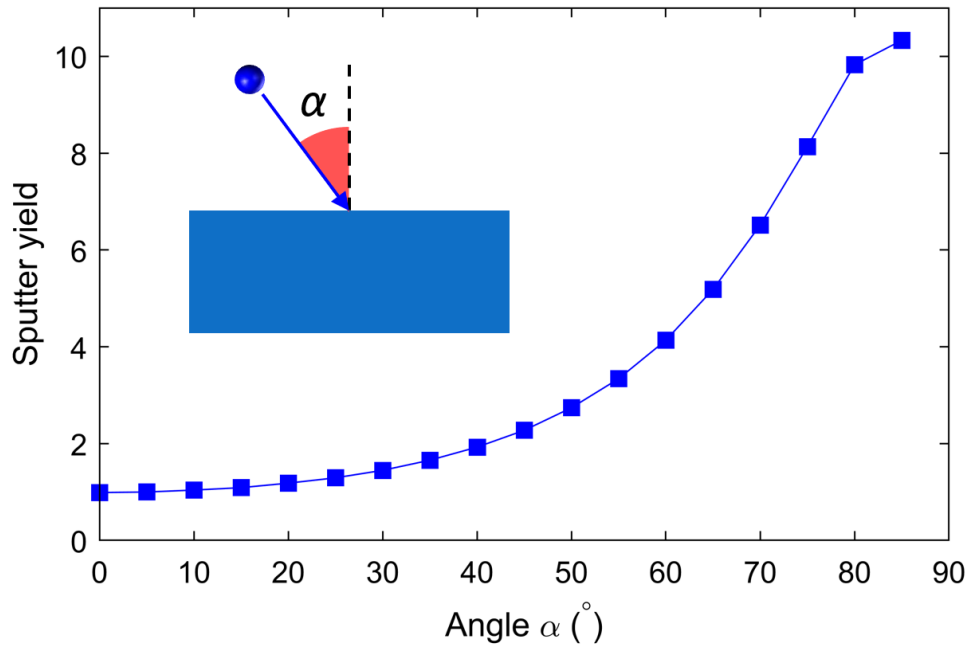


Figure 5.6: TRIDYN simulation showing sputter yield as a function of implantation angle, α , with respect to the surface normal for the implantation of 45 keV ^{28}Si at a fluence of $1 \times 10^{17} \text{ cm}^{-2}$ into $^{\text{nat}}\text{Si}$.

Fig. 5.6 shows that the sputter yield increases from a value of 1 at an angle of incidence of 0° to over 10 at 85° angle of incidence. For 45 keV ^{28}Si implanted into $^{\text{nat}}\text{Si}$, the angle at which the sputter yield is maximised appears to be just before 90° (the angle at which the projectiles would skim the surface and not be implanted). The TRIDYN simulation shows that the sputter yield is independent of the angle of incidence for angles below $\sim 10^\circ$, in agreement with previous experiments with self-implanted Si [200]. Therefore, the TRIDYN simulations performed at normal incidence to determine the sputter yield as a function of implant energy in the previous section are applicable for our experimental implants performed with a 7° tilt (commonly used to minimise ion channeling down crystallographic directions).

5.4.3 Isotopic Enrichment Dependence on Implantation Energy and Fluence

We have seen how the implantation energy affects the sputter yield, leading to regimes of deposition, erosion, one-for-one replacement and accumulation. This affects the level of isotopic enrichment that can be achieved by the implantation of ^{28}Si at a certain energy and fluence. TRIDYN was used to simulate the implantation of various energies of ^{28}Si at normal incidence into 200 nm of $^{\text{nat}}\text{Si}$ at fluences up to $5 \times 10^{18} \text{ cm}^{-2}$. A depth interval thickness of 10 Å and a precision value of 0.02 was input into the simulation, which kept the maximum relative change of layer areal density per projectile to less than 0.19%.

Fig. 5.7 shows the level of isotopic enrichment achieved with a certain fluence with each section corresponding to the following sputtering regimes; a) erosion, b) one-for-one replacement and c) accumulation, with an implant energy of 30 keV, 45 keV and 50 keV, respectively. The concentration of the remaining ^{29}Si isotope as a function of depth is shown for various fluences in each regime. The concentration profiles are plotted with the original $^{\text{nat}}\text{Si}$ surface fixed at a depth of 0 nm. Fig. 5.7a shows that 30 keV results in erosion of the surface due to a sputter yield of > 1 , indicated by the fact that the ^{29}Si concentration profiles start at increasing depths as the fluence increases. It also shows that the level of isotopic enrichment saturates at around 3500 ppm of ^{29}Si at a fluence of around $3 \times 10^{18} \text{ cm}^{-2}$, limited by self-sputtering. This is in agreement with previous work in which the isotopic enrichment was limited to 95% ^{28}Si with

an implantation energy of 20 keV.

Looking at the one-for-one replacement regime used in this work, Fig. 5.7b shows that 45 keV results in negligible erosion or accumulation on the surface due to a sputter yield of almost exactly 1. An improved level of enrichment down to around 600 ppm ^{29}Si is achieved, with no saturation limit reached for $5 \times 10^{18} \text{ cm}^{-2}$. 45 keV also produces a thicker layer of enriched Si compared to 30 keV.

Finally, 5.7c shows that 50 keV results in accumulation on the surface due to a sputter yield of < 1 . The best level of enrichment can be achieved in this accumulation regime since the enrichment is not limited by self-sputtering. A thicker layer of enriched material is also produced. Depending on the optimum transmission energy for the ion implanter and whether a planar surface is required, a ^{28}Si implant energy of greater than 45 keV may be optimum for isotopic enrichment due to the production of a thicker layer with a lower concentration of ^{29}Si .

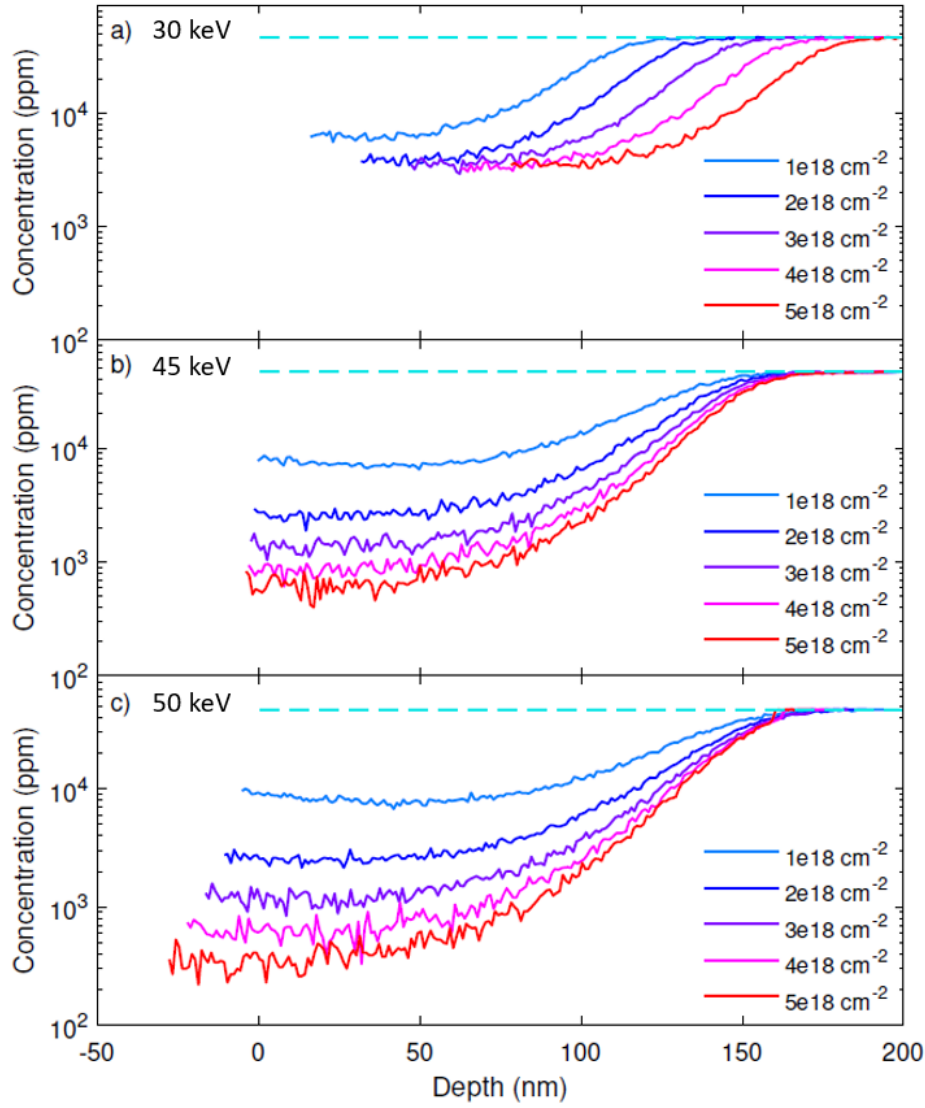


Figure 5.7: TRIDYN simulation showing the concentration of ^{29}Si with depth below the surface of $^{\text{nat}}\text{Si}$ after the implantation of ^{28}Si at normal incidence at various fluences up to $5 \times 10^{18} \text{ cm}^{-2}$ with an implantation energy of a) 30 keV, b) 45 keV and c) 50 keV in the regimes of erosion, one-for-one replacement and accumulation, respectively.

Fig. 5.8 shows how effective various ^{28}Si implant energies are at isotopically enriching the surface layer. The concentration of ^{29}Si at a depth of 20 nm below the surface of the implanted target is shown as a function of implant fluence for various implantation energies. 10 keV has the highest sputter yield and thus the concentration of ^{29}Si saturates at the highest level for the lowest implanted fluence. At fluences above $2 \times 10^{18} \text{ cm}^{-2}$, the fluence at which the isotopic enrichment level saturates increases and the resulting ^{29}Si concentration at a given fluence decreases with increasing implantation energy. Higher implantation energies (above 45 keV) are therefore found to be most effective at decreasing the level of ^{29}Si at a depth of 20 nm

but at the cost of producing a non-planar surface.

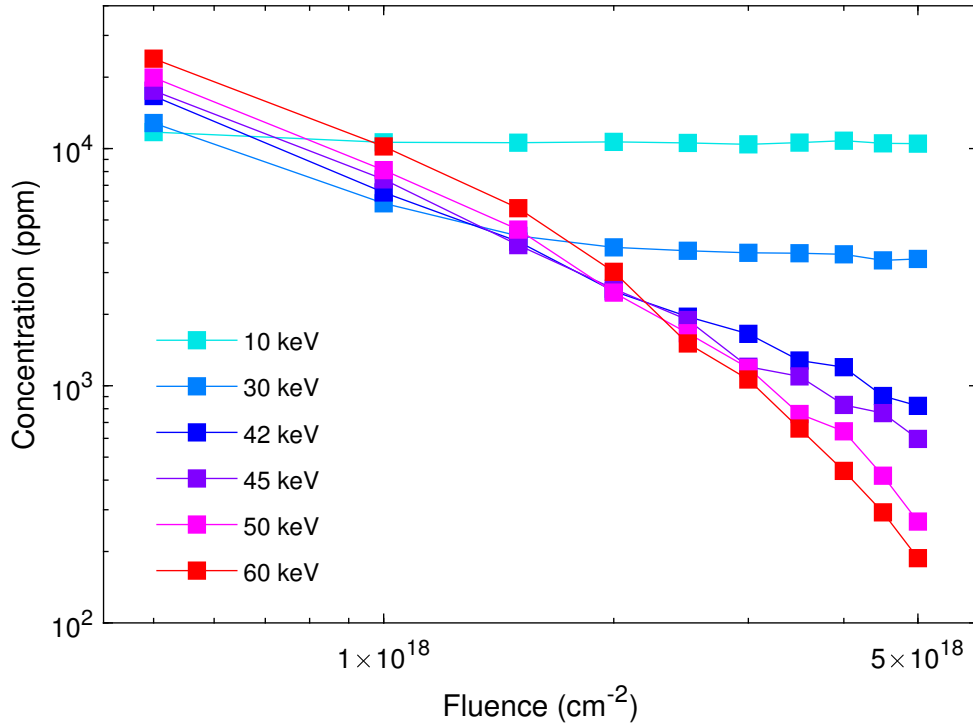


Figure 5.8: TRIDYN simulation showing the concentration of ^{29}Si at a depth of 20 nm below the surface as a function of fluence for various energies of ^{28}Si implanted into $^{\text{nat}}\text{Si}$ at normal incidence. For reference, the natural abundance of ^{29}Si is 4.67×10^4 ppm.

The depth profile of Si isotopes in $^{\text{nat}}\text{Si}$ after the simulated implantation of 45 keV ^{28}Si ions at a fluence of $5 \times 10^{18} \text{ cm}^{-2}$ is shown in Fig. 5.9a. This shows that an isotopically enriched surface layer ~ 100 nm thick is created. The resultant concentrations of ^{29}Si and ^{30}Si at a depth of 20 nm below the surface as a function of fluence of 45 keV ^{28}Si ions is shown in Fig. 5.9b. This shows the trend of an increased isotopic purity resulting from an increased implant fluence. The resultant concentration of ^{29}Si and ^{30}Si as a function of fluence can be fit by power laws in the one-for-one replacement regime, as shown on the plot. The experimental isotope concentrations at a depth of 20 nm realised in this work with an implantation of $^{28}\text{Si}^-$ ions (45 keV, $2.63 \times 10^{18} \text{ cm}^{-2}$) are indicated with star symbols in Fig. 5.9b. The degree of isotopic enrichment achieved experimentally is significantly higher than predicted with TRIDYN simulations and is discussed in section 5.7.1.

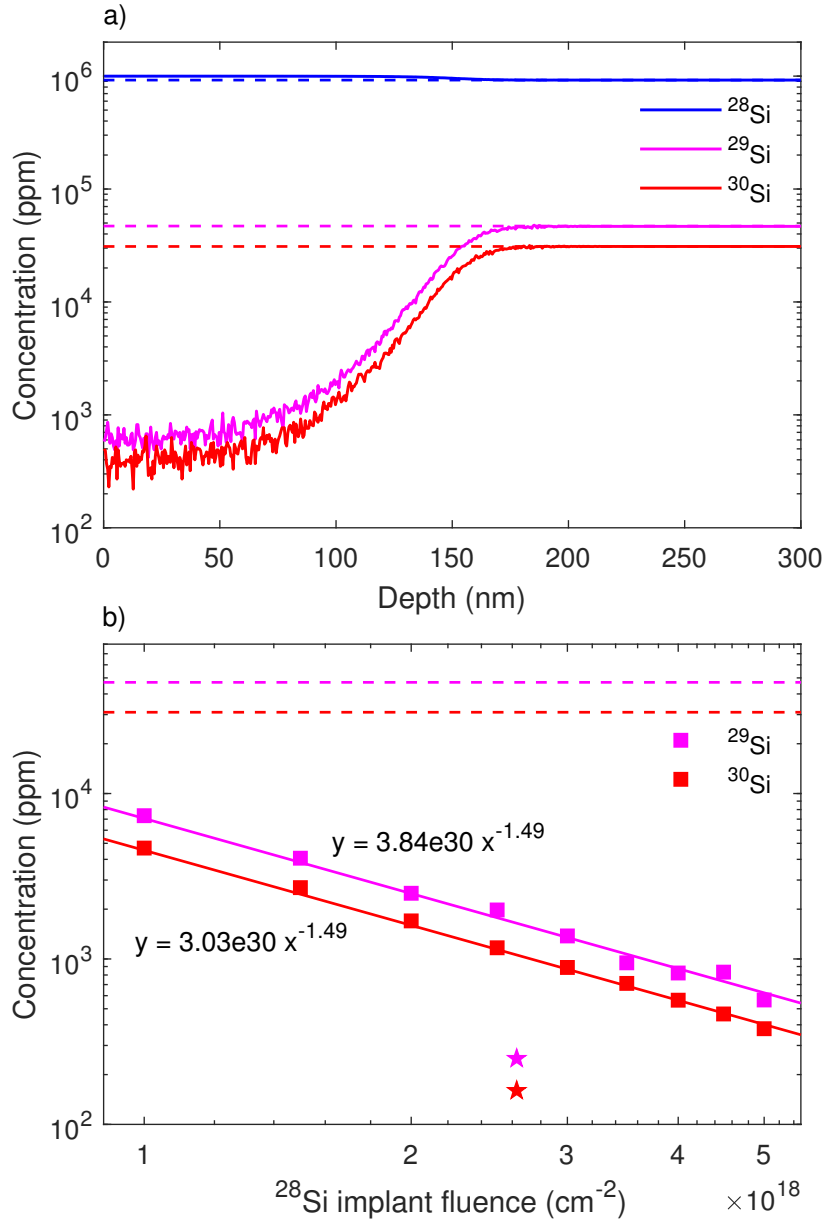


Figure 5.9: TRIDYN simulation of the implantation of 45 keV ^{28}Si ions into $^{\text{nat}}\text{Si}$ at normal incidence. The dashed lines indicate natural abundance. a) The concentration of silicon isotopes as a function of depth after an implantation fluence of $5 \times 10^{18} \text{ cm}^{-2}$. b) The concentration of ^{29}Si and ^{30}Si at a depth of 20 nm below the surface as a function of implanted fluence. Lines of best fit are displayed for both isotopes. The star symbols represent the isotope concentrations achieved in this work and are extracted from Fig. 5.19a.

5.4.4 Ion Beam Mixing

In order to create a surface layer of enriched ^{28}Si with a thickness of around 100 nm via one-for-one replacement, ^{29}Si and ^{30}Si that were originally at a depth of up to 100 nm will have to be sputtered from the surface or driven deeper into the bulk of the substrate by forward

recoils. In order to investigate the mechanism by which non- ^{28}Si isotopes initially residing deep below the surface are removed from the target, a buried layer of ^{29}Si was input into a TRIDYN simulation. 200 nm of ^{28}Si with a buried ^{29}Si layer from 50 - 60 nm was used as the input substrate, as shown in the inset of Fig. 5.10. 45 keV ^{28}Si was implanted at normal incidence with a fluence up to $5 \times 10^{18} \text{ cm}^{-2}$. A depth interval thickness of 1 nm and a precision of 0.02 was used, resulting in a maximum relative change of layer areal density per projectile of 0.21%. The concentration of ^{29}Si as a function of depth below the substrate surface is shown after various implant fluences up to $5 \times 10^{18} \text{ cm}^{-2}$ of 45 keV ^{28}Si in Fig. 5.10.

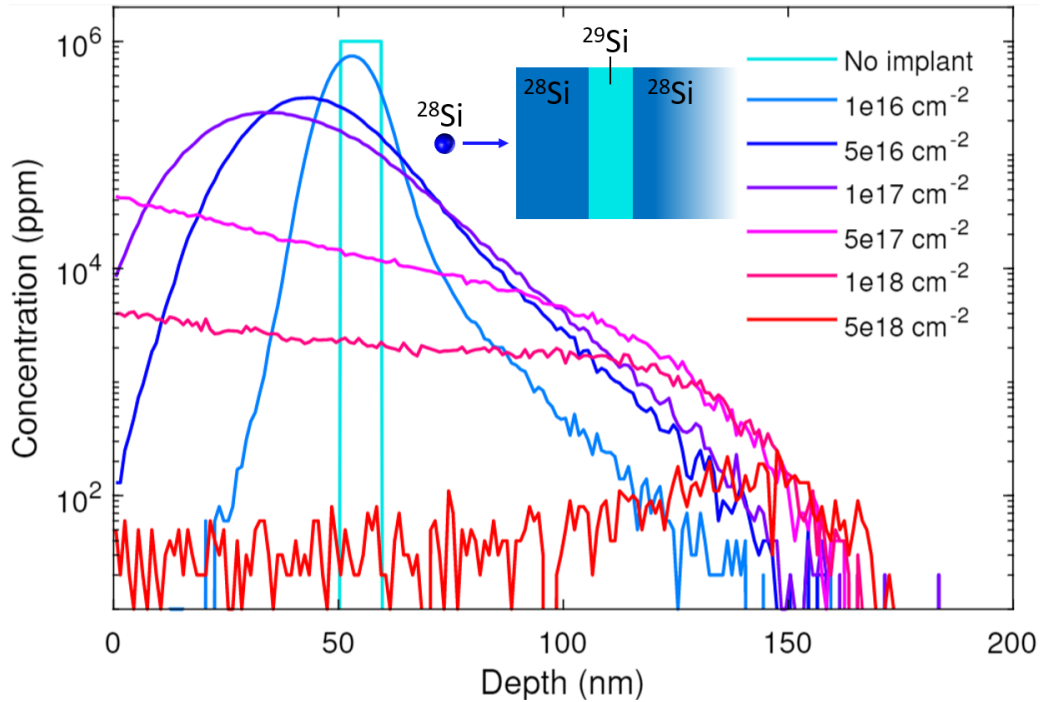


Figure 5.10: TRIDYN simulation showing the ion beam mixing of a buried ^{29}Si layer due to the implantation of 45 keV ^{28}Si . 200 nm of ^{28}Si with a buried ^{29}Si layer from 50 - 60 nm was used as the input substrate, as shown in the inset. The concentration of ^{29}Si as a function of depth below the surface is shown after various implant fluences of 45 keV ^{28}Si which shows the gradual depletion of the buried ^{29}Si layer.

Implanted 45 keV ^{28}Si has a mean range of around 67 nm, as simulated using SRIM and shown in Fig. 5.11. However, the end of range is over 150 nm. During ion irradiation, ion beam mixing will occur up to the end of range where layers in the substrate of different atomic compositions will be intermixed. Fig. 5.10 shows the buried layer spreading but with the maximum concentration of ^{29}Si moving closer towards the surface from where it will subsequently be sputtered. The vast majority of buried ^{29}Si is sputtered from the surface, with a small amount

being forward recoiled, as indicated by the peak in concentration of ^{29}Si at the end of range (around 150 nm) after the implantation of $5 \times 10^{18} \text{ }^{28}\text{Si cm}^{-2}$. This is fortuitous as it will likely result in a better donor quantum environment than if most of the ^{29}Si was forward recoiled.

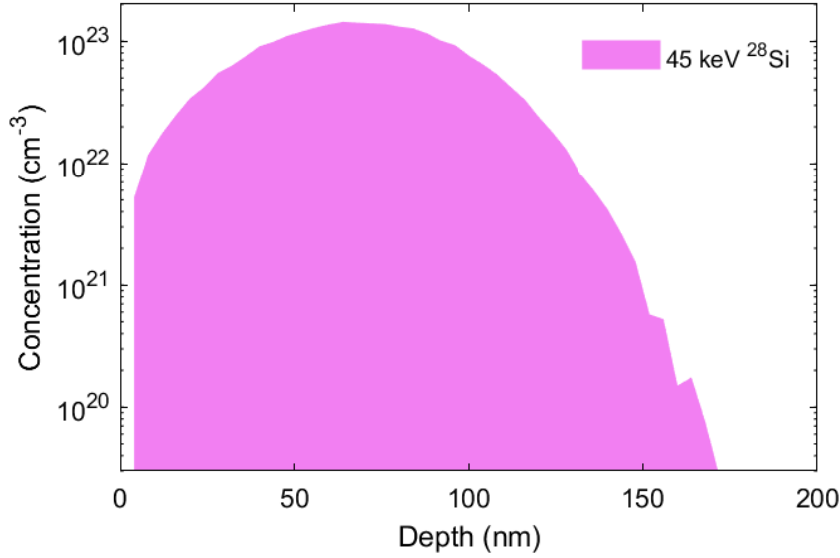


Figure 5.11: SRIM simulation showing the depth profile of 45 keV Si implanted in Si at normal incidence at a fluence of $1 \times 10^{18} \text{ cm}^{-2}$.

This TRIDYN simulation shows that the effect of ion beam mixing, combined with surface sputtering, is capable of depleting ^{29}Si from a surface layer of thickness down to the end of range of the implanted ^{28}Si ions.

5.4.5 Surface Layer Contamination

When Si is left in ambient conditions, its surface will oxidise. The growth of this native oxide is self-limited due to repulsive Van der Waals forces to a thickness of $\sim 2 \text{ nm}$ in the time frame of a few hours [94]. This native oxide can be etched away using HF acid and will not regrow if the Si substrate is placed under vacuum in the target chamber of the ion implanter immediately after etching. In some cases, it may not be practical to perform a HF etch immediately prior to ion implantation. Therefore, TRIDYN simulations were run to show the level of oxygen contamination introduced during ^{28}Si implantation through a native oxide. The implantation of 45 keV ^{28}Si at various fluences into 198 nm of ^{28}Si with a 2 nm surface layer of SiO_2 was simulated. A depth interval thickness of 1 nm and a precision of 0.02 was used, resulting in a

maximum relative change of layer areal density per projectile of 0.19%. The concentration of oxygen as a function of depth below the surface is shown after various implant fluences up to $1 \times 10^{18} \text{ cm}^{-2}$ of 45 keV ^{28}Si in Fig. 5.12.

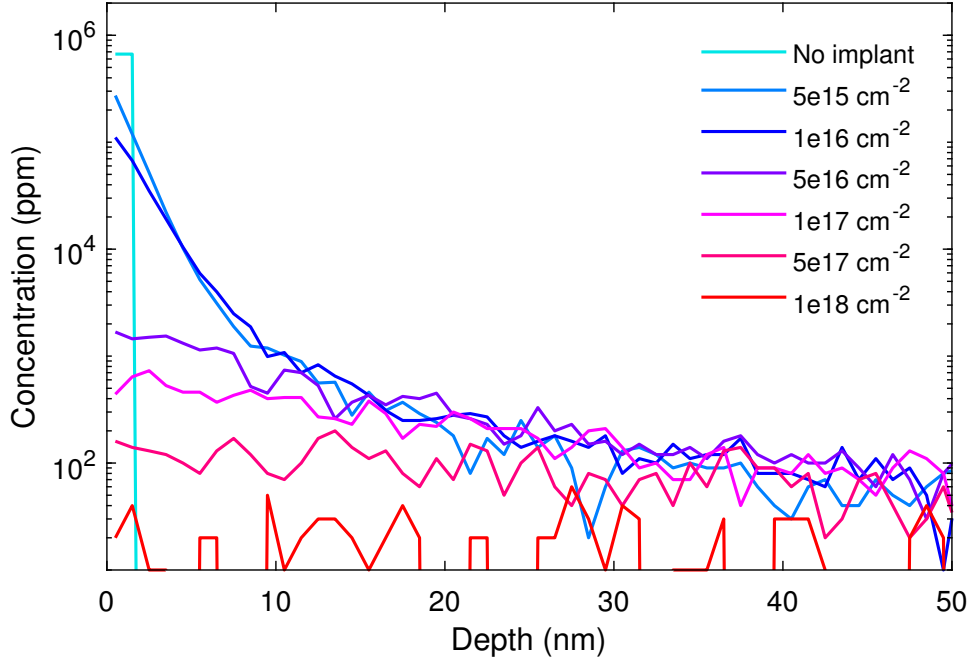


Figure 5.12: TRIDYN simulation showing the effect of a surface layer of native silicon oxide. The concentration of oxygen is shown as a function of depth below the surface after the implantation of 45 keV ^{28}Si at normal incidence through a 2 nm layer of SiO_2 on ^{28}Si at various fluences up to $1 \times 10^{18} \text{ cm}^{-2}$.

Fig. 5.12 shows that some of the oxygen from the native oxide layer is driven deeper into the ^{28}Si substrate as the concentration peak is broadened with a tail up to 50 nm. However, the total amount of oxygen present reduces with increasing implantation fluence as the oxygen is sputtered away from the surface. By $1 \times 10^{18} \text{ }^{28}\text{Si} \text{ cm}^{-2}$, the amount of oxygen introduced into the substrate is low, with an average of less than ~ 20 ppm in the surface 50 nm, corresponding to an oxygen concentration of less than $1 \times 10^{18} \text{ cm}^{-2}$. Therefore, the presence of a native oxide prior to ^{28}Si implantation should not result in a high enough level of oxygen contamination that would impede SPE due to most of the oxygen being sputtered away by the high fluence implantation required for isotopic enrichment.

If the Si substrate is not cleaned properly before ^{28}Si implantation, it could have a surface layer of hydrocarbons when entering the vacuum chamber. The effect of having a hydrocarbon layer on top of a native oxide was investigated using TRIDYN. 10 nm of $\text{C}_3\text{H}_6\text{O}$ (the chemical

formula for acetone) above a 2 nm layer of SiO_2 on a 188 nm layer of ^{28}Si was input into the simulation. A depth interval thickness of 1 nm and a precision of 0.02 was used, corresponding to a maximum relative change of layer areal density per projectile of 0.15%. The concentration of the impurities, H, C and O, as a function of depth below the surface are shown before and after the implantation of 45 keV ^{28}Si ions at a fluence of $1 \times 10^{16} \text{ cm}^{-2}$ and $1 \times 10^{18} \text{ cm}^{-2}$ in Fig. 5.13a and Fig. 5.13b, respectively. Some of the H, C and O impurities are driven into the sample to a depth of up to 200 nm by forward recoils. However, the majority of the surface contamination is sputtered away, as evidenced by the decrease in total amount of H, C and O atoms in the sample with increasing implant fluence. After the implantation of $1 \times 10^{18} \text{ cm}^{-2}$, as shown in Fig. 5.13b, the level of H is below 1000 ppm and the levels of C and O are below 100 ppm in the surface 100 nm. The maximum concentration of impurities are found around 150 nm below the surface, at a depth corresponding to the end of range of 45 keV ^{28}Si ions.

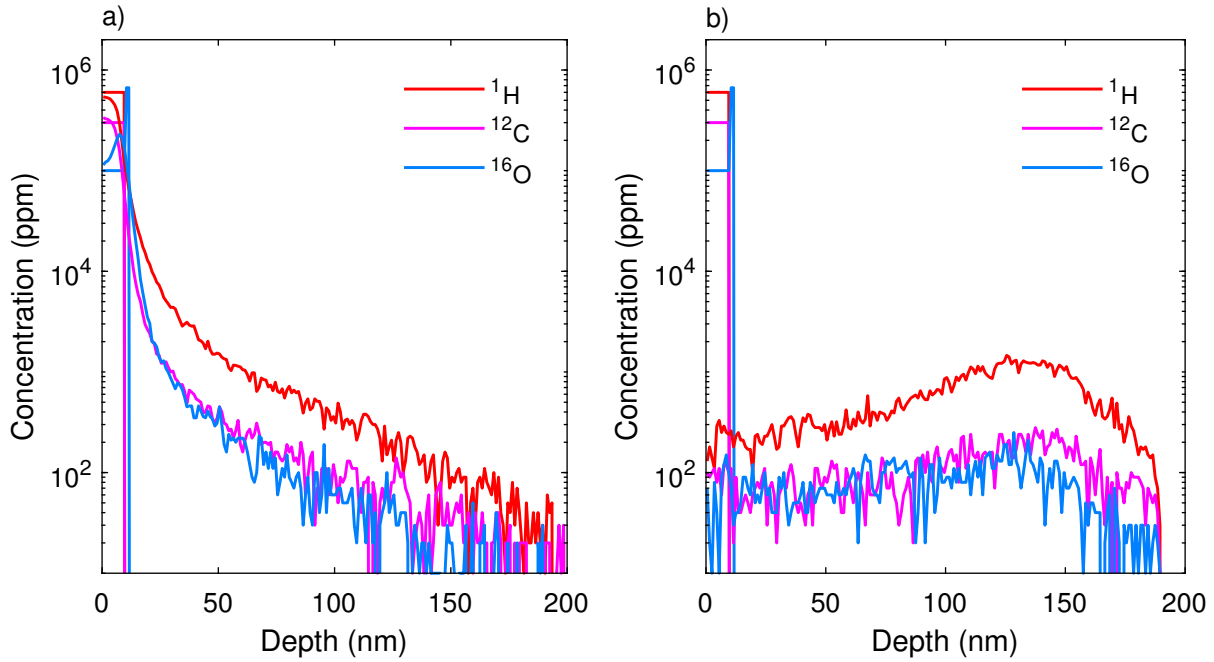


Figure 5.13: TRIDYN simulations showing the effect of surface hydrocarbon and native silicon oxide layers. The concentration of hydrogen, carbon and oxygen is shown as a function of depth below the surface of ^{28}Si with a 10 nm layer of $\text{C}_3\text{H}_6\text{O}$ (acetone) and a 2 nm layer of SiO_2 before and after the implantation of 45 keV ^{28}Si at normal incidence at a fluence of a) $1 \times 10^{16} \text{ cm}^{-2}$ and b) $1 \times 10^{18} \text{ cm}^{-2}$.

A full clean and HF etch should be given to samples to remove surface contamination and native oxide before implantation to ensure the cleanest possible result. The simulations show that failure to remove the native oxide layer produces oxygen contamination at a level of around

$1 \times 10^{18} \text{ cm}^{-3}$ in the surface 50 nm, which should be compatible with successful recrystallisation by SPE as it is comparable to that found in Czochralski-grown Si ($4 \times 10^{17} - 2 \times 10^{18} \text{ cm}^{-3}$ [87]). However, a full removal of hydrocarbons from the surface is required as a 10 nm layer would result in carbon and oxygen contamination of around $5 \times 10^{18} \text{ cm}^{-3}$, significantly higher than for the typical levels found in Czochralski-grown Si ($2 \times 10^{16} - 4 \times 10^{17} \text{ cm}^{-3}$ for C [87]). Additionally, hydrogen contamination is known to retard Si recrystallisation during SPE [202] and should be minimised.

5.4.6 Vacuum Contamination

Increasing the pressure in the vacuum chamber increases the probability that residual gases (e.g. from the air, water vapour and oil vapour from vacuum pumps) will collide with ions in the beam and alter their charge state if electrons are exchanged; thus reducing the accuracy of dosimetry and introducing energy contamination. The bombardment of residual gases can also introduce contaminants into the substrate by forwards recoils. The vacuum chamber of the EME 150 keV ion implanter used in this work is cryopumped, minimising contamination from hydrocarbon residual gases by avoiding the use of vacuum pump oil. The presence of such vacuum oil vapour would result in a darkened surface after ion implantation due to the cracking and polymerisation of hydrocarbon molecules deposited on the surface [203]. This effect is worse than having an initial surface layer of hydrocarbons, as the layer is constantly being replenished and thus results in a higher concentration of forward-recoiled impurities. TRIDYN simulations were run to show the level of contamination introduced by forward recoils during ^{28}Si implantation with residual air in the vacuum chamber. The implantation of 45 keV ^{28}Si into 200 nm of $^{\text{nat}}\text{Si}$ was simulated with a thermal flux of neutral gas (78 % N, 21 % O and 1 % Ar) included with implanted ions:neutrals = 9:1. A depth interval thickness of 1 nm and a precision of 0.02 was used, resulting in a maximum relative change of layer areal density per projectile of 0.2%. The concentration of Si isotopes and N, O and Ar contamination as a function of depth below the surface is shown after an implant of 45 keV ^{28}Si at a fluence of $2.5 \times 10^{18} \text{ cm}^{-2}$ in Fig. 5.14.

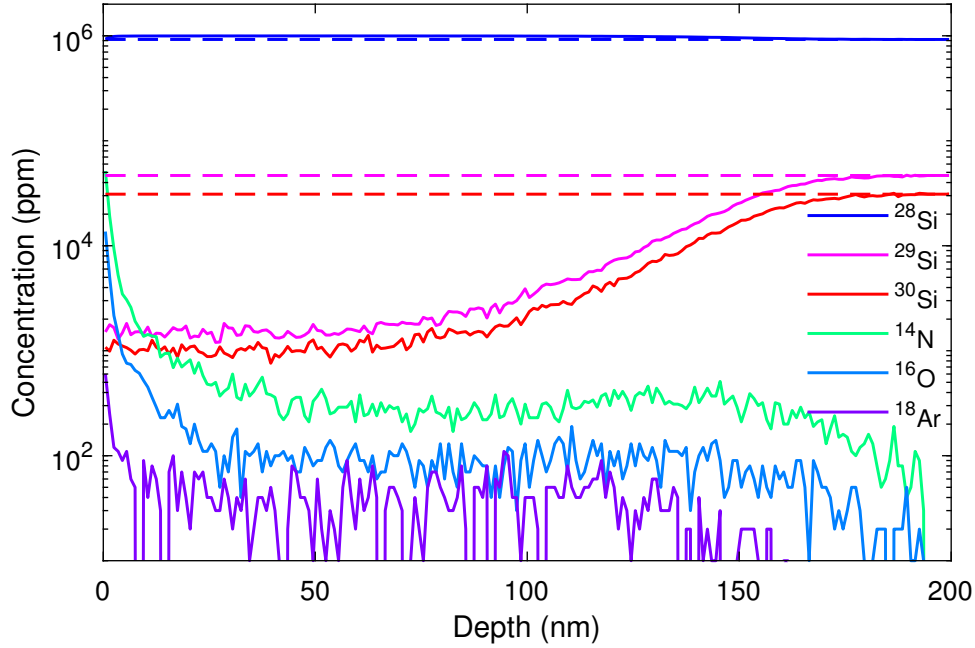


Figure 5.14: TRIDYN simulation showing the effect of vacuum level on the introduction of impurities. A thermal flux of neutral gas (78 % N, 21 % O and 1 % Ar) was included in the simulation with implanted ions:neutrals = 9:1. The concentration of Si isotopes and the impurities N, O and Ar as a function of depth are shown after the implantation of 45 keV ^{28}Si at normal incidence into $^{\text{nat}}\text{Si}$ with a fluence of $2.5 \times 10^{18} \text{ cm}^{-2}$.

As shown in Fig. 5.14, forward recoils from residual air introduce N, O and Ar contamination that extends to the end of range of 45 keV ^{28}Si with the highest concentration found in the near-surface region. The amount of contamination introduced by forward recoils increases with the residual gas pressure and implantation fluence. The increased level of contamination present in the target substrate affects the surface binding energy and was found to decrease the total sputter yield from 0.994 (for pure $^{\text{nat}}\text{Si}$) to 0.954 (for $^{\text{nat}}\text{Si}$ contaminated by forward recoils from residual gases) during the implantation of $5 \times 10^{18} \text{ }^{28}\text{Si} \text{ cm}^{-2}$. This shifts the implantation from the one-for-one replacement regime into the accumulation regime. Therefore, the contamination actually results in a slightly improved level of enrichment with less residual ^{29}Si at a depth of 20 nm. However, this improvement in enrichment level is at the cost of increased contamination, which must be limited by the use of a high vacuum level in order for successful recrystallisation by SPE. From the experimental implantation of $^{28}\text{Si}^-$ ions in this work, a vacuum level of $< 1 \times 10^{-7} \text{ Torr}$ was shown to be sufficient to avoid the incorporation of impurities at concentrations that would prevent SPE.

5.4.7 Ion Beam Contamination

An ion beam emanating from a source contains many species in addition to that which is desired for implantation, as can be observed by measuring the ion beam current whilst sweeping the mass separator magnet to collect a mass spectrum. The mass analyser selects the mass/charge ratio of ions that will be transmitted through an aperture to enter the beamline downstream. The transmitted mass range determines the mass resolution and depends on the magnet bending radius and the width of the adjustable slit forming the mass-selecting aperture. For the EME 150 keV implanter at ANU used in this work, this is 1 amu for a transmitted mass of 190 amu, with a smaller range for lower mass transmitted ions. This removes most of the contamination from the source. However, molecule ions with a mass/charge ratio almost identical to the desired implant species can be present; originating from ion source components, air and water vapour contamination in the source and previous source feed materials [204]. In the case of ^{28}Si , the isobars N_2 and CO exist; commonly present from the previously mentioned sources of contamination. TRIDYN was therefore used to simulate the co-implantation of N_2 and CO molecule ions with the same energy as ^{28}Si ions into 200 nm of $^{\text{nat}}\text{Si}$. A depth interval thickness of 1 nm and a precision of 0.02 was used, resulting in a maximum relative change of layer areal density per projectile of 0.22%. An ion beam consisting of 90% 45 keV ^{28}Si , 5% 22.5 keV N, 2.5% 19.286 keV C and 2.5% 25.714 keV O was implanted, using the valid assumption that 45 keV N_2 and CO molecular ions will dissociate upon entry and so can be simulated by separately implanting their atomic constituents with the kinetic energy distributed according to their mass fraction.

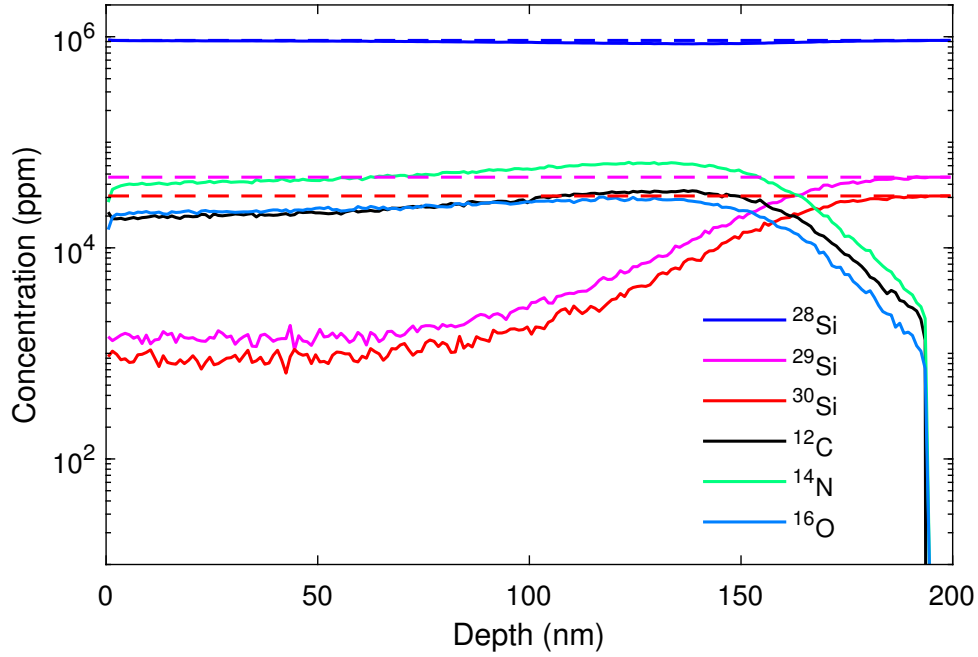


Figure 5.15: TRIDYN simulation showing the effect of a ^{28}Si beam contaminated with the isobars CO and N_2 . A 45 keV ion beam consisting of 90% ^{28}Si , 5% CO and 5% N_2 was implanted at normal incidence into $^{\text{nat}}\text{Si}$ with a fluence of $2.5 \times 10^{18} \text{ cm}^{-2}$. The concentration of Si isotopes and the impurities C, N and O as a function of depth are shown.

The concentration of the Si isotopes and impurities C, N and O as a function of depth below the surface are shown in Fig. 5.15 after the implantation of $2.5 \times 10^{18} \text{ cm}^{-2}$ of ions with ion beam composition and energy listed above. Substantial levels of contamination above 1 atomic % of C, N and O are introduced in the surface 150 nm after a high fluence implantation with a contaminated beam. The total sputter yield has been reduced to 0.953 during the implantation of $5 \times 10^{18} \text{ }^{28}\text{Si} \text{ cm}^{-2}$. The presence of these contaminants again shifts the implantation into the accumulation regime and results in a slightly lower level of residual ^{29}Si and ^{30}Si . The concentration of implanted impurities increases with fluence and the fraction of the beam that is contaminated. The contaminated fraction of a positive ion beam is likely to be less than 5%. However, high fluence implantation of a $^{28}\text{Si}^+$ ion beam containing even a small fraction of CO and N_2 molecule ions will produce unacceptably high levels of contamination that prevent recrystallisation, as observed in appendix A. Since these molecular isobars are electronically unstable in negative ion beams, a beam of $^{28}\text{Si}^-$ is strongly preferred to minimise the level of C, O and N contamination.

In summary, TRIDYN simulations allowed for the determination of how the sputter yield depends on the ^{28}Si implant energy and fluence and how the level of isotopic enrichment and thickness of the ^{28}Si surface layer depends on ^{28}Si implant energy and fluence. The phenomena of ion beam mixing was investigated to explain how the ^{28}Si ion beam can deplete unwanted isotopes from a surface layer of thickness down to the end of its implantation range. Finally, sources of contamination from surface layers, residual gases in the vacuum chamber and the ion beam were explored.

5.5 Diffusion Simulations

Fickian diffusion of ^{29}Si is simulated using Eq. 2.24, Eq. 2.25 and 2.26, with an activation energy of $E_A = 4.75$ eV and a diffusion coefficient of $D_0 = 530$ cm²s⁻¹ [196], and is shown in Fig. 5.16 for 120 min anneals at various temperatures. For the initial concentration distribution of ^{29}Si before annealing, the output of a TRIDYN simulation in which ^{28}Si (45 keV, 5×10^{18} cm⁻²) was implanted into natural Si was used.

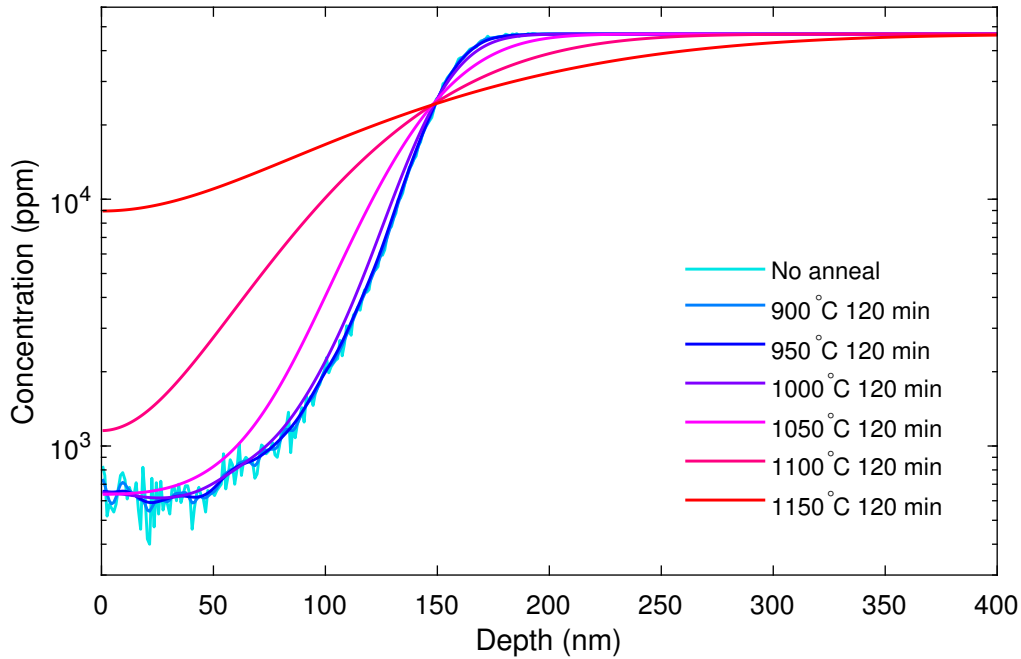


Figure 5.16: The concentration of ^{29}Si as a function of depth after simulating annealing at various temperatures for 120 min. The initial concentration distribution of ^{29}Si with no anneal is the output of a TRIDYN simulation in which ^{28}Si (45 keV, 5×10^{18} cm⁻²) was implanted into natural Si

As can be seen in Fig. 5.16, the diffusion of Si isotopes is negligible for long anneals at temperatures up to and including 1000°C. The high activation energy of the self-diffusion of Si therefore leads to negligible redistribution of Si isotopes during the solid phase epitaxial regrowth of the amorphised layer (typically performed at low temperatures around 600°C) and the rapid thermal anneal for the activation of implanted donors (typically performed at 1000°C for 5 s). This suggests the growth of a high quality thermal SiO_2 surface layer is also possible without reducing the level of isotopic enrichment in the surface layer as this process is typically performed at around 900°C for less than 2 hours.

Since the end goal of this isotope engineering is to implant donors into the enriched ^{28}Si layer for quantum device fabrication, we must be certain that the diffusion of such donors is minimised during processing. If donors are implanted into the ^{28}Si layer while still amorphous, as desired to minimise ion channeling, the thermal budget required to regrow the crystalline layer must result in negligible donor diffusion. P donors have the lowest activation energy for diffusion of any of the group V donors, with a diffusion constant described by $D = 0.074 \exp(-3.3 \text{ eV}/k_B T)$ cm^2s^{-1} for drive-in diffusion from a doped epitaxially deposited source layer [81]. The diffusion of P donors implanted into Si with an energy of 30 keV and a fluence of $6.5 \times 10^{11} \text{ cm}^{-2}$ during annealing at various temperatures for various times is shown in Fig. 5.17. The initial depth profile is simulated using SRIM.

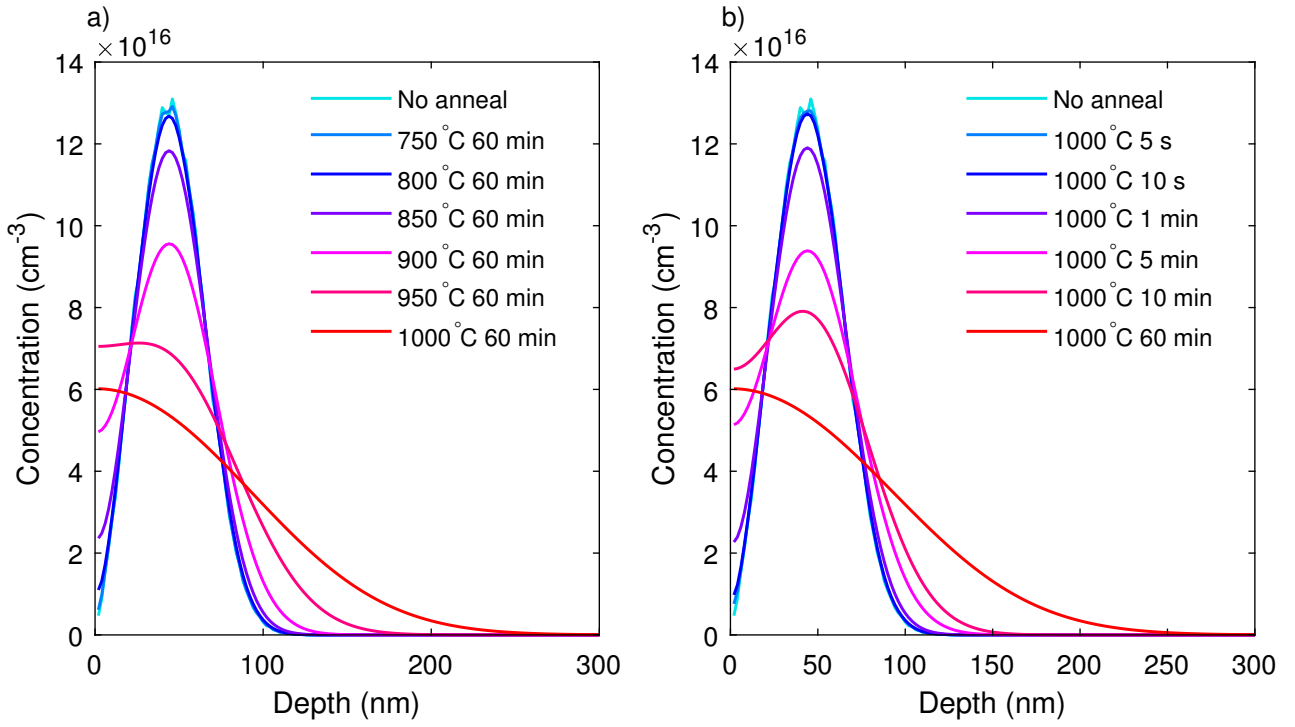


Figure 5.17: The concentration of P as a function of depth after simulating annealing at a) various temperatures for 60 min and b) 1000°C for various times. The initial concentration distribution of P with no anneal is the output of a SRIM simulation in which P (30 keV, $6.5 \times 10^{11} \text{ cm}^{-2}$) was implanted into Si

As can be seen in Fig. 5.17a, the diffusion of P in Si is negligible for long anneals at temperatures up to and including 800°C. The activation energy of P diffusion in Si is therefore high enough to result in negligible broadening of the P implant profile during solid phase epitaxy at $\sim 600^\circ\text{C}$). The growth of a high quality thermal SiO_2 surface layer at 900°C for around 1 hour should also be possible after the implantation of donors into the ^{28}Si surface layer for performing bulk measurements on the donors with, for example, EDMR since a negligible fraction of donors will diffuse out of the enriched ^{28}Si layer. A certain amount of diffusion may actually be desirable to increase the donor concentration near the surface of Si, leading to an increased number of donor spins that are accessible for EDMR measurement. In future, P donors could be implanted into the enriched ^{28}Si layer before the growth of a ~ 5 nm gate oxide required for single qubit fabrication, since this process typically requires oxidation at 800°C for which donor diffusion is shown here to be negligible. P diffusion is significant for prolonged annealing at 1000°C, however, as can be seen in Fig. 5.17b, a rapid thermal anneal at this temperature for 5 s to maximise the electrical activation of implanted donors will result in negligible diffusion.

An important caveat must be given with these results from the Fickian diffusion simulations of P in Si since the diffusion constant used was taken from drive-in diffusion experiments, in which the dopant source layer was epitaxially deposited on the Si substrate. Therefore, these results do not take into account the damage generated during ion implantation which is likely to cause transient-enhanced diffusion as P is an interstitial-assisted diffuser [84]. Therefore, the extent of P diffusion calculated here should be taken as a lower bound for that which would be expected during annealing of ion-implanted P in Si.

5.6 Experimental Methods

We have now set the scene to discuss the experimental work performed in this chapter by covering the previous experimental work performed on the isotopic enrichment of Si, the background theory of donor qubit decoherence mechanisms and by performing TRIDYN and diffusion simulations. In this section, the experimental techniques and parameters used in this work are presented. The parameters used for the fabrication of single-crystal ^{28}Si layers by high fluence ion implantation and annealing are guided by the results from the TRIDYN and diffusion simulations in the previous section. The methods used to characterise the resulting ^{28}Si layers by determining their level of isotopic enrichment, contamination, recrystallisation kinetics, crystal quality and coherence time of implanted P donors are discussed.

5.6.1 Sample Fabrication

In this work, various samples were produced by implanting $^{\text{nat}}\text{Si}$ substrates with ^{28}Si and ^{31}P followed by subsequent thermal annealing. The fabrication parameters for samples investigated in this chapter are summarised in Table 5.1. $^{28}\text{Si}^-$ implantation was used to isotopically enrich a surface layer, while $^{31}\text{P}^-$ implantation was used to incorporate donors to act as the probe for determining the quantum environment of the isotopically enriched layer by measuring their coherence time.

	Sample	
	A	B
Ion species	$^{28}\text{Si}^-$	$^{28}\text{Si}^-$
Energy (keV)	45	30
Fluence (cm^{-2})	2.63×10^{18}	4×10^{18}
Vacuum (Torr)	$< 1 \times 10^{-7}$	$< 1 \times 10^{-7}$
$^{31}\text{P}^-$ implants (keV, cm^{-2})	-	30, 6.5×10^{11} 10, 1.5×10^{11}
Anneal(s) ($^{\circ}\text{C}$, s, ambient)	620, 600, Ar 1000, 5, Ar	609, 394, air

Table 5.1: Implant parameters used to fabricate isotopically enriched ^{28}Si samples A and B.

The EME 150 keV ion implanter at ANU, equipped with a SNICS II ion source and a 90° double focusing magnet, was used for all implants performed on samples A and B. Fig. 5.1 schematically shows the mass spectrum of this implanter with a $^{\text{nat}}\text{Si}$ source, demonstrating the mass resolution of the Si isotopes. Near the start of the implantation run, the $^{29}\text{Si}^-$ and $^{30}\text{Si}^-$ ion beams contain a significant fraction of $^{28}\text{SiH}^-$ and $^{29}\text{SiH}^-$ molecular ions, respectively. Therefore, the ion beam currents for $^{29}\text{Si}^-$ and $^{30}\text{Si}^-$ relative to the $^{28}\text{Si}^-$ ion beam are initially higher than their natural abundance. $^{28}\text{Si}^-$ implants were performed at room temperature and with a 7° tilt off the incident beam axis to suppress ion channeling. A Si aperture, prepared from a wafer of $^{\text{nat}}\text{Si}$, was used to collimate the beam and prevent contamination from forward recoils of foreign atoms. A vacuum of less than 1×10^{-7} Torr was maintained in the target chamber with a cryopump to reduce impurity incorporation from residual gas by ion bombardment. The caesium oven temperature, cathode and extractor bias, magnet current, focus, einzel lens focus and horizontal and vertical alignment were adjusted to maximise the ion beam current at the sample; typically around $1 \mu\text{A}$ for a 45 keV $^{28}\text{Si}^-$ ion beam. The 3 mm beam spot is scanned across the chosen aperture to produce a homogeneous implant within the implantation area. The implantation time required is dependent on a number of factors, desired fluence, f ,

aperture area, A , and beam current on target, I , and is given as:

$$t = \frac{1.21 f A e}{I} \quad (5.4)$$

Where the factor of 1.21 is required to account for beam scattering which gives a larger effective implant area than the aperture area. Achieving a high fluence of 1×10^{18} with a $5 \text{ mm} \times 5 \text{ mm}$ aperture and a current of $1 \mu\text{A}$ takes around 12 hours.

In order to produce samples A and B, highly intrinsic (4 - 10 $\text{k}\Omega\cdot\text{cm}$) float-zone uniform high purity $^{\text{nat}}\text{Si}$ (UHPS Topsil) substrates were given a degreasing clean to remove surface hydrocarbons and a HF acid etch to remove the native SiO_2 , before being implanted with ^{28}Si ions at energies and fluences specified in Table 5.1. P donors were then implanted into the enriched layer of sample B with energies and fluences specified in Table 5.1. A piranha (4:1 98% H_2SO_4 : 30% H_2O_2 , 90 °C) and RCA-2 (5:1:1 H_2O : 30% H_2O_2 : 36% HCl , 70 °C) clean was then performed followed by annealing for SPE regrowth and donor activation, as specified in Table 5.1.

The depth profile of implanted P donors in sample B simulated using SRIM is shown in Fig. 5.18. The implant energies of 30 keV and 10 keV were chosen to spread P throughout the enriched ^{28}Si surface layer $\sim 100 \text{ nm}$ thick whilst ensuring that a P ESR signal would probe the ^{28}Si environment and not the $^{\text{nat}}\text{Si}$ substrate below. The P fluence was chosen to minimise the donor concentration (to minimise donor-donor interactions that decrease the donor coherence time and conceal the effects of reducing the concentration of ^{29}Si nuclear spins) whilst ensuring a measurable ESR signal.

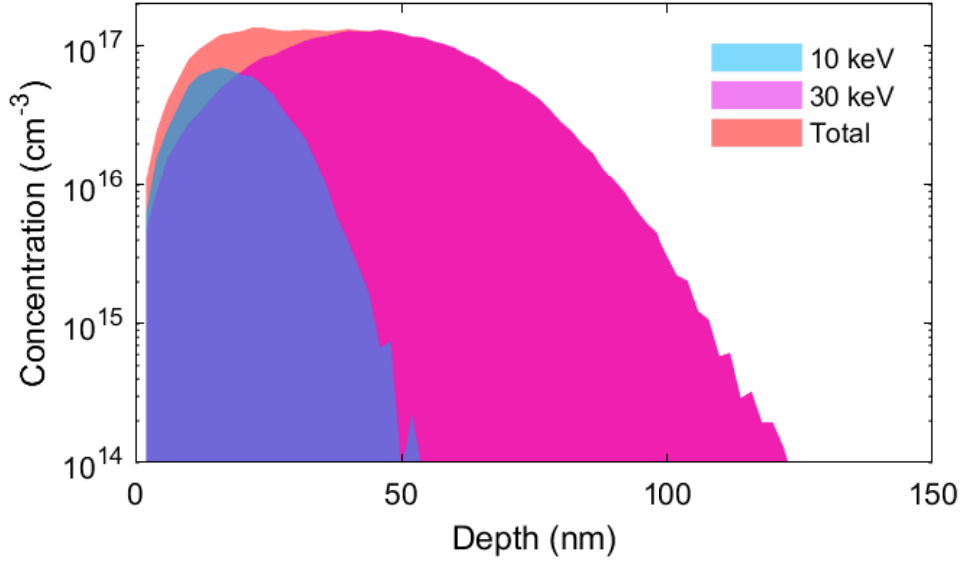


Figure 5.18: SRIM simulation of the depth profile of P implanted at 30 keV and 10 keV into Si at fluences used for sample B.

5.6.2 Isotopic Enrichment and Contamination

The composition with depth of sample A after annealing was obtained with SIMS at UNSW (IONTOF GmbH, TOF.SIMS 5). The Si isotopes were measured in positive polarity with a 1 keV O_2^+ beam used for sputtering and a 30 keV Bi^+ beam used for analysis. C and O impurities were measured in negative polarity with a 1 keV Cs^+ beam used for sputtering and a 30 keV Bi^+ beam used for analysis. The sputtered area was $300 \times 300 \mu\text{m}^2$ and the analysed area was $100 \times 100 \mu\text{m}^2$.

5.6.3 Recrystallisation Kinetics

The recrystallisation kinetics were obtained for sample B with TRR with a laser wavelength of $\lambda = 632.8 \text{ nm}$ during an anneal in air at 609°C . The rate of recrystallisation was compared to an *a*-Si standard: n-type ^{nat}Si amorphised with a much lower fluence of $^{28}\text{Si}^-$ ions with the following implantation scheme: $(0.5 \text{ MeV}, 3 \times 10^{15} \text{ cm}^{-2})$, then $(1 \text{ MeV}, 1 \times 10^{15} \text{ cm}^{-2})$ and finally $(2 \text{ MeV}, 1 \times 10^{15} \text{ cm}^{-2})$, resulting in a $2.2 \mu\text{m}$ *a*-Si layer. The SPE growth rate of this *a*-Si standard during the initial stages of the anneal was used to calibrate the temperature of the TRR hot plate. Refractive indices of $n_c = 4.086$ for *c*-Si [205] and $n_a = 4.831$ for *a*-Si [102]

were used for the SPE rate calculation.

5.6.4 Crystal Quality

TEM at Bio21 was used to determine the crystal quality of the enriched ^{28}Si layer in sample A after annealing. Before TEM lamella preparation, the sample was coated with a thin carbon layer (~ 20 nm). To prepare the sample, a focused ion beam (FEI, Nova Nanolab 200) was used to grow a 300 nm thick layer of Pt via electron-beam assisted deposition to protect the sample from ion damage. This was followed by a further $2.5\text{ }\mu\text{m}$ Pt layer deposited via a 30 keV Ga ion beam. A lamella was then extracted and thinned to a thickness of ~ 100 nm, with a final polishing step performed with a 5 keV Ga ion beam. A TEM (FEI, Tecnai TF20) was used to take high-resolution cross-sectional images in which a 200 keV electron beam was transmitted down the $[110]$ direction through the lamella to view the atomic arrangement. Raman spectroscopy with a 532 nm wavelength laser was used to confirm the crystalline nature of the enriched surface layer of sample A after annealing.

5.6.5 Pulsed Electron Spin Resonance

Pulsed electron spin resonance experiments were performed on P donors implanted in sample B. The sample was mounted onto the surface of a superconducting cavity made by dry etching a 100 nm-thick NbTiN film [206, 207]. The sample, along with the cavity, was mounted on the mixing chamber of a dilution refrigerator, with a base temperature of approximately 16 mK. Microwave pulses were sent to the cavity using a vector source at the resonant frequency of the cavity ($f = 6.028$ GHz), and the detected echo signal was then pre-amplified and measured using a digitiser. The P donor electron T_2 coherence time was measured using a standard Hahn echo pulse sequence [206], where the pulse length (400 ns for the first pulse) and power were chosen such that the spins undergo a $\pi/2$ rotation.

5.7 Results and Discussion

5.7.1 Isotopic Enrichment and Contamination

The concentration of the Si isotopes and the impurities ^{12}C and ^{16}O in sample A after annealing were measured with SIMS and are displayed as a function of depth below the surface in Fig. 5.19. Fig. 5.19a shows the high fluence ^{28}Si implantation depleted ^{29}Si and ^{30}Si to concentrations of around 250 ppm and 160 ppm, respectively, in a surface layer of thickness ~ 100 nm. The shape of the isotope concentration profiles agree well with the TRIDYN simulation shown in Fig. 5.9a. A higher level of enrichment was achieved experimentally than predicted by TRIDYN, as shown by the star symbols in Fig. 5.9b. This could be due to the experimental sputter yield being slightly less than 1, leading to the accumulation of a thicker isotopically enriched layer, as evidenced by the depth where the isotope concentrations reach natural abundance: ~ 180 nm for the TRIDYN simulation (Fig. 5.9a) and ~ 220 nm for the experimental measurement (Fig. 5.19a). This accumulation was shown to result in lower ^{29}Si and ^{30}Si concentrations, demonstrated by TRIDYN simulations implanting > 45 keV Si, as shown in Fig. 5.7c. The discrepancy in sputter yield, sensitive to the target surface binding energy, could be due to the impurity content of the substrate [201], as observed when looking at vacuum and ion beam contamination with TRIDYN simulations in sections 5.4.6 and 5.4.7, respectively. Alternatively, the actual implantation energy could have been greater than 45 keV resulting in a sputter yield of less than one. However, Fig. 5.7c shows that even if the actual implantation energy was 50 keV, a fluence of $2.63 \times 10^{18} \text{ cm}^{-2}$ should result in greater than 1000 ppm residual ^{29}Si . A smaller contribution could come from the uncertainty in the experimental implantation fluence, whereby the actual implant fluence was higher than expected.

The most important result from this SIMS measurement is that the residual ^{29}Si concentration achieved here is around 3 times lower than that found in a commercially-produced ^{28}Si wafer (Isonics) which, with 800 ppm ^{29}Si [164], has previously demonstrated dramatically increased coherence times of implanted donors [24]. This method of isotopically enriching a surface layer of $^{\text{nat}}\text{Si}$ therefore shows promise for further increasing the coherence time of implanted donor qubits.

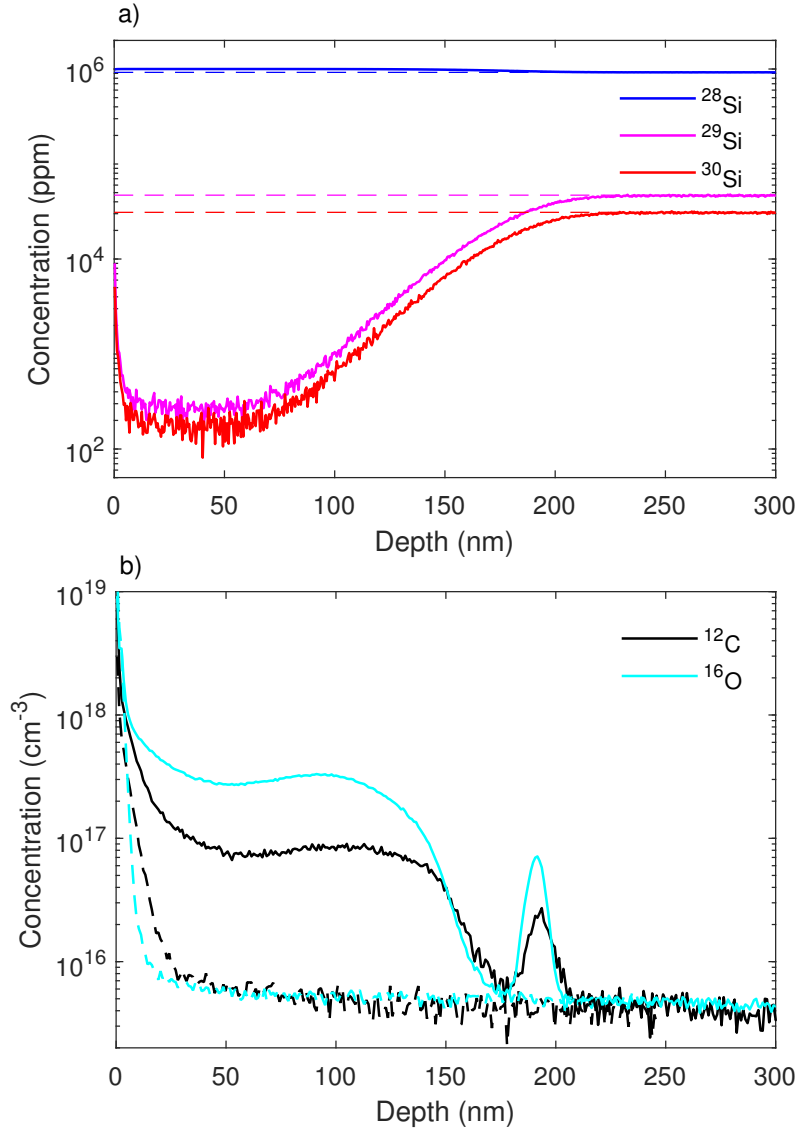


Figure 5.19: Experimental SIMS depth profiles for sample A after annealing. a) The concentration of the isotopes of ^{nat}Si as a function of depth below the surface. Natural abundance is indicated with dashed lines. b) The concentration of the impurities ^{12}C and ^{16}O as a function of depth, calibrated with typical maximum background impurity levels expected in UHPS Topsil. Dashed lines indicate the SIMS depth profiles for the non-implanted substrate.

Fig. 5.19b shows the concentrations of ^{12}C and ^{16}O in an implanted region (solid lines) and in a non-implanted region of the substrate (dashed lines). The concentrations are increased above the background levels to around $1 \times 10^{17} \text{ cm}^{-3}$ for C and $3 \times 10^{17} \text{ cm}^{-3}$ for O by the process of high fluence implantation of $^{28}\text{Si}^-$ ions and subsequent annealing. The concentrations of these impurities were calibrated by assuming that the background levels at a depth of ~ 300 nm, which are the same for the implanted and non-implanted regions, were $5 \times 10^{15} \text{ cm}^{-3}$; the maximum expected background contamination for UHPS Topsil quoted by the supplier.

An increase in impurity levels, significantly above the background level in the surface ~ 30 nm for C and surface ~ 20 nm for O, is present in the non-implanted substrate. This accounts for some of the near-surface impurity content in the implanted region. A small amount of the O contamination could have been introduced by forward recoils from a native oxide that would have been present since the HF etch of the target substrate was not performed on this sample immediately prior to entering the vacuum chamber of the implanter. However, as shown in section 5.4.5, the majority of O in the oxide layer will be sputtered away during the high fluence implantation, therefore, this is unlikely to be the dominant source of the O contamination. The Si aperture reduced forward recoils of impurities, with no trace of heavy metals detected with high-resolution Rutherford backscattering spectrometry (not shown). The majority of the C and O contamination is therefore proposed to have been incorporated into the implanted layer from the imperfect vacuum, as seen before with high fluence implantation in a cryopumped target chamber [208].

Despite this, our isotopically enriched sample meets our criterion for success where these levels of contamination are comparable to Czochralski-grown Si ($4 \times 10^{17} - 2 \times 10^{18} \text{ cm}^{-3}$ for O and $2 \times 10^{16} - 4 \times 10^{17} \text{ cm}^{-3}$ for C [87]) and indeed are shown to be low enough to allow for the successful recrystallisation of the enriched layer by SPE. A peak in the concentration of C and O impurities occurs at around 190 nm below the surface of Si. This depth is significantly shallower than the depth of the end of range defects (~ 290 nm) visible with TEM as a dark band of dislocation loops, as shown in Fig. 5.21a. The peak in impurity concentration at an intermediate depth between the surface and the end of range could be explained by open volume defects, invisible to TEM, in this region of vacancy excess behaving as gettering centres during annealing [209, 210]. Additionally, the gradual increase of the C and O concentration after implantation towards the surface in Fig. 5.19b indicates the preferential diffusion of C and O towards the surface, known to be a vacancy-rich region after ion implantation [211].

5.7.2 Recrystallisation Kinetics

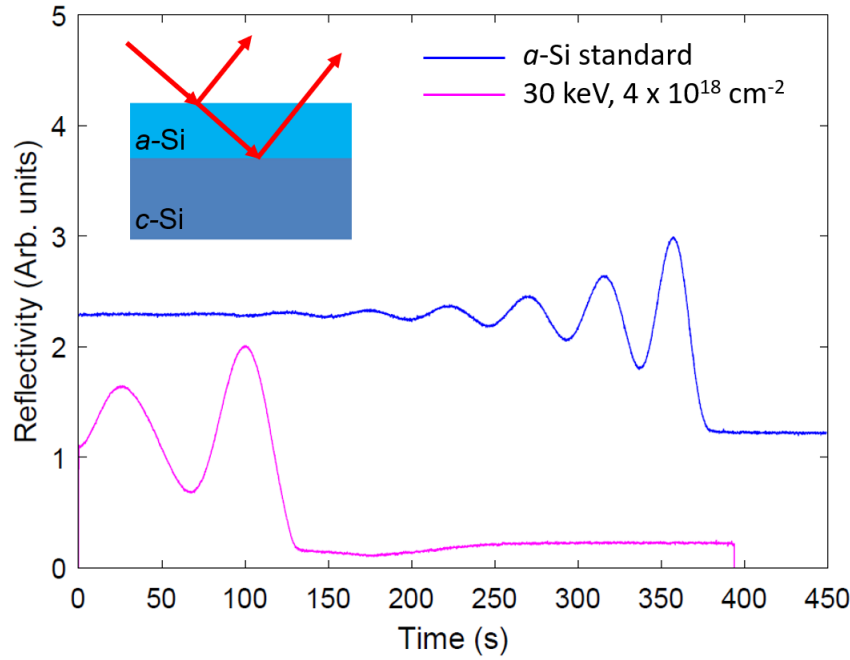


Figure 5.20: TRR curves showing the oscillating reflectivity due to the interference of a laser reflected off the surface and the advancing amorphous/crystalline (a/c) interface (as shown in the inset) during SPE. The a -Si standard and sample B were annealed on a hotplate at 609 °C during the measurement.

TRR curves collected during the annealing of the a -Si standard and sample B are shown in Fig. 5.20. During annealing, the amplitude envelope of the reflectivity oscillations increases due to the laser absorption in the a -Si layer of diminishing thickness. Each reflectivity oscillation corresponds to a distance of $\lambda/2n_a$ that the a/c interface has progressed. Sample B displays fewer oscillations due to the thinner a -Si layer. SPE is a thermally activated process and the intrinsic SPE rate is described by the Arrhenius relationship:

$$v_i = v_0 \exp(E_A/k_B T) \quad (5.5)$$

with $E_A = 2.70$ eV and $v_0 = 4.64 \times 10^{16}$ Å/s [194]. The SPE rate of the a -Si standard was calculated from the TRR curve to be 17.3 Å/s, whereas that of sample B was 8.9 Å/s. This SPE rate is lower due to the increased level of impurities [173] and open-volume defects [195] introduced by the high fluence implantation which slows the progression of the a/c interface.

5.7.3 Crystal Quality

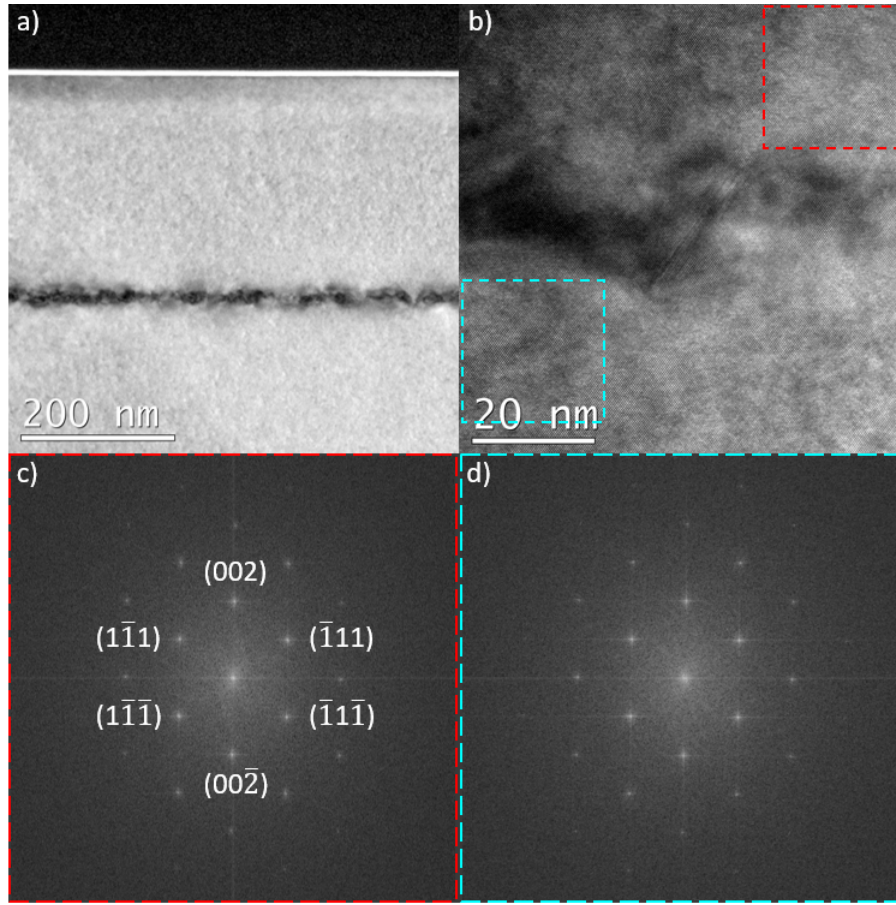


Figure 5.21: Cross-sectional TEM images of a lamella of sample A after annealing. a) The end of range defects are visible as a dark band ~ 290 nm below the surface. b) High-resolution TEM image showing the successful repair of the crystal lattice in the implanted layer. Crystal diffraction patterns of c) the implanted region (highlighted in red) and d) the non-implanted region (highlighted in cyan).

The crystal quality of sample A after annealing was determined using cross-sectional TEM, shown in Fig. 5.21. End of range defects, visible as a dark band ~ 290 nm below the surface in Fig. 5.21a, indicate the location of the amorphous/crystalline (a/c) interface before annealing. The a -Si layer is extended to greater depths during continued ion bombardment above the Si amorphisation threshold [212] (typically around $1 \times 10^{15} \text{ cm}^{-2}$ for keV Si ions [213]). The excess of interstitials at the end of range produced during ion implantation can evolve into dislocation loops during SPE regrowth of the a -Si layer [214]. These dislocation loops are stable up to temperatures of 1100°C [215], whereby they release self-interstitials into the surrounding substrate. This could cause undesired transient-enhanced diffusion [216] of implanted phosphorus donor qubits in this enriched layer and so lower annealing temperatures, well suited for SPE,

are preferred. Fast Fourier transforms (FFTs) of regions of the TEM image in Fig. 5.21b were taken to give diffraction patterns indicating the crystal structure of the lamella. The diffraction pattern for the implanted region, shown in Fig. 5.21c, indicates a high-quality crystal structure that is comparable to that of the non-implanted *c*-Si substrate beneath, shown in Fig. 5.21d. The crystallinity of the surface of sample A after annealing was confirmed using Raman spectroscopy (not shown).

These measurements show the success of the recrystallisation of the isotopically enriched Si surface layer during post-implantation annealing. The contamination level introduced during the high fluence implantation is therefore low enough to avoid the formation of a polycrystalline ^{28}Si layer, which would otherwise contain undesirable charge traps and dangling bonds at grain boundaries [217]. This single crystal layer of ^{28}Si should therefore provide a ‘semiconductor vacuum’ environment for implanted donor qubits with long coherence times. This is tested in the following section with electron spin resonance measurements of P donors implanted into an isotopically enriched surface layer.

5.7.4 P Donor Coherence Time

The isotopic enrichment level of sample B after annealing was measured using SIMS. The left axis of Fig. 5.22a shows the high fluence 30 keV $^{28}\text{Si}^-$ implantation depleted ^{29}Si and ^{30}Si to concentrations of around 3000 ppm and 2000 ppm, respectively, in a surface layer of thickness ~ 50 nm. $^{31}\text{P}^-$ was implanted into the ^{28}Si layer with a depth profile, simulated using SRIM, shown on the right axis of Fig. 5.22. The maximum P concentration was confirmed to lie below the SIMS detection limit ($\sim 2 \times 10^{17} \text{ cm}^{-2}$).

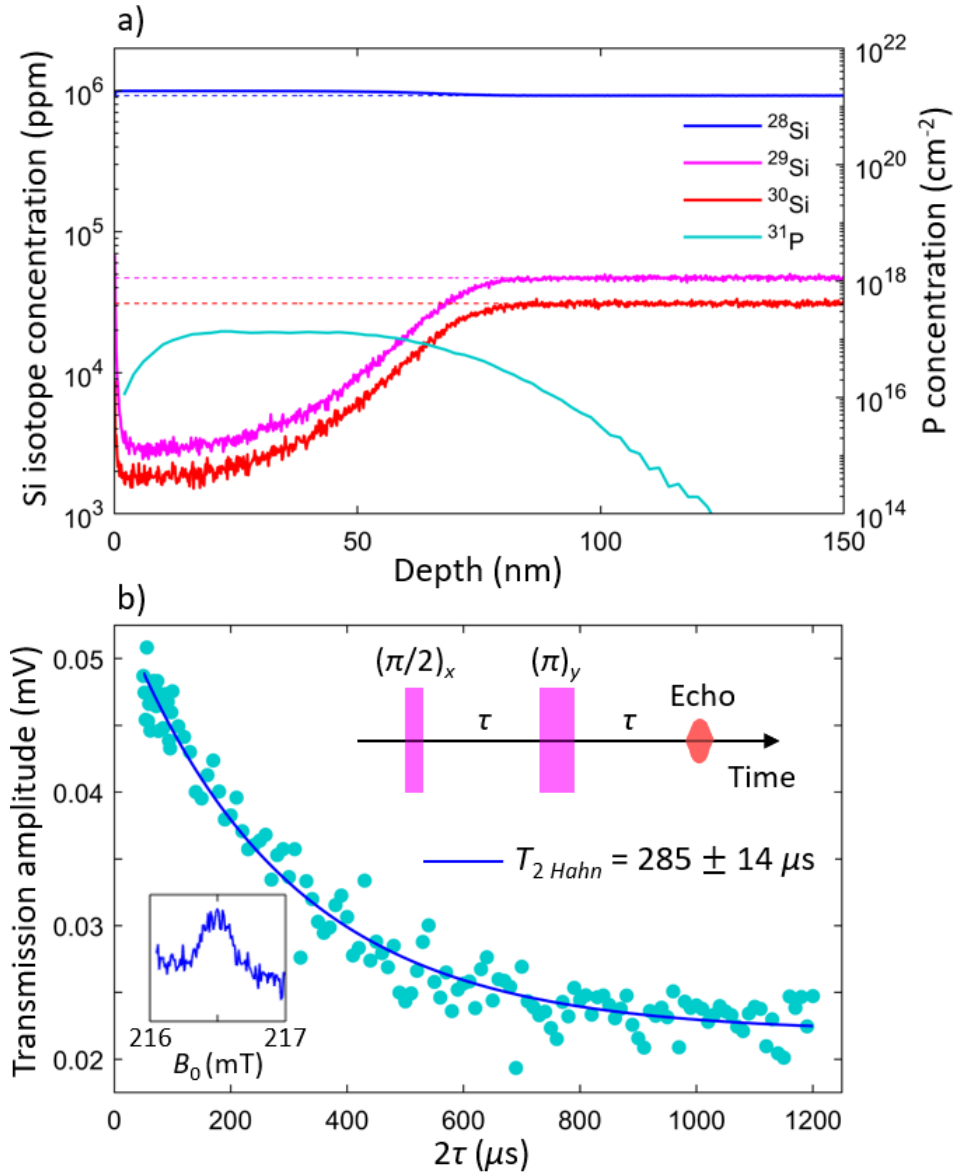


Figure 5.22: Experimental data for sample B after annealing. a) Left axis: SIMS depth profiles showing the concentration of the isotopes of $^{\text{nat}}\text{Si}$ as a function of depth below the surface. Natural abundance is indicated with dashed lines. Right axis: SRIM simulation of the implanted P depth profile. b) Pulsed ESR measurement of the implanted P donors. The Hahn echo is fit with an exponential decay, indicative of a ^{28}Si substrate, giving $T_2 = 285 \pm 14 \mu\text{s}$. The pulse sequence is shown in the top right and the upper hyperfine-split P ESR peak, collected with $\tau = 5 \mu\text{s}$, is shown in the bottom left.

Pulsed ESR experiments with a Hahn echo pulse sequence were performed to measure the coherence time of the implanted P donors, as shown in Fig. 5.22b. The transverse relaxation time T_2 obtained using the Hahn echo pulse sequence gives $T_2 = 285 \mu\text{s} \pm 14 \mu\text{s}$, which is comparable to previous reports [218, 193] and longer than the coherence time obtained in $^{\text{nat}}\text{Si}$ for similar doping concentrations ($\sim 100 \mu\text{s}$ [218]). Moreover, the echo decay is mono-

exponential which is consistent with the instantaneous diffusion between the donor electrons being the dominant decoherence mechanism here, instead of the spectral diffusion caused by ^{29}Si nuclear spins which dominates in $^{\text{nat}}\text{Si}$ [218, 193, 55]. The Hahn echo of P in $^{\text{nat}}\text{Si}$ is better fit by an exponential decay containing an additional cubic term:

$$\propto \exp\left(\frac{-\tau}{T_{2e}} - \frac{\tau^3}{T_{2s}^3}\right) \quad (5.6)$$

where T_{2e} is the characteristic decay time due to instantaneous diffusion caused by interactions between donor electrons and T_{2s} is the characteristic decay time due to spectral diffusion caused by interactions with ^{29}Si nuclear spins.

It is important to note that our measured T_2 of $\sim 285 \mu\text{s}$ is much shorter than the value predicted for a ^{29}Si concentration of 3000 ppm ($\sim 800 \mu\text{s}$) shown previously in Fig. 5.4. However, this is due to the concentration of P donors being much higher ($\sim 1 \times 10^{17} \text{ cm}^{-3}$) in our experiment than in the previous study [23] ($\sim 1 \times 10^{14} \text{ cm}^{-3}$) which decreases the coherence time by instantaneous diffusion of P donor electrons.

These ESR measurements demonstrate that the P donors have been implanted into an isotopically enriched ^{28}Si environment and successfully activated. In future, the concentration of P and the residual ^{29}Si can be reduced to improve the coherence time of implanted donors, with the optimum sample containing around $1 \times 10^{16} \text{ cm}^{-3}$ of P and 250 ppm or less of residual ^{29}Si . Therefore, we expect that the single crystal layer of isotopically enriched ^{28}Si will provide an ideal environment for implanted donor qubits, with high electrical activation and long coherence times.

5.8 Summary

In conclusion, a high fluence implant of $^{28}\text{Si}^-$ ions (45 keV, $2.63 \times 10^{18} \text{ cm}^{-2}$) into $^{\text{nat}}\text{Si}$ results in a depletion of ^{29}Si down to 250 ppm in a surface layer of thickness $\sim 100 \text{ nm}$, as measured with SIMS. The drastically reduced concentration of ^{29}Si spin-1/2 nuclei in this isotopically enriched layer should further extend the coherence time of implanted donors beyond that achieved with

commercial Isonics epilayers. Care was taken to limit the level of contamination introduced during high fluence implantation and concentrations were found to be below $1 \times 10^{17} \text{ cm}^{-3}$ for C and $3 \times 10^{17} \text{ cm}^{-3}$ for O, comparable to those in Czochralski-grown Si. The levels of contamination introduced during the high fluence enrichment process were found to be low enough to allow for successful recrystallisation via SPE, the activation of implanted P donors and their lengthy coherence times for the given level of P doping. The quality of the single crystal surface layer of ^{28}Si was shown to be equivalent to the non-implanted region of the *c*-Si substrate using high-resolution TEM, in which the end of range defects were still visible after annealing. A Hahn echo measurement of P donors implanted into a ^{28}Si layer produced by high fluence implantation with a higher level of residual ^{29}Si ($\sim 3000 \text{ ppm}$) was fit with a mono-exponential decay, suggesting an isotopically enriched ^{28}Si donor environment. The extracted coherence time of $T_2 = 285 \pm 14 \text{ }\mu\text{s}$ is longer than that obtained for $^{\text{nat}}\text{Si}$ at a similar doping concentration and can be increased in future with a lower concentration of P and residual ^{29}Si . This work shows the high fluence implantation of $45 \text{ keV } ^{28}\text{Si}^-$ ions as an effective method for isotopic enrichment which could be incorporated *in-situ* into the fabrication of ion implanted donor spins in ^{28}Si for quantum devices with increased coherence times.

5.9 Acknowledgements

I would like to acknowledge the following people for work performed in this chapter: Dr Brett Johnson for his assistance with ion implantation at the Australian National University, Dr Cassandra Chua, Dr Benoit Voisin, Dr Sacha Kocsis and Prof Sven Rogge for the pulsed ESR and SIMS measurement performed in this work at UNSW, Prof Dane McCamey for useful discussions on the pulsed ESR results, A/Prof Sergey Rubanov for the TEM measurements performed in this work at Bio21 and Simon Robson for his high-resolution RBS measurements at the University of Melbourne.

Chapter 6

Electrically Detected Magnetic Resonance of P in Si

6.1 Introduction

The quantum environment of donor electrons, i.e. the spins in their surroundings that they couple to and the magnetic and electric fields that they experience, strongly affects their coherence time which in turn determines their suitability for high fidelity qubits [24]. We desire to measure the coherence times of donors implanted into our isotopically enriched single crystal ^{28}Si material to see whether the high fluence implantation enrichment process produces a ‘semiconductor vacuum’ by depleting ^{29}Si nuclear spins without introducing paramagnetic defects such as dangling bonds or impurities with nuclear spin, for example ^{13}C . We can get an idea for the true donor coherence time T_2 by measuring the linewidth of a magnetic field-swept continuous-wave ESR transition since it gives a lower bound to the effective coherence time T_2^* [219], which in turn sets a lower limit for T_2 . This effective T_2^* results principally from inhomogeneity in the local magnetic field. The presence of ^{29}Si nuclei in the vicinity of donors broaden the donor ESR transition linewidth since they create an inhomogeneous magnetic field and so each donor will have a slightly different resonance condition [220].

Conventional ESR systems that employ resonant cavities, like that used to measure bismuth

donors in chapter 4, typically require at least 10^{10} donors to measure donor spin transitions from a change in magnetisation of the substrate [221]. Since our isotopically enriched ^{28}Si layer is on the order of 100 nm thick and the donor concentration is required to be low to prevent linewidth-broadening donor-donor interactions [222], the sensitivity of conventional ESR is too low to measure spin transitions from the small number of donors that would fit inside an ESR cavity. As a higher sensitivity alternative, we aim to use EDMR to measure donor spin transitions from a change in substrate conductivity. Since EDMR was first demonstrated with Si:P [114], the limits of sensitivity are being pushed down to the single spin, with less than 100 implanted P donors producing a spin transition signal via a change in photocurrent [115]. This is approaching the sensitivity of the measurement of a single donor spin achieved via spin-to-charge conversion by coupling the donor to the island of a single electron transistor (SET) [16]. A comparison of the sensitivity of the different measurement techniques discussed here for probing donor spin transitions is given in table 6.1.

	Conventional ESR	EDMR	SET
N_{spins}	$\sim 10^{10}$	< 100	1

Table 6.1: A comparison of the sensitivity of conventional ESR with a resonant cavity, EDMR and spin-to-charge conversion using an SET for the measurement of donor spin transitions. In each case, the minimum number of spins, N_{spins} , required to produce a measurable signal is given.

EDMR has previously been demonstrated as a suitable tool for observing the effect of isotopic enrichment of Si on the linewidth of the donor spin transition at the required sensitivity [223]. EDMR therefore provides an attractive solution to probing the quantum environment of a small number of donors implanted into ^{28}Si . The spin flips of these donors could be excited with an on-chip microwave stripline, as shown schematically in Fig. 6.1, and detected as a change in photocurrent flowing between biased source and drain electrodes.

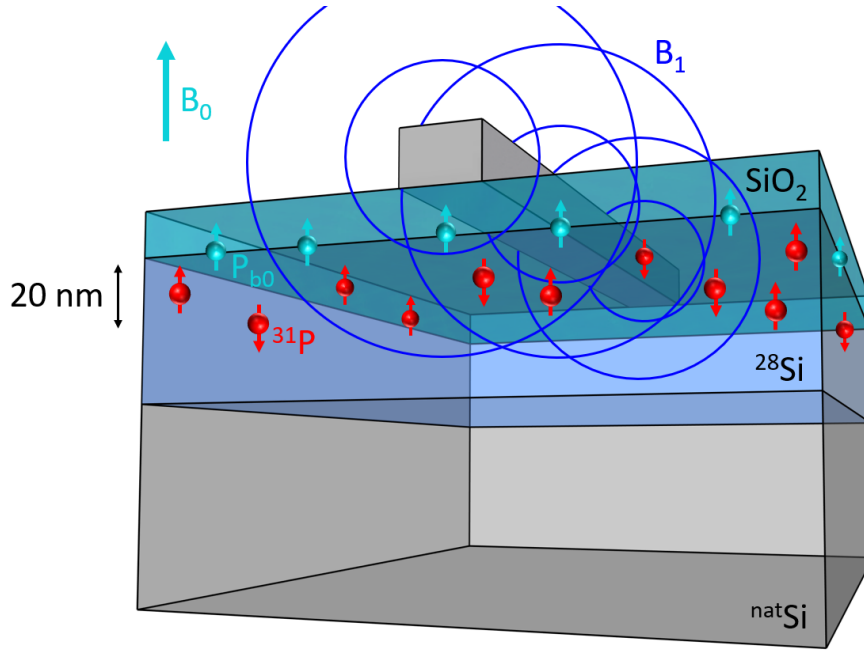


Figure 6.1: Spin transitions of ^{31}P donors (red) implanted into the near surface (~ 20 nm) region of an isotopically enriched layer of ^{28}Si can be probed using EDMR by the spin-dependent recombination pathway involving P_{b0} dangling bonds at the Si/SiO₂ interface (blue). This schematic shows an on-chip microwave stripline, electrically insulated from Si with SiO₂, capable of delivering an oscillating magnetic field B_1 that can drive transitions between spin states of electrons bound to donor nuclei, Zeeman-split by an external magnetic field B_0 .

In this work, an EDMR setup with lock-in amplification was designed and implemented with the aim of measuring spin transitions from donors in Si with a high sensitivity. EDMR devices were fabricated on a background-doped $^{\text{nat}}\text{Si}:\text{P}$ substrate as a proof of concept and to optimise the sensitivity of the system by adjusting experimental parameters. Various spin transitions were detected by collecting EDMR spectra, by measuring the photocurrent as a function of external magnetic field, at various microwave frequencies. The effects of donor freeze-out and the dependence of the EDMR signal amplitude and linewidth on the microwave power and microwave frequency modulation amplitude were explored.

Ultimately, this work provides a demonstration of the measurement of P donor spin transitions with this EDMR setup. The sensitivity of the setup can be increased further, with suggestions given in the Further Work section of chapter 7, to enable spin transitions from a low concentration of P donors implanted into our isotopically enriched Si layers to be probed. By measuring the linewidth of these EDMR signals, a lower bound can be placed on the donor coherence time, demonstrating the effect of ^{29}Si depletion on the donor quantum environment.

6.2 Theory

6.2.1 Electrically Detected Magnetic Resonance

EDMR achieves high sensitivity for probing donor spin transitions by electrically measuring the change in conductivity of a doped semiconductor that occurs during spin-dependent recombination of photo-excited electrons and holes through the pathway of paramagnetic donor and acceptor levels in the semiconductor band gap. An incident above-band gap light source is used to excite photoelectrons from the valence band to the conduction band, generating electron-hole pairs in the semiconductor. If a source-drain voltage is applied, this generates a steady-state photocurrent, where the optical excitation rate is balanced by the carrier recombination rate. If any of the carrier recombination pathways are spin-dependent, a resonant microwave excitation of any one of the spin species involved in those pathways will modulate the recombination rate and cause a transient change in the photocurrent [224]. In the case of measuring spin transitions of donors in Si, the P_{b0} centre (a dangling bond (coordination defect) at the interface between *c*-Si and its oxide caused by lattice mismatch [225]) acts as the acceptor in the spin-dependent recombination pathway. The shallow P donor and deep P_{b0} centre energy levels are shown between the conduction and valence bands of Si in Fig. 6.2.

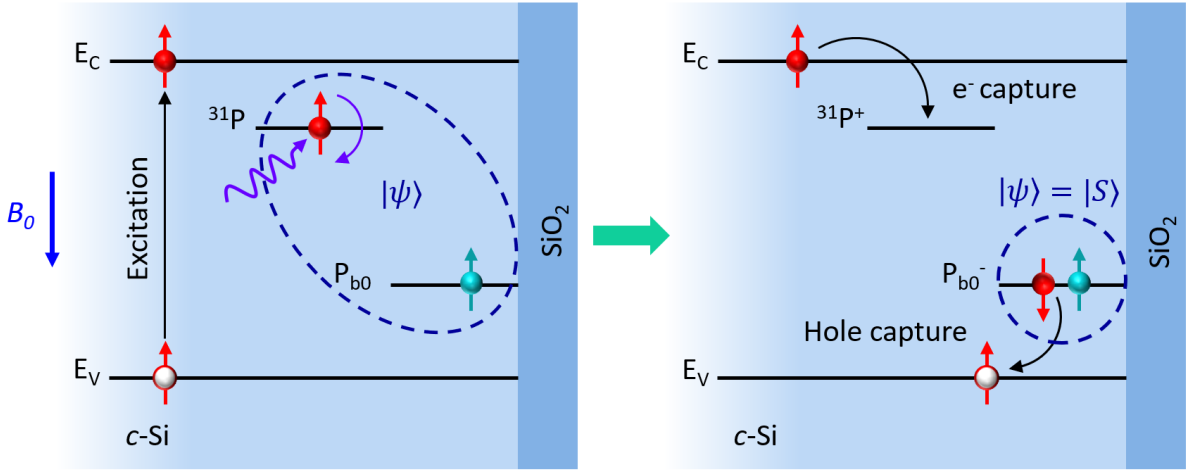


Figure 6.2: Band diagram of the Si/SiO₂ interface showing the spin-dependent recombination mechanism in Si:P EDMR. Optical excitation generates electrons in the conduction band and holes in the valence band of Si. A P donor electron in close proximity to a P_{b0} centre at the interface forms a spin pair $|\psi\rangle$. Resonant microwave excitation (purple) of the P donor electron induces a spin pair transition into the singlet state $|S\rangle$. The Pauli spin blockade is therefore lifted, allowing the P donor electron to transfer to the P_{b0} centre. The subsequent change in electron-hole recombination rate causes a measurable change in conductivity.

If a P donor electron is nearby a P_{b0} dangling bond electron in an external magnetic field, they will form a coupled spin pair [226], whose wavefunction $|\psi\rangle$ is a superposition of any of its four eigenstates: the three triplet states $|T_+\rangle$, $|T_0\rangle$ and $|T_-\rangle$, with total spin $S = 1$, and the singlet state $|S\rangle$, with total spin $S = 0$. The eigenstates of the spin pair consist of the triplet states that are independent of the spin-spin coupling strength:

$$|T_+\rangle = |\uparrow\uparrow\rangle \quad (6.1)$$

$$|T_-\rangle = |\downarrow\downarrow\rangle \quad (6.2)$$

and the admixed states that depend on the coupling strength:

$$|1\rangle = a|S\rangle + b|T_0\rangle = a(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) + b(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \quad (6.3)$$

$$|2\rangle = b|S\rangle - a|T_0\rangle = b(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) - a(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \quad (6.4)$$

where the first arrow in the ket represents the spin of the P donor electron and the second arrow represents the spin of the P_{b0} electron. In the strong coupling regime, when the P donor and P_{b0} electron are close together, $a \rightarrow 1$ and $b \rightarrow 0$, whereas in the limit of very weak coupling, when the P donor and P_{b0} electron are far apart, $a = b = 1/\sqrt{2}$. This spin pair $|\psi\rangle$ can relax into a lower energy state by transferring the P donor electron to the P_{b0} level, forming a negatively charged P_{b0}^- . Due to Pauli's exclusion principle, this doubly-occupied P_{b0}^- has to be diamagnetic (with a total spin of $S = 0$). The conservation of total spin angular momentum, resulting from the small spin-orbit interaction of Si, ensures that only the singlet component of the spin pair can relax into the lower energy state, making the carrier recombination rate via this pathway proportional to $|\langle S | \psi \rangle|^2$ [227].

During steady-state optical excitation, most spin pairs are pumped into the states $|T_+\rangle$ or $|T_-\rangle$ since all of the states are generated at the same rate but states $|1\rangle$ and $|2\rangle$ recombine the most quickly due to their singlet component. Resonant microwave excitation of either the P donor electron spin or the P_{b0} electron spin induces transitions from states $|T_+\rangle$ and $|T_-\rangle$ to states $|1\rangle$ or $|2\rangle$, thus increasing the carrier recombination rate via this pathway [228]. This leads to a transient decrease in conductivity, measurable as a change in photocurrent.

The spin dependent recombination pathway involving P donors is primarily dominated by P_{b0} centres [226]. Donor electrons interact with adjacent P_{b0} centres at the interface through either dipolar or exchange interactions [228], which set the length scale over which the spin pair is coupled. P donors in the first 20 nm below the oxide interface have been shown to be sensitive to EDMR [229], bounding the active volume of the device. Preliminary experiments to determine the optimal areal concentration of P_{b0} centres suggest that the EDMR signal is maximised when it matches that of the P donors in the sensitive region of the device [95]. Too high a concentration of P_{b0} centres (for example at the interface with a low quality native oxide) and the P donors will be ionised, too few P_{b0} centres (for example at a hydrogen-terminated Si surface produced by HF etching to remove SiO_2) and the recombination pathway will not be available. A thermally grown oxide with an intermediate areal concentration of P_{b0} centres may therefore be optimal depending on the concentration of P in the active region of the device.

Low temperatures, below the donor ionisation energy, are required during EDMR measure-

ments for carrier freeze-out [230] to ensure the donor electrons are bound to the donor nuclei. If the number of P donor spins in the active region of the device is low, lock-in amplification techniques are required to increase the EDMR signal to noise in the photocurrent. In order to excite carriers, the photon energy used must be greater than the Si band gap. The EDMR signal to noise is also affected by the power and wavelength of the light source used to excite a photocurrent [228]. Therefore, it is important to optimise the device fabrication and operating parameters, such as P_{b0} concentration, temperature, lock-in amplification and laser parameters, to maximise the sensitivity of the EDMR system.

6.2.2 The P Donor Spin Hamiltonian

In the previous section we have seen how when the substrate is irradiated with microwaves of a particular frequency that corresponds to the resonance frequency of the P donor electron, a spin transition is induced which alters the carrier recombination rate and results in an EDMR signal. The resonance frequency of a P donor electron depends on the size of the Zeeman-splitting due to the applied magnetic field and the alignment of the P nuclear spin in this magnetic field. In this work, the microwave frequency is fixed and the magnetic field strength is scanned to alter the strength of the Zeeman interaction. In order to determine the resonant magnetic fields at which the 2 P donor EDMR signals (corresponding to the 2 spin orientations of the spin-1/2 P nucleus) will appear, we need to map how the transition frequencies between the different P donor energy levels depend on the applied magnetic field. For this, we first need to find the energy levels of the P donor spin Hamiltonian.

The spin Hamiltonian of the P donor system in an external magnetic field, B_0 , is given in frequency units as:

$$\frac{\hat{H}}{h} = \gamma_e B_0 \hat{S}_z - \gamma_n B_0 \hat{I}_z + A \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \quad (6.5)$$

where $\gamma_e \approx 28$ GHz/T is the electron gyromagnetic ratio [231], $\gamma_n \approx 17.2$ MHz/T is the P nuclear gyromagnetic ratio [232] and $A \approx 117.5$ MHz is the hyperfine constant [122]. The eigenenergies of this Hamiltonian are plotted using the Breit-Rabi formula, previously derived

in Eq. 2.16, in Fig. 6.3a. The eigenstates of this Hamiltonian are:

$$|1\rangle = |\uparrow\uparrow\rangle \quad (6.6)$$

$$|2\rangle = \alpha |\downarrow\uparrow\rangle + \beta |\uparrow\downarrow\rangle \quad (6.7)$$

$$|3\rangle = \alpha |\uparrow\downarrow\rangle - \beta |\downarrow\uparrow\rangle \quad (6.8)$$

$$|4\rangle = |\downarrow\downarrow\rangle \quad (6.9)$$

where the nuclear magnetic projection $m_I = 1/2$ ($-1/2$) is represented by $\uparrow$ ($\downarrow$) and the electron magnetic projection $m_s = 1/2$ ($-1/2$) is represented by $\uparrow$ ($\downarrow$). The spin state coefficients are:

$$\alpha = \cos \eta/2 \quad (6.10)$$

$$\beta = \sin \eta/2 \quad (6.11)$$

where η is the angle between the magnetic field B_0 and the electron and nuclear spins precession axis, given by:

$$\tan \eta = \frac{A}{\gamma_e B_0 - \gamma_n B_0} \quad (6.12)$$

The magnetic field dependence of the spin state coefficients α and β are shown in Fig. 6.3b.

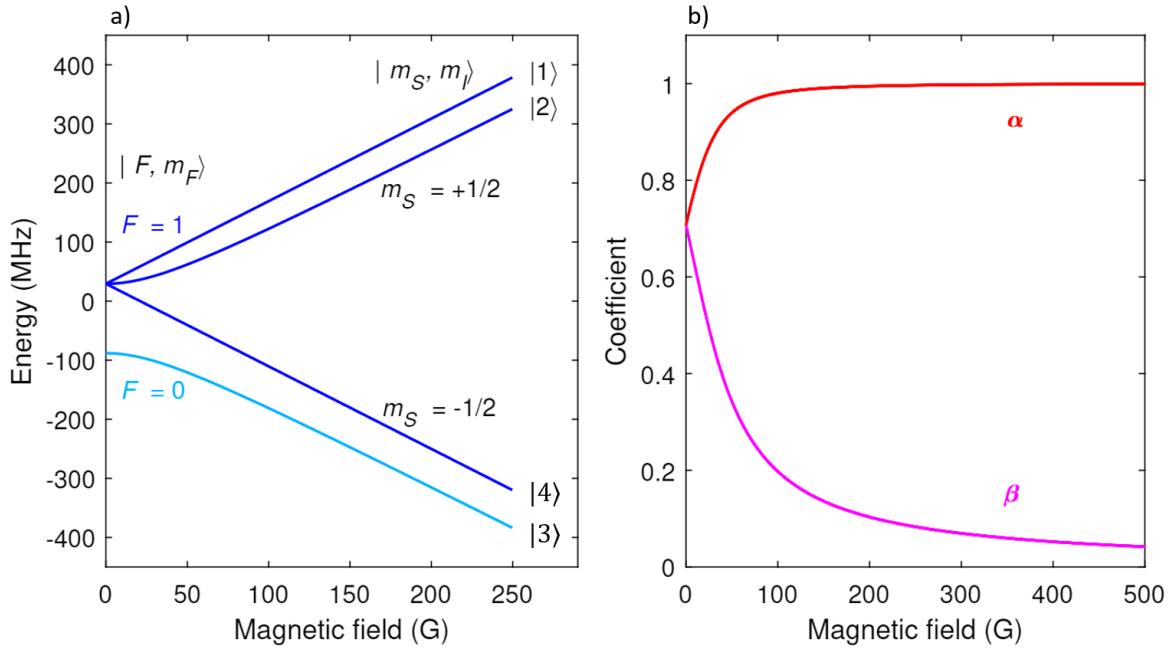


Figure 6.3: a) The $(2I + 1)(2S + 1) = 4$ energy levels, in frequency units, of the P donor spin states as a function of magnetic field. The states are described by the good quantum numbers $|F, m_F\rangle$ in the low field regime (when $B \leq 200$ G) and $|m_S, m_I\rangle$ in the high field regime. b) The spin state coefficients, α and β , as a function of magnetic field.

In the high field regime ($B_0 \gg 200$ G), $\alpha \rightarrow 1$ and $\beta \rightarrow 0$ and the four eigenstates simply become $|\uparrow\uparrow\rangle$, $|\downarrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$ and $|\downarrow\downarrow\rangle$. In this regime, the ESR allowed transitions are given by the selection rules $m_s = \pm 1$ and $m_I = 0$, i.e. $|1\rangle \Leftrightarrow |3\rangle$ and $|2\rangle \Leftrightarrow |4\rangle$. In the low field regime ($B_0 < 200$ G), α and β are both non-zero and eigenstates $|2\rangle$ and $|3\rangle$ are both in a superposition of spin states. Therefore, transitions that are forbidden in the high field regime contain a component of the allowed ESR transitions and can be observed at low field. All possible transitions are shown in Fig. 6.4a, with their transition frequency dependence on magnetic field shown in Fig. 6.4b.

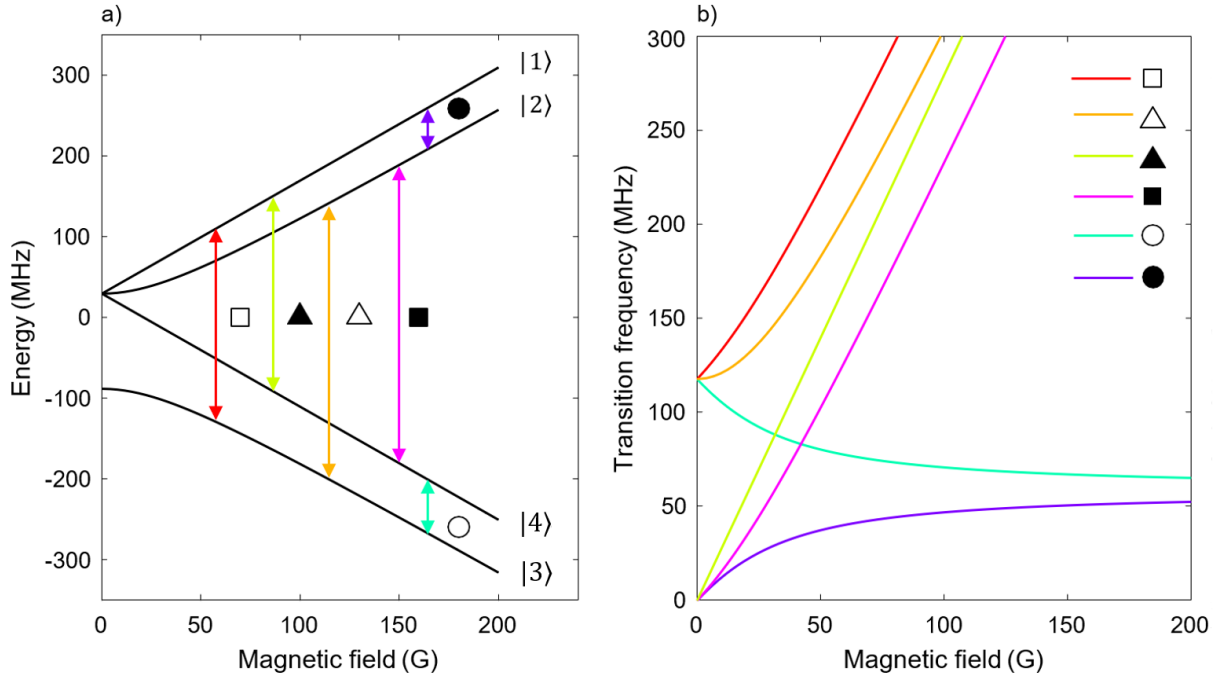


Figure 6.4: Breit-Rabi simulations for P in Si. a) Energy levels of the spin states as a function of magnetic field. The symbols represent all possible spin transitions. b) Resonance frequency of the various spin transitions as a function of magnetic field.

6.2.3 Electron Spin Resonance Linewidth

Spin transition linewidths provide an important insight into the spin environment in the vicinity of the spin species undergoing ESR. As detailed in section 5.3.1, the presence of ^{29}Si causes spectral diffusion, resulting in a decreased donor coherence time T_2 . Each donor electron is coupled to its surrounding ^{29}Si nuclear spins with varying hyperfine interaction strengths due to the random distribution of ^{29}Si in the Si crystal. The resonance frequency of each donor is therefore shifted by a slightly different amount, resulting in a broadening of the hyperfine-split lines present in the ESR spectra of an ensemble of donors in Si. The ESR linewidth has been found to show a different dependence on the fraction of ^{29}Si , f , in two different regimes [220]. In the high- f regime ($f > 10\%$), the ESR transition has a Gaussian line shape with a FWHM of $\Delta B_G \propto f^{1/2}$ [233]. In the low- f regime ($f < 10\%$), the ESR transition has a Lorentzian line shape with a FWHM of $\Delta B_L \propto f$ [234].

A lower bound estimation of the inhomogeneous coherence time T_2^* can be extracted from the intrinsic peak-to-peak linewidth, ΔB_L , of the first derivative Lorentzian CW-ESR peak, in

which no artificial broadening effects take place, since:

$$T_2^* \gtrsim \frac{2}{\sqrt{3}} \frac{1}{\gamma_e \Delta B_L} \quad (6.13)$$

This sets a lower limit for the coherence time T_2 of the donor electron [219].

This implies that in future the effect of the depletion of ^{29}Si in our isotopically enriched Si surface layers can be determined by measuring the linewidth of the EDMR signals produced by P donors implanted in this layer.

6.3 Experimental Review

6.3.1 EDMR of P Donors in Si

The detection of P donor ESR by a change in electrical conductivity of a bulk-doped Si substrate was first observed in 1966 [114]. Since then, spin transitions of donors in Si have been measured using EDMR for bulk-doped [235, 236, 226, 237, 238, 239, 240, 223, 228] and implanted donors [115, 241, 242] in both $^{\text{nat}}\text{Si}$ [235, 236, 115, 226, 237, 238, 239, 240, 242, 228] and ^{28}Si [223, 241]. Most of these experiments involve the electrical measurement of a photocurrent to obtain an EDMR spectrum. High sensitivities, with EDMR signals being produced by spin transitions of less than 100 implanted donors in Si, have been demonstrated [115].

In one such experiment with bulk-doped P donors in $^{\text{nat}}\text{Si}$ [239], EDMR devices were fabricated on n-type Si with a P concentration of $\sim 10^{16} \text{ cm}^{-3}$ with ohmic contacts prepared by As implantation (25 keV, $2 \times 10^{15} \text{ cm}^{-2}$ followed by annealing at 980°C for 25 s) and vacuum deposition of 5 nm palladium and 50 nm gold. The sample was placed in a cryostat in an externally applied magnetic field and irradiated with a white halogen lamp and RF from an irradiation coil. A pair of current-carrying coils was used to modulate the magnetic field for lock-in detection of the sample photoconductivity. EDMR spectra were collected by measuring the fractional change in sample photoconductivity, $\Delta\sigma/\sigma$, as a function of external magnetic field for various RF frequencies, as shown in Fig. 6.5a. Each EDMR peak is indicated with a

symbol which corresponds to one of the spin transitions shown in Fig. 6.4a. Two allowed ESR transitions of the P donor electrons (squares), 3 forbidden transitions of the P donor electrons (2 circles and one triangle) and one ESR transition of the P_{b0} dangling bond electron (asterisk) are observed in the low-field regime. The remaining forbidden transition (black triangle) is not observed as it is masked by the P_{b0} allowed ESR transition.

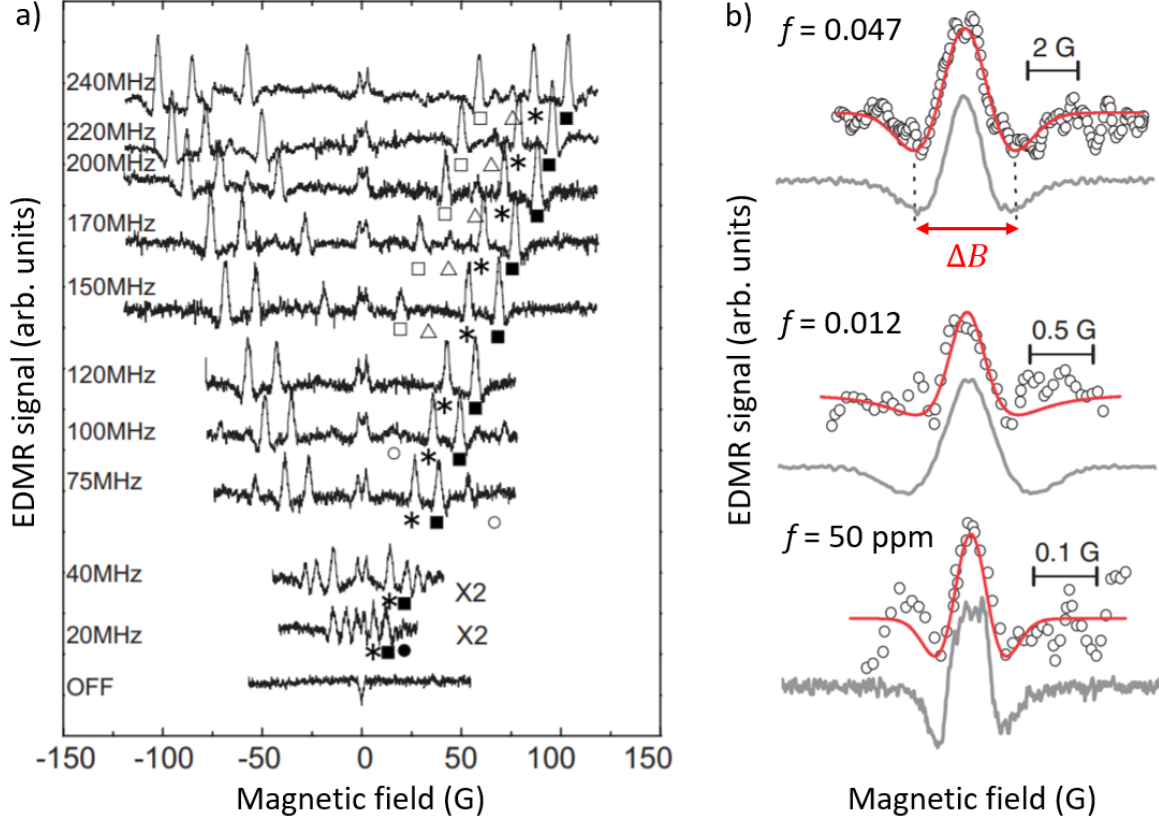


Figure 6.5: Previous experimental work on bulk-doped Si:P EDMR in the low-field regime. a) EDMR spectra for ^{nat}Si with $[P] \sim 10^{16} \text{ cm}^{-3}$ at various RF frequencies [239]. The symbols mark various spin transitions (see text for details). b) Upper hyperfine P EDMR peaks showing the linewidth, ΔB , for Si with $[P] \sim 10^{15} \text{ cm}^{-3}$ and various fractions of ^{29}Si , f . The EDMR data (black circles) is fit with a second derivative Gaussian or Lorentzian (red curve) and compared to the corresponding ESR spectrum (grey line) for each case [223].

The intrinsic linewidth of ESR transitions contain information about the spin-spin interactions present in the paramagnetic species, as mentioned in section 6.2.3. This has been probed by measuring the photoconductivity in a low-field EDMR experiment for isotopically controlled $c\text{-Si}$, background-doped with $\sim 10^{15} \text{ P cm}^{-3}$ with various fractions of ^{29}Si , f , [223], as shown in Fig. 6.5b. The linewidth ΔB was found to decrease from 2.2 G at $f = 0.047$ to 0.52 G at $f = 0.012$. The linewidth at $f = 50 \text{ ppm}$ of 62 mG was limited by the inhomogeneity of

the electromagnet. The linewidth obtained by this EDMR experiment was found to agree with that measured using a conventional X-band ESR spectrometer. This shows that there are no additional linewidth broadening mechanisms introduced with the EDMR measurement that are not also present in conventional ESR systems.

EDMR therefore provides a sensitive method for probing the electron spin transitions of donors implanted in Si that could be used to determine the success of electrically activating implanted donors and to show the effect of our ^{28}Si enrichment method on the quantum environment of donors implanted into this layer.

6.4 Experimental Methods

We have now covered the background theory on the phenomenon of EDMR caused by spin-dependent recombination, specifically with P donors in Si, how the EDMR signal linewidth can be used to extract a lower bound for the donor coherence time and the previous experimental work performed on Si:P EDMR. This section will now describe the design and fabrication of EDMR devices, the implementation of the EDMR setup and the measurement protocol performed in this work for the measurement of electron spin transitions of P donors in Si.

6.4.1 Device Fabrication

EDMR devices were designed with an on-chip microwave stripline (in this work, microwaves are used interchangeably with RF, although technically microwaves have a frequency of at least 300 MHz), source and drain electrodes and a surrounding ground plane. The microwave stripline is surrounded by a ground plane to form a coplanar waveguide, with the spacing between the central signal-carrying conductor and the surrounding ground plane conductors chosen to impedance match the stripline to the $50\ \Omega$ coaxial cables. This minimises the microwave power transmission loss through the device, however this is more significant at higher frequencies in the GHz range. Various electrode geometries are shown in the false-colour KLayout design in Fig. 6.6a-c. The EDMR devices were fabricated using photolithography, an example is shown

Fig. 6.6d.

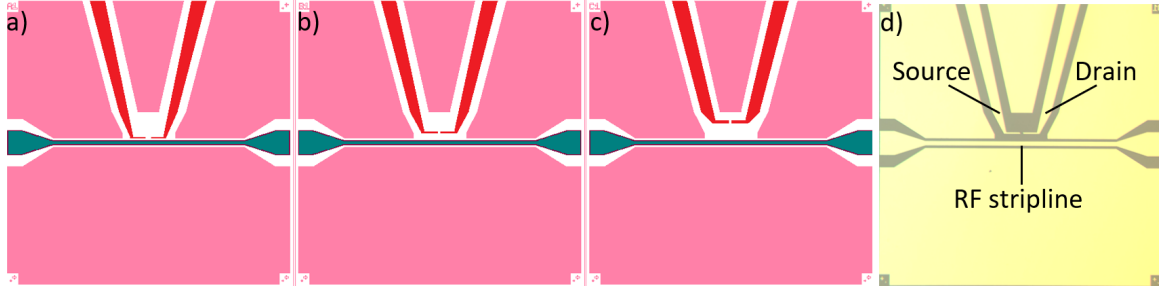


Figure 6.6: a)-c) EDMR devices were designed using KLayout with source and drain electrodes (red), an RF stripline (teal) and a ground plane (pink). Different electrode geometries are shown. The sensitive region of the EDMR device is located in the gap between the source and drain electrodes. d) Optical image showing an example of an EDMR device design produced using photolithography.

The substrate selected for EDMR device fabrication was n-type, P-doped ^{nat}Si with a resistivity of 0.1-0.5 $\Omega\cdot\text{cm}$, corresponding to a P concentration of $2.4 \times 10^{17} - 3.19 \times 10^{16} \text{ cm}^{-3}$. This substrate, containing a large number of P spins and thus capable of producing a large EDMR signal, was used to set up the EDMR measurement protocol and adjust experimental parameters to increase measurement sensitivity.

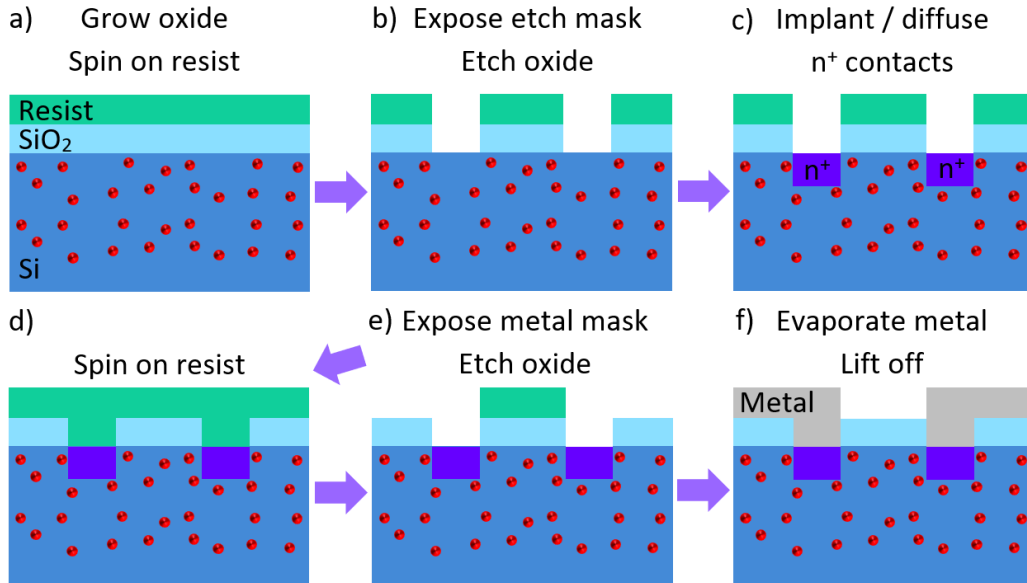


Figure 6.7: Simplified fabrication process flow for EDMR devices. The substrate is background doped with P donors (red).

A simplified EDMR device fabrication process flow is shown in Fig. 6.7 and is as follows: The substrate is first cleaned before a ~ 20 nm-thick thermal silicon oxide is grown in a Si furnace with oxidation at 900 $^{\circ}\text{C}$ for 20 min. Negative photoresist is then spun onto the surface,

UV-exposed through an etch mask and developed to reveal the pattern. The exposed SiO_2 is etched away using HF acid in the regions of the source and drain contacts. Heavily n-type ohmic contacts are then formed by either implanting or drive-in diffusing As into the source and drain contact regions. In order to produce the metal pattern, negative photoresist is first spun onto the surface. This resist is then patterned by UV-exposing through the metal mask (aligned with the etched regions) before developing. A quick 5 s HF etch is then performed to remove any native SiO_2 that has grown over the ohmic contact regions. Finally, the metal can be deposited in a vacuum by e-beam evaporating 50 nm Au, with a 10 nm Pt inter-layer for surface adhesion. The metal pattern is then revealed during the lift off process that removes the resist. The EDMR devices are then laser cut, mounted and wire bonded to a chip carrier that is attached to a probe that is inserted into the JANIS cryostat for measurement. A more detailed fabrication process flow is given in Appendix C.

6.4.2 Microwave Power Dissipation Simulation

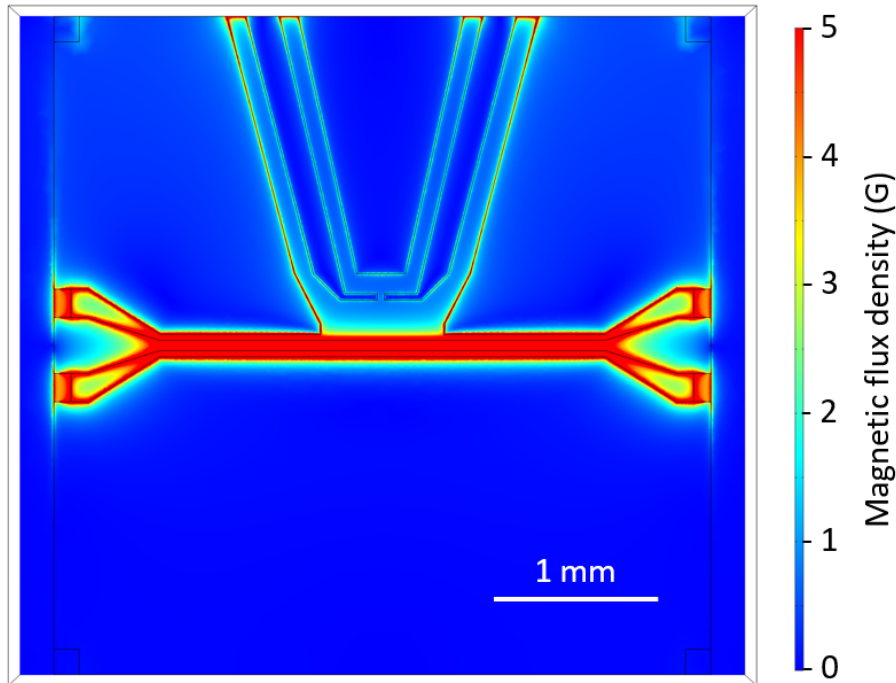


Figure 6.8: COMSOL simulation showing how the magnetic flux density, B_1 , produced by the transmission line carrying RF with a frequency of 150 MHz and a power of 20 dBm varies across the EDMR device used in this work. This shows a magnetic field strength of ~ 1 G in the sensitive region of the device between the source and drain electrodes.

In this work, the device geometry shown in Fig. 6.6c was used for EDMR measurements. This design was chosen as it has the largest area between the source and drain electrodes and thus contains the greatest number of donor spins in the sensitive region of the device which should yield the highest signal to noise ratio. A microwave signal of frequency ν is sent along the transmission line to provide an alternating magnetic field, B_1 , to induce donor spin transitions when the Zeeman splitting, ΔE , matches the energy of the microwaves, $h\nu$. A COMSOL simulation showing the magnetic flux density produced by microwaves flowing along the transmission line with a frequency of 150 MHz and a power of 20 dBm is shown in Fig. 6.8. The dimensions of the EDMR device simulated with COMSOL were the same as used in the experiment with a total device area of 4 mm x 4 mm. The presence of the ground plane minimises the dissipation of the microwave power and this simulation shows that it concentrates the magnetic field, B_1 , in the regions between the transmission line and the ground plane. The ground plane can be seen to shield the active region of the device from the microwave power dissipated by the transmission line. This simulation shows that microwaves with a frequency of 150 MHz and a power of 20 dBm produce a magnetic field strength, B_1 , of around 1 G in the active region of the EDMR device between the source and drain electrodes. A stronger magnetic field, B_1 , could be produced in the active region of the device by moving the source and drain electrodes closer to the transmission line and removing the ground plane. This would excite more spin transitions and produce EDMR signals with larger amplitudes, however, care would have to be taken to avoid power broadening of EDMR signal linewidth.

6.4.3 EDMR Setup

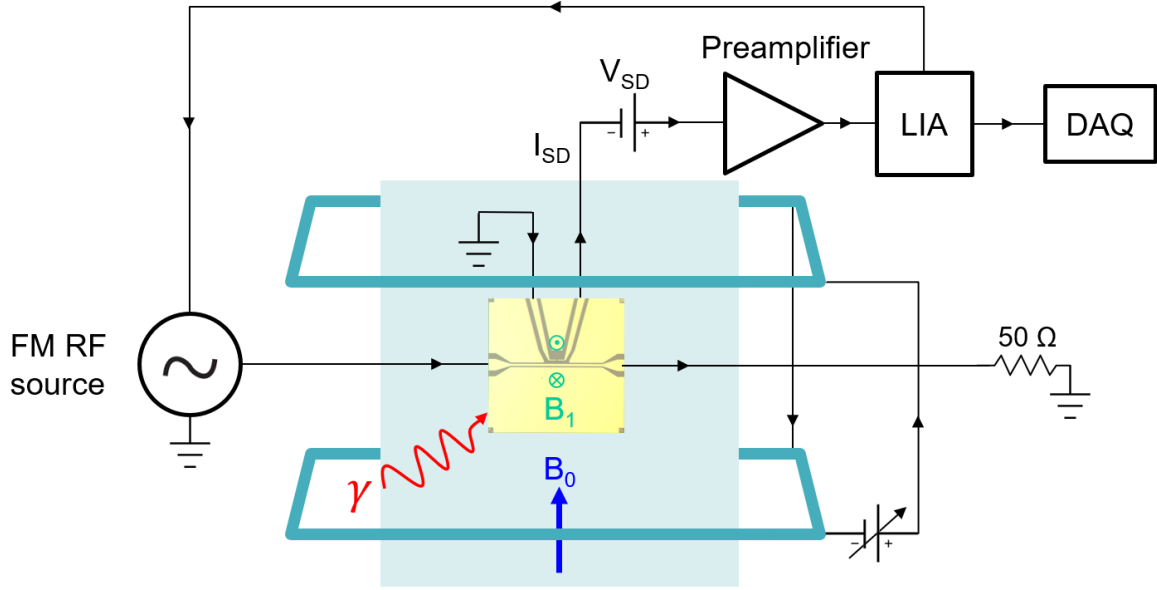


Figure 6.9: Block diagram showing the EDMR setup. See text for details.

A simplified view of the EDMR setup is shown in the block diagram in Fig. 6.9. The EDMR device is placed in the JANIS cryostat which maintains the sample at temperatures down to 5 K. A 633 nm red laser is shone through an optical window onto the active region of the device to generate electrons and holes in the Si substrate. The source electrode is grounded on the EDMR chip carrier and the drain electrode is connected to a preamplifier (FEMTO, DLPCA-200) which applies a source-drain voltage, V_{SD} . This causes carriers to flow through the active region of the EDMR device. This source-drain photocurrent, I_{SD} , is amplified and converted into a voltage with the low-noise preamplifier. Lock-in amplification is used to increase the signal to noise ratio by frequency modulating (FM) the microwaves applied and only detecting signals at that modulation frequency. A lock-in amplifier (LIA) (Stanford Research, SR830) is used to supply a reference signal that modulates the frequency of microwaves generated by a signal generator (Rohde & Schwarz, SMC100A). This frequency modulated microwave signal flows along the on-chip radio frequency (RF) stripline, generating an alternating magnetic field, B_1 , that will induce spin flips in the substrate when the microwave frequency is on resonance with the Zeeman-split energy levels of a certain spin species. To prevent the microwave signal from being reflected, one end of the RF stripline is connected to a 50 Ω RF load terminator, external to the fridge. The Zeeman energy splitting is created by external Helmholtz coils that

generate a magnetic field, B_0 . The current flowing through these solenoids is swept to sweep B_0 whilst the lock-in amplified photocurrent is collected with a data acquisition (DAQ) system (National Instruments, USB-6003) to generate an EDMR spectrum.

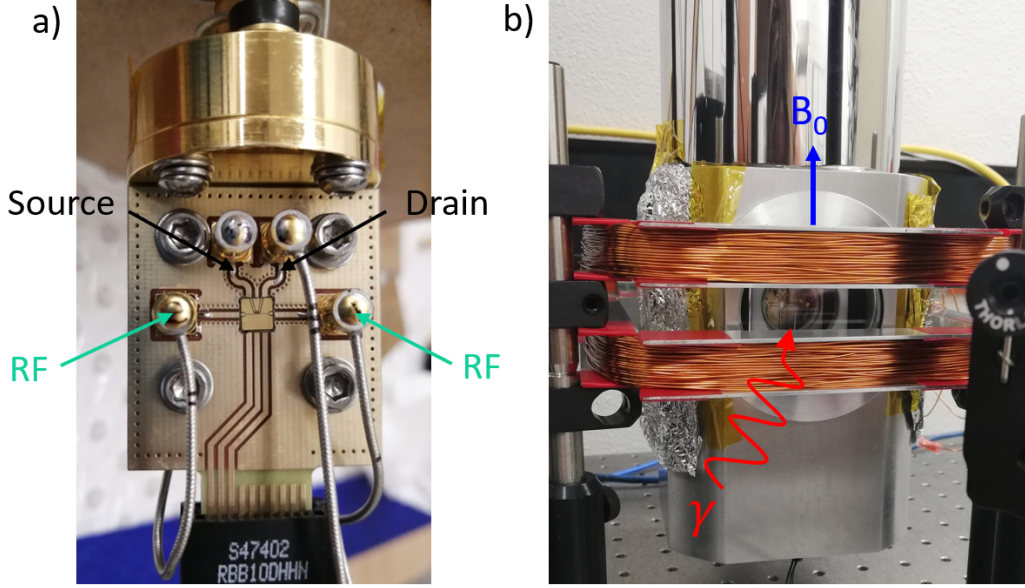


Figure 6.10: EDMR experimental setup. a) The EDMR device is mounted and wire bonded to a chip carrier with a source, drain and RF feedthroughs. The chip carrier is mounted to a probe that is inserted into the cryostat. b) The Janis cryostat with an optical window through which a laser is shone on the EDMR device. Externally mounted Helmholtz coils sweep the magnetic field B_0 during an EDMR measurement.

The EDMR device is shown mounted on a chip carrier and attached to the JANIS cryostat probe in Fig. 6.10a. Double wire bonds connect both sides of the RF stripline to the two RF coaxial cables, all ground plane conductors to the chip carrier ground, the source electrode to a short circuit to the chip carrier ground and the drain electrode to a coaxial cable that carries the source-drain current. The probe is then inserted in the JANIS cryostat, shown in Fig. 6.10b, with an optical window for the illumination of the EDMR device with a red laser and the externally mounted copper wire solenoids for sweeping the magnetic field B_0 .

6.4.4 External Magnetic Field Simulation

In this work, square Helmholtz coils were mounted externally to the cryostat in order to sweep the applied magnetic field B_0 during the EDMR measurement. A COMSOL simulation showing the magnetic field density produced by square Helmholtz coils is shown in Fig. 6.11. The

dimensions of the coils were the same as used in the experiment: an inner square edge length of 13 cm, a coil cross-sectional width of 1.5 cm, a coil separation of 5 cm from the centres and 200 turns of wire per coil. This simulation shows that a current sweep of ± 3 A achieves a magnetic field sweep of $\pm \sim 80$ G. Square Helmholtz coils produce magnetic fields with a greater homogeneity than circular Helmholtz coils and allow for a better use of volume [243].

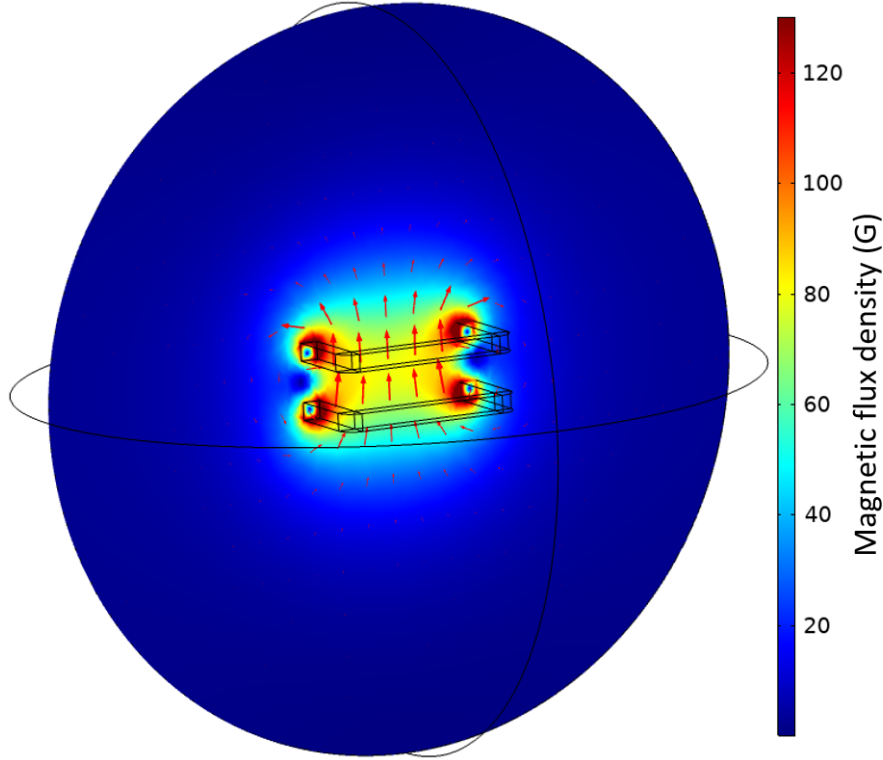


Figure 6.11: COMSOL simulation showing the magnetic flux density produced by square Helmholtz coils used to apply an external magnetic field B_0 during the EDMR measurement. Each coil has 200 turns and carries a current of 3 A.

6.4.5 EDMR Measurement

EDMR measurements were performed on the n-type P-doped substrate ($0.1\text{--}0.5\ \Omega\cdot\text{cm}$) with a 20 nm thermal oxide, drive-in diffused heavily doped As ohmic contacts and 10 nm Pt / 50 nm Au metallisation with a device geometry as shown in Fig. 6.6c. This EDMR device design was selected as the source and drain electrodes are the furthest away from the RF stripline, minimising the B_1 gradient and thus reducing the EDMR signal linewidth broadening effect. However, a larger signal to noise ratio would probably have been achieved with the device design showed in Fig. 6.6a.

The lock-in amplified photocurrent was detected in quadrature with both of the X and Y components collected during the magnetic field B_0 sweep. Multiple magnetic field sweeps were performed and both the X and Y components were averaged to obtain EDMR spectra with suitable signal to noise ratios. For all of the EDMR measurements, the following experimental parameters were used: The red laser was shone through the optical window by reflecting off multiple mirrors. The laser spot position was adjusted to the active region of the EDMR device by maximising the source-drain photocurrent whilst adjusting a movable mirror. The laser current was set to 40 mA, corresponding to a laser power of $340 \mu\text{W}$ just before the optical window of the cryostat. The source-drain voltage supplied by the preamplifier was adjusted to maximise the source-drain photocurrent. $V_{SD} = 7.15 \text{ V}$ was used to give $I_{SD} \sim 100 \text{ nA}$ measured with a DC coupled preamplifier and with the microwave power set to 20 dBm. The offset of the preamplifier was then adjusted to set the DC output voltage to zero. The EDMR signal was collected with an AC coupled preamplifier with a gain of $1 \times 10^7 \text{ V/A}$ and a low pass bandwidth of 50 kHz.

Lock-in amplification was used that measured an AC coupled voltage referenced to ground with 2 notch filters (at frequencies of 50 Hz and 100 Hz to attenuate noise from the power lines), a time constant of 100 ms, a 12 dB/oct filter, a sensitivity of 1V and a normal reserve. The lock-in amplifier output a reference signal with a modulation frequency of $f_{mod} = 1.93 \text{ kHz}$ and a sine amplitude of $0.706 \text{ V}_{\text{rms}}$. The 2nd harmonic of the signal was detected with auto phase on to maximise the signal in the X quadrant and minimise the signal in the Y quadrant. The X and Y signals were auto offset to 0 V and were both expanded by a factor of 100 to improve the signal to noise ratio. The reference signal from the lock-in amplifier was used to modulate the frequency of the microwave source.

An RF amplifier with +50 dBm was used to increase the power of the microwave signal. The magnetic field was swept with a time period of 25.25 s using a 100% symmetrical ramp signal to sweep the current in the solenoids between -0.2 V and 2.8 V. For each magnetic field sweep, 830k samples of both X and Y data were acquired at a rate of 33k samples/s with a trigger set to the solenoid current ramp signal. The X and Y components of the EDMR signal were averaged over 100 sweeps of the magnetic field to provide a suitable EDMR signal to noise

ratio for the given substrate doping and device geometry. Each EDMR spectrum therefore took around 42 minutes to collect.

EDMR measurements were performed at various microwave frequencies to determine how the transition frequency of a given spin species depends on magnetic field in order to aid the classification of the spin species. EDMR spectra were collected whilst the substrate was irradiated with microwaves of various frequencies between 10-160 MHz with 10 MHz intervals. For this experiment, the temperature of the cryostat was set to 10 K, the microwave power was set to 19 dBm and the modulation amplitude of the microwave frequency was set to 4 MHz.

In order to observe the effect of EDMR signal linewidth power broadening and signal amplitude enhancement, EDMR measurements were performed at various microwave powers between 1-22 dBm with 1 dBm intervals. For this experiment, the temperature of the cryostat was set to 10 K, the microwave frequency was set to 100 MHz with a modulation amplitude of 2.5 MHz.

The effect of the modulation amplitude of the microwave frequency on the EDMR signal amplitude and linewidth was also investigated by collecting EDMR spectra with various modulation amplitudes between 0.5-4 MHz with 0.5 MHz intervals. For this experiment, the temperature of the cryostat was set to 10 K, the microwave frequency was set to 100 MHz and the microwave power was set to 19 dBm.

Finally, the effect of temperature on the strength of EDMR signals produced by the P donor and P_{b0} centre electrons was investigated by collecting EDMR spectra at various cryostat temperatures between 5-30 K with 1 K intervals. For this experiment, the microwave frequency was set to 150 MHz with a modulation amplitude of 4 MHz and a microwave power of 19 dBm.

6.5 Results and Discussion

6.5.1 Si:P EDMR Frequency Dependence

To confirm the presence of P donors in the active region of the device, the EDMR signal was measured as a change in photocurrent as a function of externally applied magnetic field under the irradiation of different microwave frequencies. The microwave power was set to 19 dBm, the microwave frequency was modulated with an amplitude of 4 MHz and the measurements were performed at 10 K. The X and Y components of the lock-in amplified signal measured in quadrature are shown in Fig. 6.12 and Fig. 6.13, respectively.

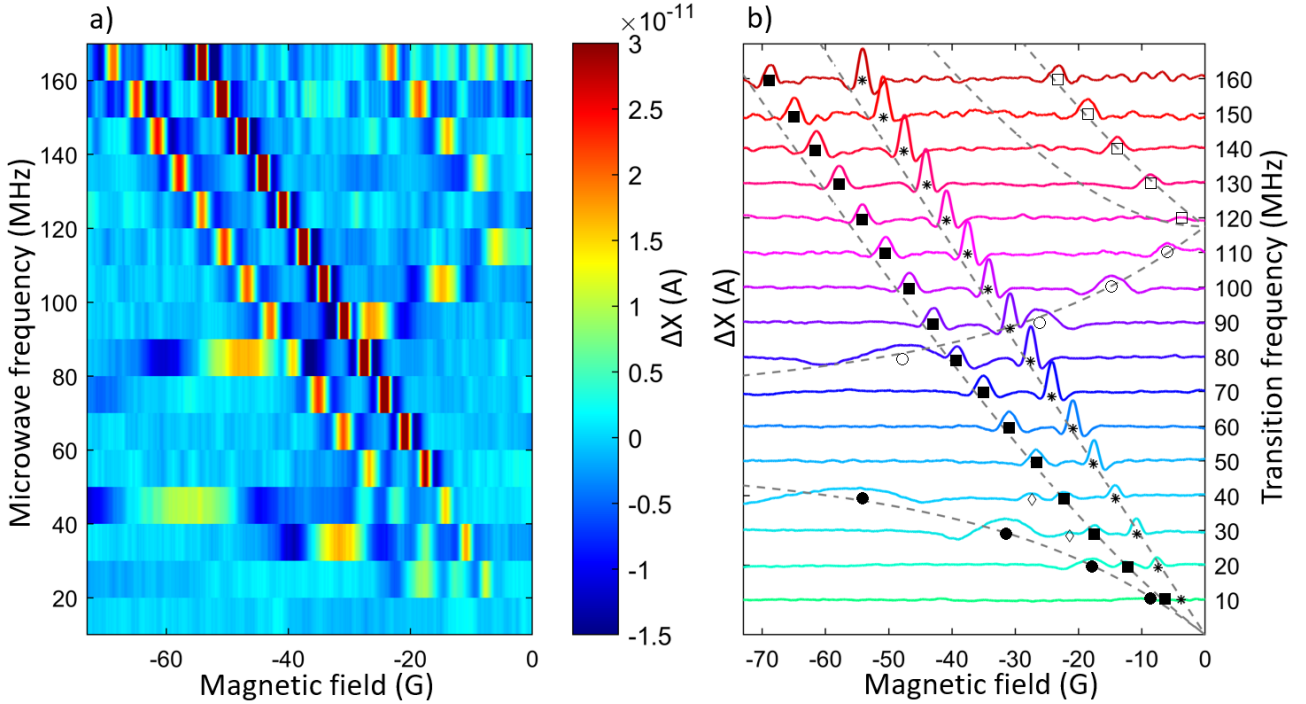


Figure 6.12: EDMR spectra from P in $^{\text{nat}}\text{Si}$ showing the change in photocurrent as a function of magnetic field for various microwave frequencies between 10-160 MHz. The X component of the lock-in amplified signal is shown. The sample was measured at 10 K while irradiated with microwaves at a power of 19 dBm, frequency modulated with an amplitude of 4 MHz. a) The change in photocurrent is represented with colour. b) The EDMR peaks are marked with symbols corresponding to transitions, including those from the P donor system as shown in Fig. 6.4. The dashed lines give the simulated transition frequencies as a function of magnetic field.

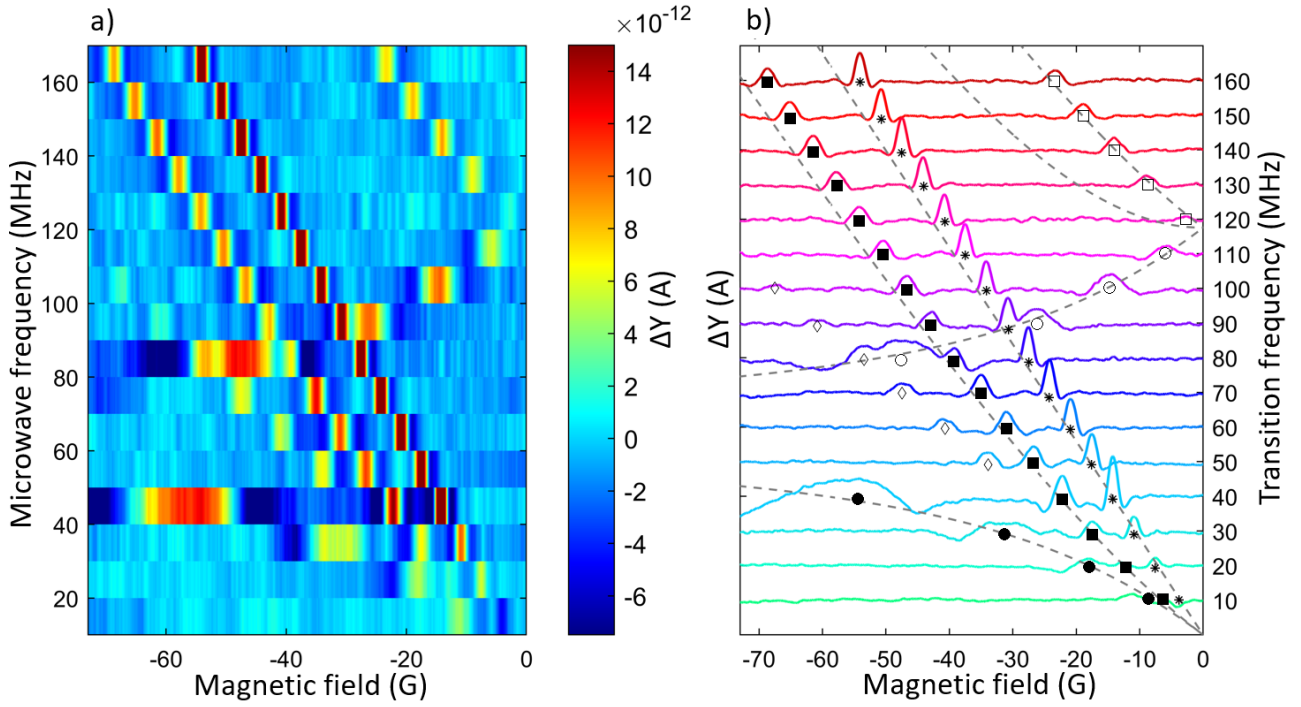


Figure 6.13: The same as for Fig. 6.12 but with the Y component of the lock-in amplified signal shown.

The position of the EDMR peaks move with microwave frequency, as can be seen in the colour plots shown in Fig. 6.12a and Fig. 6.13a where the colour represents the change in photocurrent. We can compare the positions of these EDMR peaks to the predicted transition frequency of the various spin transitions for P donors as a function of magnetic field, seen before in Fig. 6.4. The predicted transition frequencies as a function of magnetic field are overlaid with grey dashed lines on the right axes of Fig. 6.12b and Fig. 6.13b. From this, we can see that the collected EDMR spectra contain two ESR transitions of the P donor system (marked with squares) and two transitions of the P donor system that are forbidden in the high field regime (marked with circles). The width of the EDMR peaks can be seen to be inversely related to the gradient of the transition frequency as a function of magnetic field at the position of the peak, particularly visible with the broad peaks observed for the forbidden transitions (marked with circles) at higher magnetic fields. This makes sense due to the resonance condition scanning a larger magnetic field range for a given microwave frequency modulation, in this case ± 4 MHz, when the gradient of the transition frequency with magnetic field is shallower.

The position of the peak with the largest height closely matches that predicted for another forbidden transition of the P donor system (marked with a black triangle in Fig. 6.4), however,

this transition is expected to be weaker than the P donor ESR transitions (marked with squares) and the P donor first order-forbidden transitions (marked with circles) as it is only allowed in the second order. Therefore, this strong signal can be concluded to be caused by ESR of the P_{b0} centres at the Si/SiO₂ interface, which are likely to be present as they are a key part of the dominant spin dependent recombination pathway. Further evidence for this peak being caused by P_{b0} centres is given later in section 6.5.2 where this transition remains at higher temperatures than the P donor transitions. This P_{b0} ESR transition is therefore marked with an asterisk instead of the black triangle.

An additional peak (highlighted with a diamond symbol) which does not follow the position of any predicted P donor transition can be observed in some of the EDMR spectra. The position of this peak corresponds to that predicted for an As donor transition ($m_I = -3/2, m_S = \pm 1/2$). It is possible that some As donors exist in the active region of the EDMR device due to lateral diffusion during the formation of the ohmic contact regions by drive-in diffusion from a spin on dopant. Judging from the EDMR signal amplitude of this As peak, it is likely that the concentration of As donors in the sensitive region near the source and drain electrodes is substantial (on the order of the P concentration of around $1 \times 10^{17} \text{ cm}^{-3}$) as a result of lateral diffusion during the drive-in doping anneal. The presence of this As peak highlights the importance of using an alternative donor species to create the ohmic contacts so as not to interfere with the donor species intentionally present in the active region of the EDMR device. It also opens up the possibility of measuring EDMR signals from donors other than P with this EDMR system and for introducing donors to the active region by diffusion instead of substrate background doping or ion implantation.

The EDMR peak positions marked with symbols are not always perfectly aligned with the predicted values (traced by the grey dashed lines), particularly for increased magnetic fields. This is likely due to the imperfect calibration of the current flowing around the Helmholtz coils with the magnetic field strength at the active region of the EDMR device. The calibration was performed by first measuring the magnetic field strength as a function of solenoid current with a Hall probe mounted to the JANIS probe and inserted in the cryostat. The position of the Hall probe may not have been exactly at the location of the active region of the EDMR device

and the Hall probe voltage response to the magnetic field strength may also have a slightly miscalibrated proportionality factor.

The strength of the EDMR signals are larger in the X component than the Y component as can be seen by comparing the scale bars for the change in photocurrent in Fig. 6.12a and Fig. 6.13a. The absolute value of the photocurrent is larger in the X component than the Y component due to the auto phasing of the lock-in amplified signal before each measurement. It is interesting to note that the EDMR peak from the As donor transition (marked with a diamond) appears mostly in just the Y component of signal. This could be due to a phase shift of the EDMR signal at the transition.

The signs of the X and Y components of the EDMR peaks (i.e. whether they appear as peaks or troughs) appeared to change arbitrarily for different microwave frequencies. This could be due to the change in phase of the measured quadrature signal with respect to the reference signal at different microwave frequencies. The phase of continuous-wave EDMR spectra has been shown to have a complex dependence on experimental parameters such as temperature, microwave power and modulation frequency [244]. In the plots shown in Fig. 6.12 and Fig. 6.13, the sign of the change in photocurrent was chosen such that the EDMR signals appear as peaks for both the X and Y components of the signal.

6.5.2 Si:P EDMR Temperature Dependence

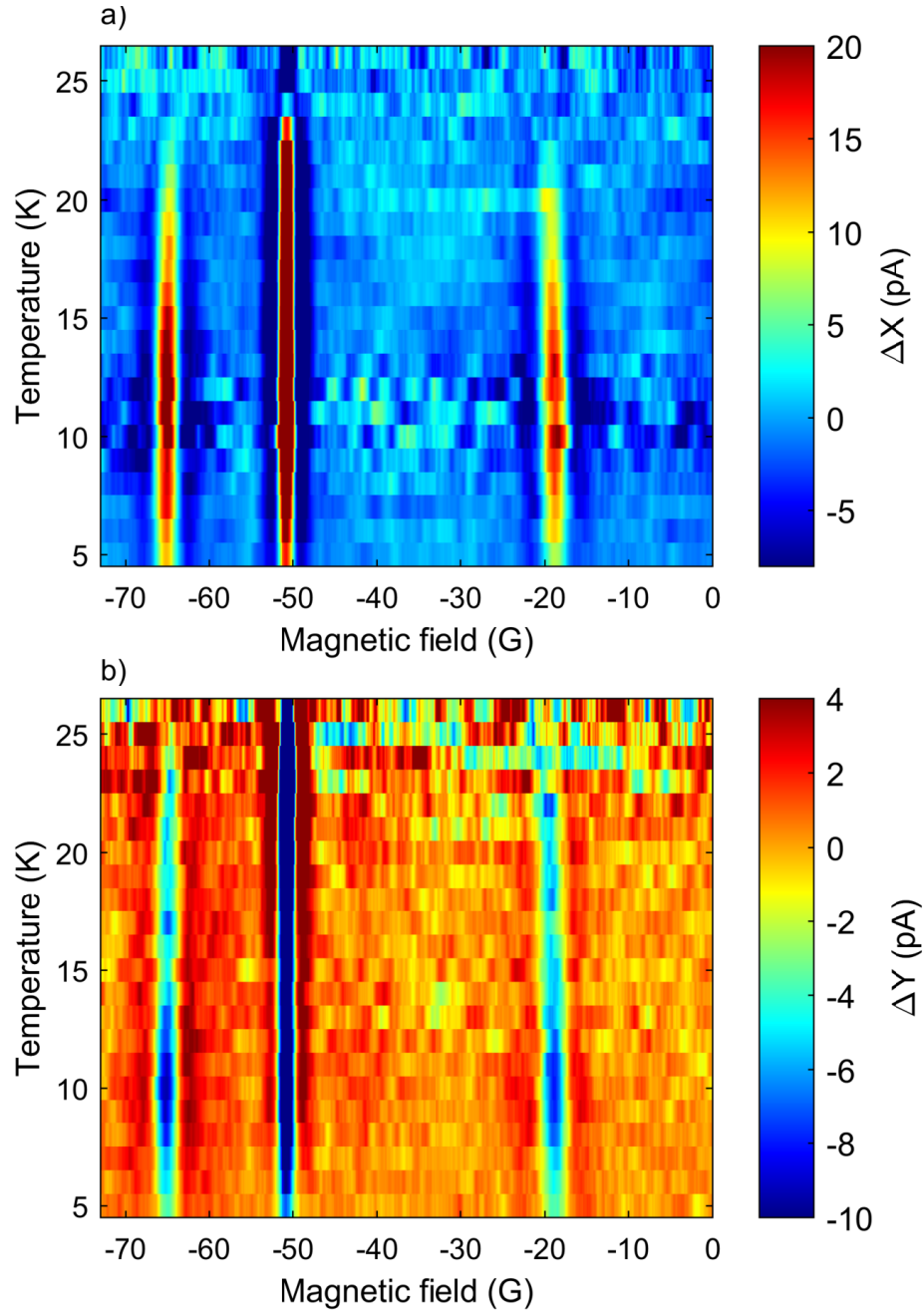


Figure 6.14: EDMR spectra from P in $^{\text{nat}}\text{Si}$ showing the change in photocurrent as a function of magnetic field under the irradiation of 19 dBm 150 MHz microwaves, frequency modulated with an amplitude of 4 MHz, at various temperatures from 5-26 K. The X and Y components of the lock-in amplified signal are shown in a) and b), respectively.

The EDMR signal was measured as a change in photocurrent as a function of externally applied magnetic field at various temperatures controlled by the cryostat. The microwave power was set to 19 dBm and the microwave frequency was modulated about 150 MHz with an amplitude of 4 MHz. The X and Y components of the lock-in amplified signal measured in quadrature

are shown in Fig. 6.14a and Fig. 6.14b, respectively.

Fig. 6.14 shows the 2 P donor ESR transitions with a central stronger signal from the P_{b0} centres. The P ESR signals get weaker with increasing temperature above 10 K and diminish into the noise at temperatures around 22 K. We have therefore observed the effect of carrier freeze-out [245] of P donor electrons, where the donor electrons are confined to orbit the P nuclei at temperatures below ~ 22 K. The freeze-out temperature is lower for heavily doped semiconductors than lightly doped ones. If the doping concentration is above the metal insulator transition level, the semiconductor will not contain single donor energy levels, but rather an impurity band which overlaps with the conduction band and so freeze-out effects are eliminated as free carriers exist even at 0 K. The dopant concentration studied here ($3.19 \times 10^{16} - 2.4 \times 10^{17} \text{ cm}^{-3}$) is well below the metal insulator transition for Si:P with a critical density of $3.74 \times 10^{18} \text{ cm}^{-3}$. The freeze-out temperature found here is in agreement with previous ESR measurements of $1.3 \times 10^{17} \text{ cm}^{-3}$ doped Si:P, which saw a vanishing of the P hyperfine ESR lines at temperatures above 20 K [246].

The central signal from the P_{b0} centres appears to remain at temperatures above 25 K in the Y component of the EDMR signal. The sign of the P_{b0} centre ESR signal appears to change at temperatures above 25 K, which may be due to the phase shifting of the measured signal with respect to the reference signal for different temperatures [244]. The P_{b0} centre occurs at a deeper energy level below the conduction band of Si and so has a higher ionisation energy than the shallow level P donors. A higher thermal energy is therefore required to ionise the P_{b0} centres, resulting in a higher freeze-out temperature. P_{b0} centres are known to be electronically stable over a wide temperature range, with ESR of P_{b0} centres being observed at room temperature [247]. The dependence of signal intensity I on temperature T was found to follow the paramagnetic law ($I \propto T^{-1}$) down to 4.2 K.

It is interesting to note that the P_{b0} centre transition is still present at temperatures above the P donor freeze-out temperature. The P donors are ionised in this regime and so cannot contribute to the spin-dependent recombination mechanism that produces the EDMR signal. However, P_{b0} centres are amphoteric [248], meaning they can behave as both a donor and an acceptor. Therefore, they can produce an EDMR signal even when there are no P donors present

since they introduce two energy levels into the Si bandgap and so create a spin-dependent recombination pathway by themselves.

The magnitude of the EDMR signals from both the P donors and the P_{b0} centre decrease at temperatures below 10 K. This could be due to the condensation of the free electron gas into electron-hole droplets [249] upon a decrease in temperature when the laser power is sufficient to produce a large density of electron-hole pairs. The exciton (a bound state of an electron and hole) lifetime in Si was found to decrease at temperatures below ~ 10 K [250], leading to an increased carrier recombination rate. This would decrease the change in substrate conductivity due to carrier recombination via the spin-dependent pathways of interest, resulting in smaller EDMR signals.

This experiment suggests that the optimal P donor EDMR signal to noise is found at temperatures around 10 K, above the temperature of electron-hole droplet condensation and below the temperature of donor electron freeze out.

6.5.3 Si:P EDMR Microwave Power Dependence

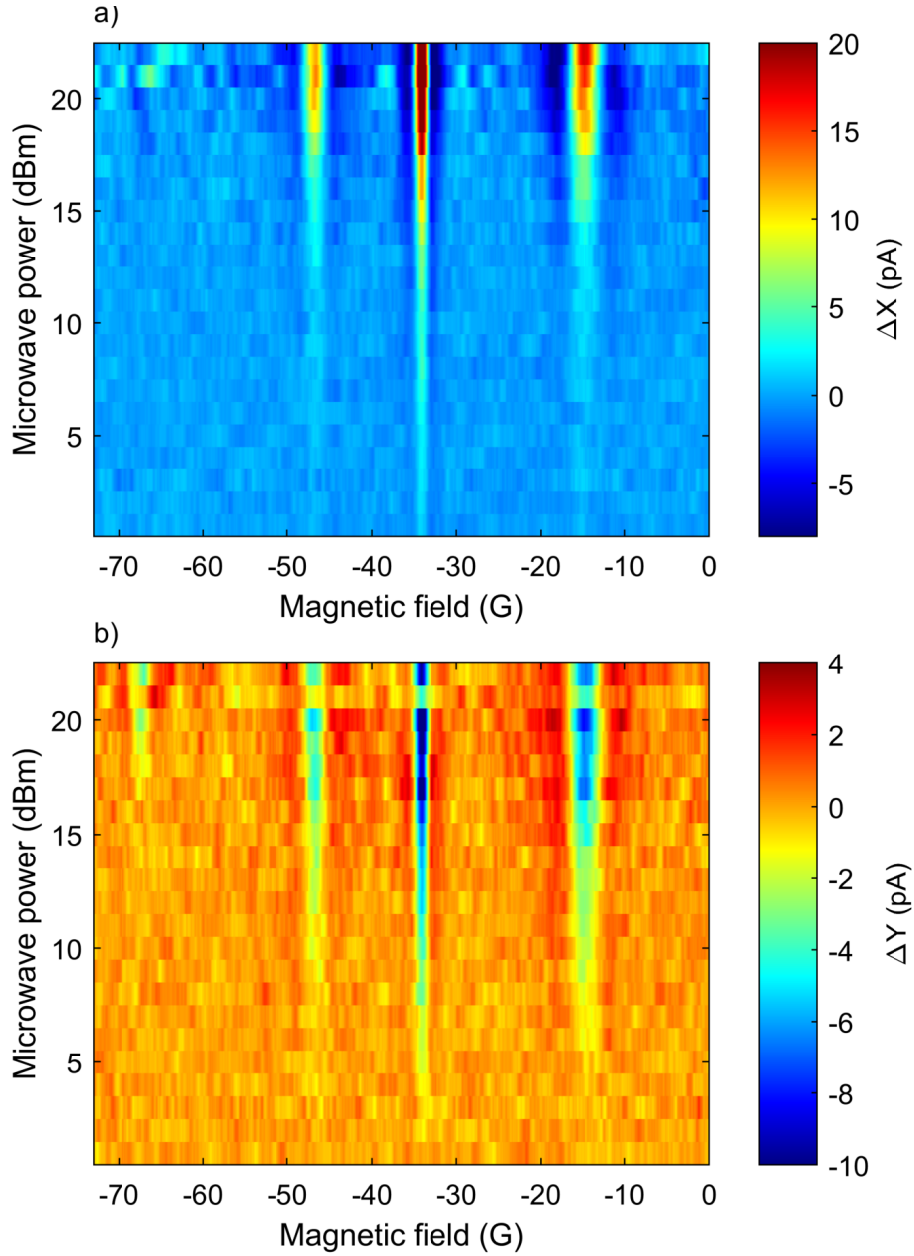


Figure 6.15: EDMR spectra from P in $^{\text{nat}}\text{Si}$ as a function of magnetic field at various microwave powers between 1 dBm and 22 dBm. The sample was measured at 10 K while irradiated with 100 MHz microwaves, frequency modulated with an amplitude of 2.5 MHz. The X and Y components of the lock-in amplified signal are shown in a) and b), respectively.

Studies to enhance the EDMR signal to noise ratio and increase the sensitivity of this EDMR setup for future measurements with smaller numbers of donors in the active region of the device were carried out. First, the EDMR signal was measured as a change in photocurrent as a function of externally applied magnetic field at various microwave powers. The microwave frequency was modulated about 100 MHz with an amplitude of 2.5 MHz and the EDMR

measurements were performed at 10 K. The smaller value of the modulation amplitude (2.5 MHz instead of the 4 MHz used previously) was chosen to see the effects of microwave power broadening more clearly, at the expense of a smaller signal to noise ratio. The X and Y components of the lock-in amplified signal measured in quadrature are shown in Fig. 6.15a and Fig. 6.15b, respectively.

EDMR signal strength can be increased up to a saturation point by increasing the microwave power. This is demonstrated in Fig. 6.16a in which the amplitude ΔI of the X component of the EDMR signal produced by the P_{b0} centre, measured as the height of the peak above zero, is plotted as a function of microwave power P . Increasing the microwave power increases the transition probability and so increases the number of donor transitions that are excited, resulting in a larger change in photocurrent. In the low microwave power regime, it was found that $\Delta I \propto P$ and above 100 mW, the signal amplitude saturated at $\Delta I \approx 30.1$ pA. This result agrees with previous studies on Si:P EDMR, where the signal intensity was found to be proportional to the microwave power in mW (which is proportional to the square of the microwave magnetic field, B_1) around the origin and saturates at microwave powers around 100 mW and above [239].

Although the signal to noise ratio is not high enough to get an accurate measure of the full width at half maximum for the EDMR signals from the P donors, particularly at low microwave powers, a measure of the linewidth ΔB of the stronger P_{b0} EDMR signal was extracted as the distance between the two minima of the signal for various microwave powers to see if a relationship can be determined. Fig. 6.16b shows that for higher microwave powers P , the linewidth ΔB appears to follow the square root law, $\Delta B \propto P^{1/2}$. Measuring this effect up to higher microwave powers would have produced a stronger correlation, however 22 dBm (~ 158.5 mW) was the maximum possible microwave irradiation power without causing the cryostat to heat above 10 K and the wirebonds to blow up. At low microwave powers, the linewidth is expected to reach a minimum limit due to the intrinsic linewidth of the spin species caused by the surrounding magnetic environment, the gradient of the applied magnetic fields, B_0 and B_1 , across the active region of the device and the modulation amplitude. At a modulation amplitude of 2.5 MHz, the intrinsic linewidth appears to be $\Delta B \approx 2.71$ G, however, the linewidth was

increasingly difficult to measure accurately at low microwave powers due to the decrease in signal to noise ratio. As we shall see in the next section, a lower modulation amplitude of 2 MHz or less may be required to obtain the intrinsic linewidth, free from modulation amplitude broadening effects. The dependence of the observed linewidth ΔB_{obs} on the microwave power P found here is in agreement with that predicted for a field swept continuous wave ESR signal [251]:

$$\Delta B_{\text{obs}} = \Delta B_{\text{int}} \sqrt{1 + \alpha P} \quad (6.14)$$

where ΔB_{obs} tends to the intrinsic linewidth ΔB_{int} in the limit of low microwave power and increases proportional to $\sqrt{P}$ in the limit of high microwave power, with α being a constant of proportionality.

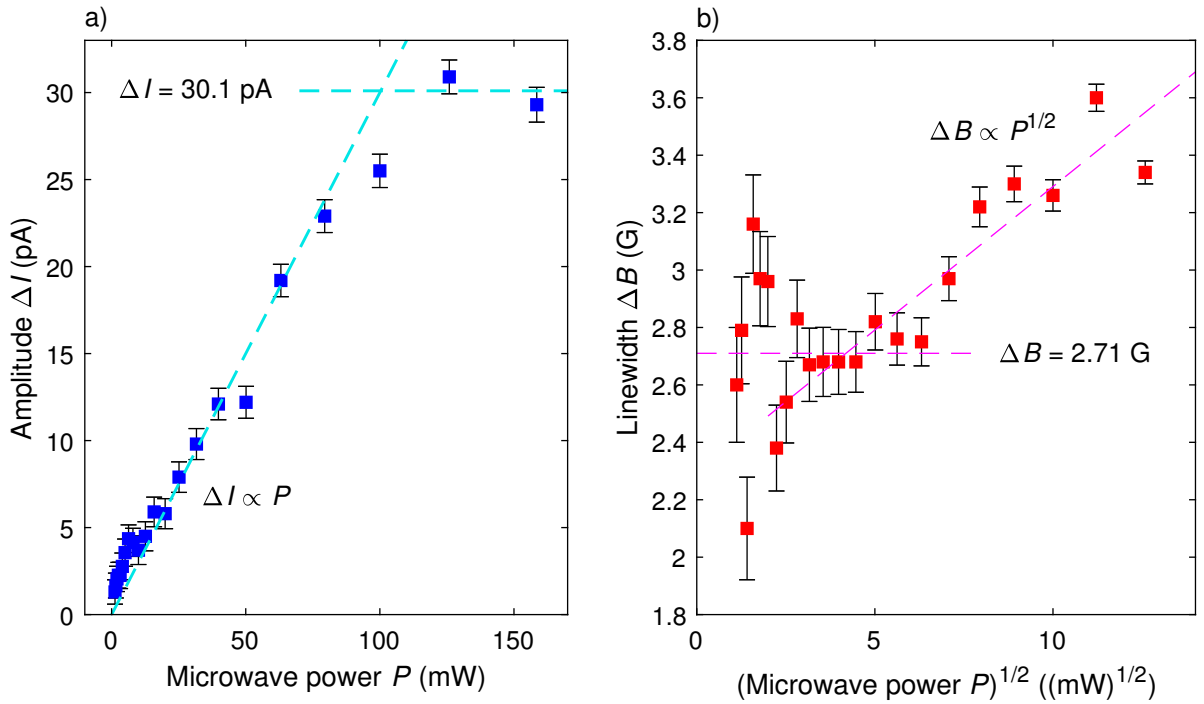


Figure 6.16: Measurements taken of a) the amplitude and b) the linewidth of the X component of the EDMR signal from P_{b0} centres as a function of microwave power. The $^{\text{nat}}\text{Si:P}$ sample was measured at 10 K while irradiated with 100 MHz microwaves, frequency modulated with an amplitude of 2.5 MHz.

6.5.4 Si:P EDMR Modulation Amplitude Dependence

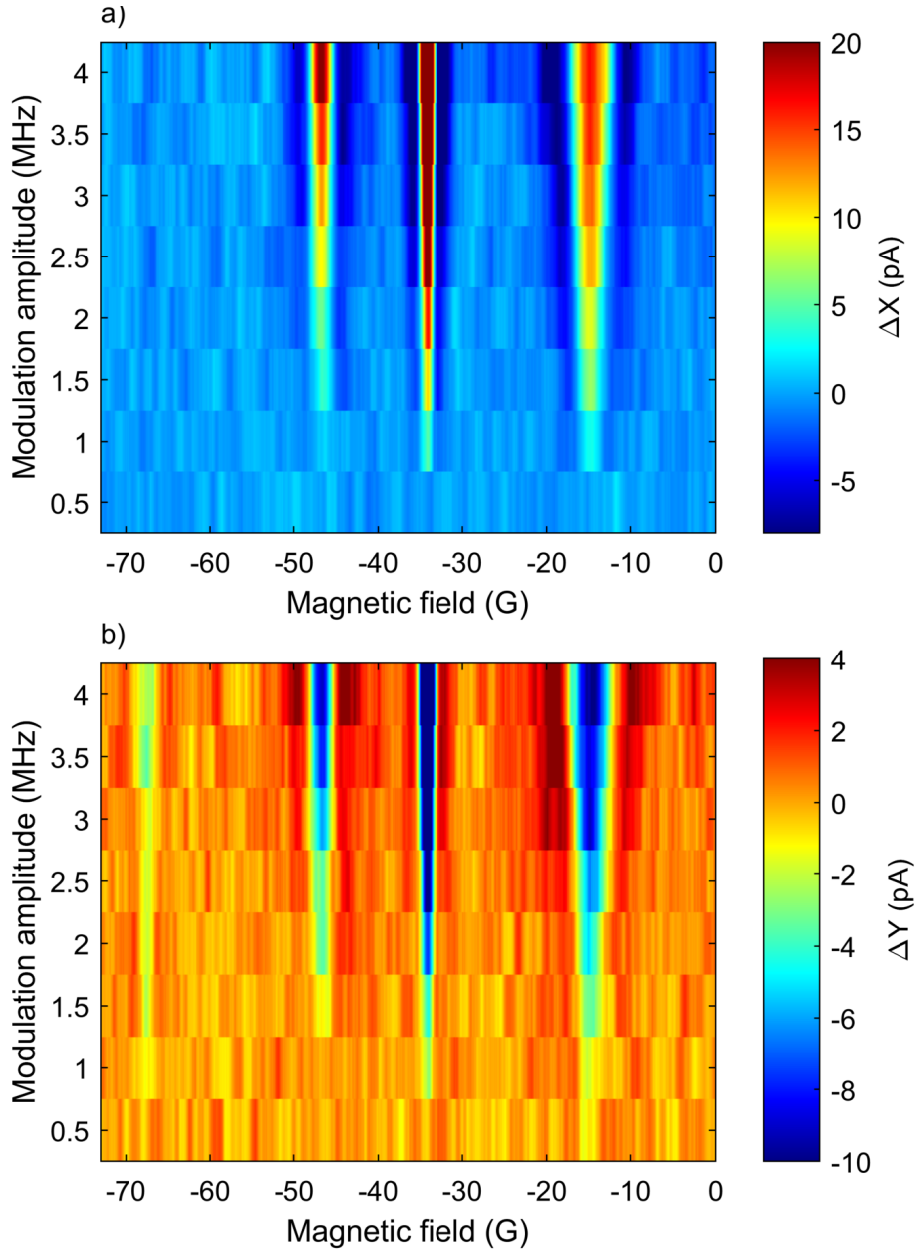


Figure 6.17: EDMR spectra from P in $^{\text{nat}}\text{Si}$ showing the change in photocurrent as a function of magnetic field under the irradiation of 19 dBm 100 MHz microwaves, frequency modulated with various modulation amplitudes from 0.5 MHz to 4 MHz, measured at 10 K. The X and Y components of the lock-in amplified signal are shown in a) and b), respectively.

As a second study on EDMR signal enhancement, the EDMR signal was measured as a change in photocurrent as a function of externally applied magnetic field at various microwave frequency modulation amplitudes. The microwave power was set to 19 dBm and the microwave frequency was modulated about 100 MHz. The EDMR spectra were collected at 10 K. The X and Y components of the lock-in amplified signal measured in quadrature are shown in Fig. 6.17a and

Fig. 6.17b, respectively.

The EDMR signal strength is increased by increasing the modulation amplitude. This is demonstrated in Fig. 6.18a and Fig. 6.18c in which the amplitude ΔI of the X component of the EDMR signal produced by ESR of P_{b0} centres and the P donor forbidden transition (marked with a white circle in Fig. 6.12b), respectively, measured as the height of the peak above zero, is plotted as a function of modulation amplitude A_{mod} . Increasing the modulation amplitude increases the strength of the lock-in detected photocurrent signal. For the P_{b0} centre, it was found that $\Delta I \propto A_{\text{mod}}$ over the full range of $0.5 \leq A_{\text{mod}} \leq 4$ MHz. However, for the P donor forbidden transition, ΔI dropped below the linear relationship with A_{mod} at modulation amplitudes higher than 2.5 MHz. This could be due to the significant increase in signal linewidth at higher modulation amplitudes resulting in a decrease in signal amplitude to conserve the signal area. These results are in agreement with previous EDMR measurements of dangling bonds in micro-crystalline Si:H which found that above a certain modulation amplitude, the EDMR signal amplitude became sub-linear, corresponding with a simultaneous broadening of the linewidth [252].

The linewidth ΔB of the X component of the EDMR signals from P_{b0} ESR and P donor forbidden transitions were extracted by measuring the distance between the two minima of the signals for various modulation amplitudes, as shown in Fig. 6.18b and Fig. 6.18d, respectively. The linewidth ΔB was found to vary much more with modulation amplitude for the P donor forbidden transition than the P_{b0} ESR transition due to the significantly shallower gradient of the transition frequency as a function of magnetic field, as shown in fig. 6.12b, resulting in a larger range of magnetic fields that will meet the resonance condition over the range of microwave frequencies. For the P_{b0} transition, 6.18b shows that for higher modulation amplitudes A_{mod} , $\Delta B \propto A_{\text{mod}}$ and that for low modulation amplitudes, the linewidth reaches a minimum of $\Delta B \approx 3.16$ G for a microwave power of 19 dBm. Whereas for the P donor forbidden transition, the linewidth did not reach a minimum limit and $\Delta B \propto A_{\text{mod}}$ down to a modulation amplitude of 0.5 MHz. Lower modulation amplitudes around a microwave frequency of 100 MHz would therefore be required to determine the intrinsic linewidth of this forbidden transition. The same trend exists with magnetic field modulation instead of frequency

modulation, where the observed linewidth ΔB_{obs} follows Poole's equation [253]:

$$\Delta B_{\text{obs}} = \sqrt{4\Delta B_{\text{int}}^2 + B_{\text{mod}}^2} - \Delta B_{\text{int}} \quad (6.15)$$

where ΔB_{obs} tends to the minimum intrinsic value ΔB_{int} for low modulation amplitudes B_{mod} and increases linearly for high modulation amplitudes [251, 252].

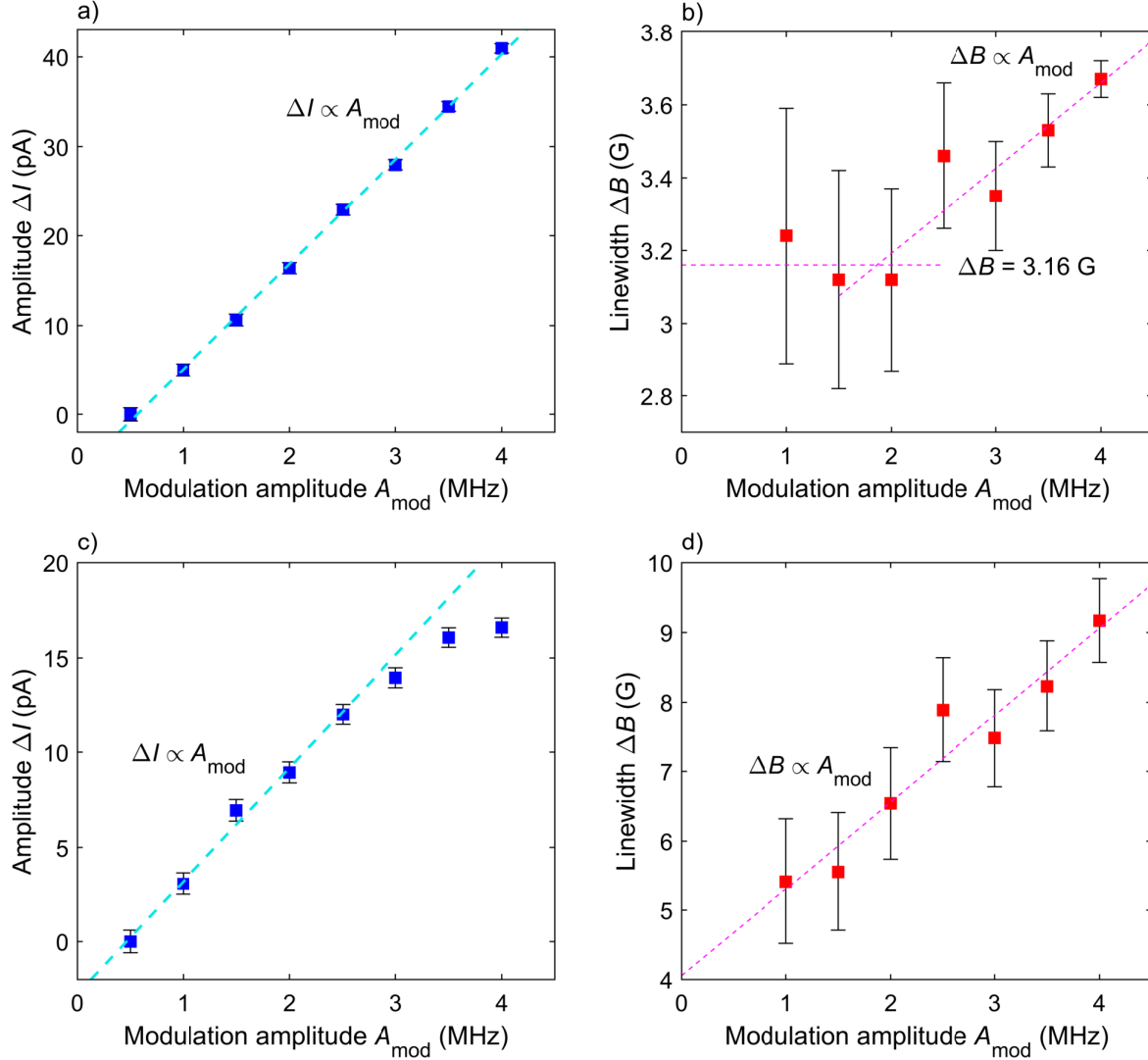


Figure 6.18: Measurements taken of a) the amplitude and b) the linewidth of the X component of the EDMR signal from P_{b0} centres as a function of modulation amplitude. c) The amplitude and d) the linewidth of the X component of the EDMR signal from the P donor forbidden transition were also measured as a function of modulation amplitude. The $^{\text{nat}}\text{Si:P}$ sample was measured at 10 K while irradiated with 100 MHz microwaves at a power of 19 dBm.

In future, a large modulation amplitude will be useful to produce a large signal to noise to first locate the EDMR signal but small modulation amplitudes will be required to determine

the intrinsic linewidth of a P donor transition, particularly in isotopically enriched ^{28}Si where the broadening effect from nearby ^{29}Si nuclear spins is drastically reduced.

6.6 Summary

In conclusion, an in-house custom EDMR setup was designed and implemented for the measurement of quantum spin transitions of donors in Si. The ultimate aim of this system is to be able to measure spin transitions from a low concentration of implanted donors in our isotopically enriched ^{28}Si material to probe their quantum environment. This work tests the suitability of the EDMR setup by measuring EDMR devices (designed with an on-chip microwave stripline and source and drain electrodes) fabricated on background-doped $^{\text{nat}}\text{Si}:\text{P}$ substrates with a P concentration of $\sim 3 \times 10^{16} - 2 \times 10^{17} \text{ cm}^{-3}$; high enough to produce a large signal to noise allowing for experimental parameters to be adjusted to optimise the signal. EDMR spectra were collected at various microwave frequencies to confirm the detection of the two hyperfine split P donor allowed ESR transitions along with two P donor forbidden transitions that are allowed in the low-field regime ($< 200 \text{ G}$) probed with this EDMR setup. Additionally, a strong signal was observed from the ESR transition of P_{b0} dangling bonds found at the Si/SiO₂ interface. An As donor transition was also observed, with its presence due to the formation of ohmic contacts via the in-diffusion of As. The effect of P donor carrier freeze out was observed at temperatures below $\sim 22 \text{ K}$. In order to maximise the signal to noise without unwanted linewidth broadening, the effect of microwave power and modulation amplitude was investigated on the EDMR signal amplitude and linewidth. The area between the source and drain electrodes of $40 \mu\text{m} \times 40 \mu\text{m}$ and the estimated sensitive depth of between 14-20 nm below the Si/SiO₂ interface [229], corresponds to around 10^5 P donors in the active region of the device which produce strong EDMR signals. This EDMR system is therefore already around 5 orders of magnitude more sensitive than a conventional ESR system. In order to accurately determine the EDMR signal linewidth from a low concentration of donors implanted in ^{28}Si , low microwave powers and modulation amplitudes will be necessary. The implementation of modifications to the EDMR system (suggested in Chapter 7) should further increase the sensitivity that is required to achieve a suitable signal to noise for this future investigation.

6.7 Acknowledgements

I would like to acknowledge the following people for work performed in this chapter: Dr Brett Johnson for his assistance with setting up the EDMR system at the University of Melbourne, Dr Daniel Creedon for his help with the COMSOL simulation of the microwave power dissipation and help setting up lock-in amplification on the EDMR system at the University of Melbourne, Stephen Gregory for the wirebonding of EDMR devices and Chris Lew for useful discussions on the EDMR setup.

Chapter 7

Conclusions

Two main fabrication techniques for donor in Si qubit devices were investigated in this thesis, namely, the implantation of Bi donors and the isotopic enrichment of ^{28}Si layers. A measurement technique for donors in Si was also explored using electrically detected magnetic resonance. This chapter summarises the key achievements of each of the three experimental projects covered in this thesis; the activation and electron spin resonance of near-surface implanted Bi in Si, the isotopic enrichment of Si by high fluence ion implantation and the development of an electrically detected magnetic resonance system for the measurement of donors in Si. Since a PhD is never truly finished, I will also give suggestions on fruitful avenues of further work for each of these experimental projects. To conclude, the ultimate goal of this work is given, along with how much progress was made towards this in my experimental research.

7.1 Activation and ESR of Near-Surface Implanted Bi in Si

Bi donors offer many possible advantages over conventional P donors as Si spin qubits. However, implanted Bi donors are notoriously difficult to activate due to the large amount of Si lattice damage caused and the large covalent radius mismatch. In order to function as an operational qubit, Bi donors must be substitutional in the Si lattice and electrically activated. It is

therefore important to find the optimum implantation and annealing strategy that maximises the electrical activation yield to give the highest chance of fabricating operational qubits.

7.1.1 Achievements

Chapter 4 presented a thorough annealing study of near-surface bismuth donors implanted at fluences above and below the amorphisation threshold of Si into both crystalline and pre-amorphised Si. This enables the optimum implantation and annealing strategy to be chosen for the activation of Bi donor qubits, within the parameter space investigated.

26 keV Bi was implanted to a mean depth of ~ 20 nm at fluences of 1×10^{14} and 6×10^{12} cm $^{-2}$ into *c*-Si and *a*-Si. Various thermal anneals were performed for 5 minutes at a range of temperatures and at 1000°C for a range of times. The Hall effect was used to determine the Bi electrical activation yield and RBS was used to determine the substitutional fraction and diffusion of Bi after these anneals. From these experiments, the Bi electrical activation yield was maximised at 64% and 46% for implantation above and below the Si amorphisation threshold by SPE at 600°C for 5 min and a RTA at 1000°C for 60 s, both following pre-amorphisation of the Si substrate, respectively.

The highlight of this work was the measurement of spin transitions of Bi donor electrons. The full hyperfine spectrum of near-surface implanted Bi donors, with all 10 of the ESR transitions appearing at their expected magnetic field for the given microwave frequency, was collected to confirm the success of the anneal to repair the damaged Si lattice and electrically activate a significant fraction of the Bi donors.

7.1.2 Further Work

From previous experiments, it would appear that the ease of activating Bi donors is greater for Bi implanted to a deeper depth [133]. It would be interesting to investigate this further to determine how the Bi electrical activation yield changes with implanted Bi depth in the near-surface region. One could perform a series of Bi implants at different energies to place Bi at a

range of depths below the surface. This will determine if the proximity of the interface limits the electrical activation of Bi, for example by an increased concentration of defects and charge traps, strain and electric fields. Although this would be interesting, the optimal donor depth for the initialisation, control and readout of the donor spin by surface nanocircuitry is around 20 nm below the Si/SiO₂ interface. Therefore, the electrical activation of Bi donors implanted to this depth with an energy of 26 keV, as investigated in this work, is of most relevance to donor qubit fabrication.

In this work, Bi was implanted into ^{nat}Si and so it would be interesting to repeat the annealing study on Bi donors implanted into isotopically enriched layers of ²⁸Si. The electrical activation yield and substitutional fraction could be measured to determine if the high fluence ²⁸Si⁻ implantation enrichment process reduces these, for example by the addition of a higher concentration of impurities. This would determine the suitability of Bi donors implanted in our isotopically enriched Si for the use as operational spin qubits. The ESR measurement could be repeated for Bi donors implanted in ²⁸Si. If the artificial broadening of the linewidth produced by the microwave power and the magnetic field inhomogeneity inside the solenoid is first reduced, this would have the advantage of producing ESR peaks with a greatly reduced linewidth due to the removal of the variation in local magnetic field caused by the presence of ²⁹Si spins. This would result in greater signal amplitudes, by the conservation of signal area, and could allow for much smaller magnetic field ranges to be swept to enclose each of the 10 Bi hyperfine peaks, reducing the ESR measurement time.

A higher sensitivity technique could be used to measure the spin transitions of Bi donors with a greater signal to noise, such as EDMR. The present low-field EDMR system in the School of Physics, University of Melbourne is unsuitable for measuring ESR transitions from Bi donors due to their large zero-field splitting ($\Delta W = A(I + 1/2) \approx 7.4$ GHz), with the exception of the $m_I = -9/2$ transition which has an energy gap that goes to zero as the magnetic field goes to zero. Microwave frequencies higher than the zero-field splitting would be required to probe the ESR transitions corresponding to all 10 of the Bi nuclear magnetic moment projections. However, in future the EDMR system could be upgraded by replacing the microwave source with one capable of irradiating the substrate with microwaves of a much higher frequency. The

present solenoids would also have to be upgraded with a more powerful electromagnet capable of sweeping a much greater magnetic field range (up to around 600 mT) to excite all 10 of the Bi donor ESR transitions.

The next key step in this work would be to use the large zero-field splitting of Bi to its advantage and demonstrate new and interesting physics with a hybrid qubit device. By nature, the energy splitting between the clockwise and anticlockwise current states of superconducting flux qubits closely match the zero-field splitting of Bi donors. This hybrid qubit system could make use of the fast processing times of superconducting qubits and the use of Bi donor qubits as quantum memories due to their long coherence times. A Superconducting Quantum Interference Device (SQUID) could be fabricated on the surface of a Si substrate and a Bi donor then implanted and activated such that the donor qubit resides close to the Josephson junction of the SQUID. Fabrication steps would have to be carefully chosen for the successful realisation of a coupled hybrid qubit device. An electrically insulating oxide would be required between the Si substrate and the SQUID to prevent the ionisation of the Bi donor, a post-implantation anneal compatible with the surface metallisation would have to be chosen to activate the donor and the hybrid qubit device would have to be operated at a magnetic field below the critical field of the superconductor.

Finally, the suitability of deterministic ion implantation via the IBIC technique for the fabrication of Bi donor qubit arrays could be tested. Bi donors could be implanted to a technologically useful depth into the construction site of IBIC detectors and their detection fidelity could be determined. This would allow the ion-solid interactions and stopping mechanisms to be probed and would determine if the Funsten correction, in which the dense plume of ionisation generated by the implantation of the heavy mass Bi ion results in increased carrier recombination, limits the number of electron-hole pairs generated.

7.2 Isotopic Enrichment of Silicon by $^{28}\text{Si}^-$ Ion Implantation

The dominant decoherence mechanism in $^{\text{nat}}\text{Si}$ is caused by the dipolar fluctuation of ^{29}Si spin-1/2 nuclei that cause perturbations in the local magnetic field of donor spin qubits. The production of a spin-free ^{28}Si substrate is therefore required for Si qubits with long coherence times, suitable for high fidelity quantum computing. The existing methods of Si isotopic enrichment require specialised equipment, such as a centrifuge for producing $^{28}\text{SiF}_4$ that is reduced to isotopically pure silane gas that can be deposited as ^{28}Si epilayers via Chemical Vapour Deposition (CVD) or Molecular Beam Epitaxy (MBE) or an UHV ion implanter to deposit low energy ^{28}Si ions, mass-separated from a natural source. The method investigated here has the advantage of neither relying on isotopically enriched source materials or a specialised UHV implanter and thus increases the accessibility of ^{28}Si .

7.2.1 Achievements

Chapter 5 investigates a method for the isotopic enrichment of surface layers in natural silicon substrates using high fluence $^{28}\text{Si}^-$ ion implantation that depletes ^{29}Si and ^{30}Si isotopes by sputtering. This method requires only standard ion implanter technology, can be integrated with the fabrication of qubits by donor ion implantation and was shown to provide a single-crystal ^{28}Si environment capable of increasing donor qubit coherence times.

TRIDYN simulations were performed to determine how the sputter yield and resulting level of isotopic enrichment depends on ion implant energy and to investigate various sources of contamination. A $^{28}\text{Si}^-$ ion implant energy of 45 keV was chosen to result in one-for-one replacement (a sputter yield of 1). A fluence of $2.63 \times 10^{18} \text{ cm}^{-2}$ $^{28}\text{Si}^-$ ions were implanted at this energy, resulting in a depletion of ^{29}Si down to 250 ppm in a surface layer of thickness $\sim 100 \text{ nm}$, as measured with SIMS. This ^{29}Si concentration is more than 3 times lower than that found in commercial Isonics epilayers, which have already demonstrated record-holding solid state coherence times [24].

The concentration of C and O impurities were found to be comparable to that found in Czochralski-grown Si and were sufficiently low to allow for successful recrystallisation via SPE. The quality of the single-crystal ^{28}Si surface layer was found to be equivalent to the *c*-Si substrate below using high-resolution TEM.

In order to measure the coherence time of donors in our isotopically enriched Si, P donors were implanted into a ^{28}Si layer produced by high fluence 30 keV $^{28}\text{Si}^-$ implantation resulting in ~ 3000 ppm of residual ^{29}Si in a surface layer of thickness ~ 50 nm. The Hahn echo signal produced by the P spins was fit with a mono-exponential decay, indicative of an isotopically enriched ^{28}Si donor environment. The measured coherence time of $T_2 = 285 \pm 14 \mu\text{s}$ is longer than that obtained for $^{\text{nat}}\text{Si}$ at a similar doping concentration. This represents the key achievement of this work by proving that our method of isotopic enrichment can extend donor coherence times which can be further increased by reducing the concentration of P and residual ^{29}Si .

7.2.2 Further Work

The repeating of the pulsed ESR measurement to probe the coherence time of donors implanted in our isotopically enriched ^{28}Si layer with an optimum sample containing a lower level of residual ^{29}Si (ideally to 250 ppm, as already demonstrated, or lower) and a lower concentration of implanted P donors (ideally $1 \times 10^{16} \text{ cm}^{-3}$ or lower) is necessary to be able to extract a much longer coherence time that should be possible with this method. The Hahn echo measurement in this work was performed on a non-optimal sample with a P concentration of around $1 \times 10^{17} \text{ cm}^{-3}$, which, although increasing the signal to noise, would have reduced the coherence time via instantaneous diffusion, and with a ^{29}Si concentration of around 3000 ppm, which reduced the coherence time via spectral diffusion.

In this work, 45 keV $^{28}\text{Si}^-$ was chosen for its one-to-one replacement. However, if the requirement for a planar surface post implantation and anneal is relaxed, higher energy ions could be implanted to reduce the sputter yield below one and result in a higher level of isotopic enrichment, as demonstrated with TRIDYN simulations. A series of high fluence implants could be performed at various energies above 45 keV, after which the thickness of the enriched layer

and the level of ^{29}Si depletion could be determined using SIMS. If a hard mask was used on the surface of the Si substrate during the implantation, the step height from the $^{\text{nat}}\text{Si}$ region to the isotopically enriched region could be determined before and after annealing with a Dektak profilometer. A $^{\text{nat}}\text{Si}$ substrate could be used as the hard mask to avoid forward recoils of heavy metal impurities. After considering the maximum step height that could be tolerated by Electron Beam Lithography (EBL) fabrication techniques, this may allow for the selection of a $^{28}\text{Si}^-$ ion implant energy higher than 45 keV in future to produce thicker ^{28}Si surface layers with a lower concentration of residual ^{29}Si . This greater thickness of enriched material would allow for a greater number of spins to be probed by the pulsed ESR technique with an on-chip cavity, increasing the signal to noise of the measurement.

Future investigations into the whether the presence of the end of range defects cause deleterious effects on the implanted donor qubits are necessary. A series of pre-amorphisation $^{28}\text{Si}^-$ implants at a lower fluence of around $1 \times 10^{15} \text{ cm}^{-2}$ could be performed at a range of energies that place the a/c interface much deeper in the substrate before the high fluence enrichment process. This would move the end of range defects much further away from the implanted donor qubits and reduce their influence.

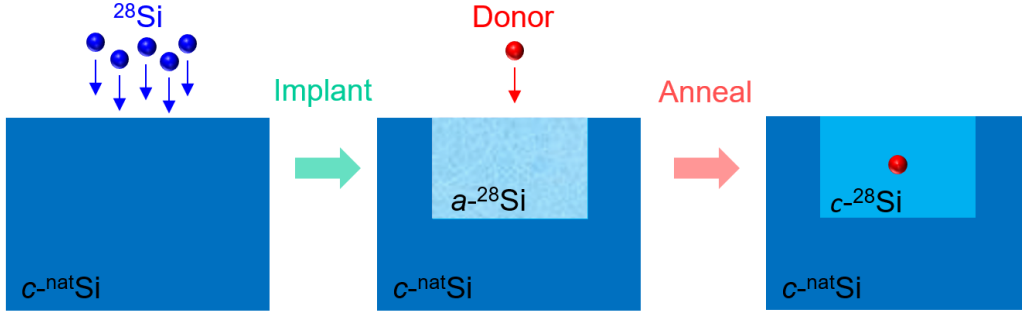


Figure 7.1: A focused ^{28}Si ion beam could be used to locally enrich islands of the surface region of a $^{\text{nat}}\text{Si}$ substrate, into which donors could be implanted for the fabrication of quantum computing architectures.

Islands of locally enriched ^{28}Si could be produced using a FIB to drastically speed up the high fluence implantation process. Donors could then be implanted into the enriched amorphous regions before annealing to limit ion channeling. This is shown schematically in Fig. 7.1. Since a FIB is capable of implanting only positive ^{28}Si ions, the C, O and N contamination levels in the ion beam will be required to be very low. Measurements of these contamination levels

using SIMS after enrichment and the assessment of single-crystal quality using TEM after annealing will be required. The areal dimensions of the enriched islands will also have to be much greater than their thickness to ensure solid phase epitaxy progresses predominantly from the *c*-Si substrate below instead of from the sides as well, which would result in crystal grain boundaries.

Of great importance is the determination of whether this silicon enrichment method is compatible with deterministic implantation of donor qubits using the ion beam induced charge method. Ideally, donors would be implanted into the amorphous ^{28}Si layer to reduce ion channeling and hence increase placement precision. Experiments in which the active region of an IBIC detector is locally enriched using a FIB should be performed. The charge collection efficiency of this detector with an *a*-Si substrate could be obtained to see if a suitable number of electrons and holes can be collected by the biased electrodes before they recombine in the amorphous region. Perhaps the annealing of the ^{28}Si layer is required before the deterministic implantation of donors, in which case, a suitable solid phase epitaxy anneal compatible with the detector metallisation will be required, unless the substrate is isotopically enriched before the fabrication of an IBIC detector. In the case of the later, the detector fabrication process flow will have to avoid the diffusion of ^{29}Si back into the enriched layer and any oxide growth steps will have to avoid consuming a large amount of the enriched layer.

Before the measurement of a single donor qubit in ^{28}Si , a lower bound for the donor coherence time could first be measured with an EDMR device fabricated on an isotopically enriched layer of ^{28}Si implanted with P donors, as discussed in the further work portion of the next section. The criterion for success of the high fluence implantation enrichment process would be a significant increase in donor coherence time over those implanted in $^{\text{nat}}\text{Si}$ to the same dopant concentration. The final step would be to determine the fidelity of a single donor qubit implanted into this isotopically enriched material and to see how much the donor coherence time is extended over the results for donor qubits implanted in commercially-available ^{28}Si epilayers containing 800 ppm ^{29}Si .

7.3 Electrically Detected Magnetic Resonance of P in Si

Conventional ESR can measure transition signals from a minimum of $\sim 10^{10}$ spins. Due to the small volume of our isotopically enriched ^{28}Si surface layers and the requirement for a low concentration of implanted donors to observe the effect of ^{29}Si depletion, a higher sensitivity system capable of measuring transitions from a smaller number of spins is required. EDMR provides a promising solution to this, with the previous demonstration of sensitivity down to less than 100 spins [115], in which the linewidth of a continuous-wave EDMR measurement can be used to extract a lower bound on the donor coherence time.

7.3.1 Achievements

In chapter 6, a low-temperature system for the measurement of electron spin transitions via the change in photoconductivity of the substrate was designed and implemented. This EDMR system enables the measurement of donors in Si with a greater sensitivity than conventional ESR, important for the quality control of future isotopically enriched ^{28}Si layers by determining the coherence time of implanted donors.

A low-temperature, low-field EDMR setup capable of measuring donor spin transitions in Si at temperatures down to 5 K, irradiated with microwaves of frequencies up to ~ 200 MHz with a magnetic field range of $\sim \pm 100$ G was designed and implemented. The small signal produced by the change in photocurrent was enhanced by modulating the frequency of the microwaves and using lock-in amplification. EDMR devices, designed with an on-chip microwave stripline and source and drain electrodes, were fabricated on background-doped $^{\text{nat}}\text{Si:P}$ substrates with a P concentration of $\sim 3 \times 10^{16} - 2 \times 10^{17} \text{ cm}^{-3}$. This doping level was high enough to produce EDMR signals from P donor transitions with a high signal to noise ratio to allow for the optimization of experimental parameters. Additionally, a large EDMR signal produced by transitions of P_{b0} centres (dangling bonds at the interface of Si and its oxide), responsible for the spin-dependent recombination mechanism, was observed.

EDMR measurements were carried out at various temperatures in order to observe the

effect of P donor carrier freeze out at temperatures below ~ 22 K. Additionally, various microwave powers and modulation amplitudes were used during the collection of EDMR spectra to determine their effect on EDMR signal amplitude and linewidth.

The implementation of this EDMR system and measurement of devices fabricated on background-doped Si:P substrates leads the way for the future measurement of donors implanted into isotopically enriched ^{28}Si surface layers. The doping level and active volume of the EDMR device corresponds to around 10^5 P donors contributing to the spin transitions measured in this work, which is already around 5 orders of magnitude more sensitive than a conventional ESR system.

7.3.2 Further Work

It is important to further increase the sensitivity of this EDMR system for the future measurement of spin transitions from a smaller number of implanted donors. A greater number of spin transitions can be excited by increasing the strength of the oscillating magnetic field B_1 , corresponding to increasing the microwave power. The EDMR device design could be optimised to increase the amplitude of the EDMR signals by performing COMSOL simulations that map the microwave power dissipation across the active region of the device. The ground plane could be removed since low microwave frequencies of around 200 MHz are being used. This would prevent the active region of the device being shielded from the microwave power and would increase the signal to noise. Similarly, the source and drain electrodes could be moved closer towards the microwave stripline to increase the strength of the oscillating B_1 magnetic field in the active region of the device. The source and drain electrodes could also be made thicker and moved further apart to increase the active volume of the device to include a greater number of donor spins that produces a stronger EDMR signal. The gradient of the B_1 magnetic field across the active region of the device will have to be determined using COMSOL simulations to ensure that the EDMR signal linewidth will not be artificially broadened by this source.

The collection of additional EDMR spectra at various laser powers, modulation frequencies and source-drain voltages would allow for further optimization of the EDMR signal. The

isolation of cables to reduce the vibrational noise caused by the Janis compressor would also increase the signal to noise of the system and hence its sensitivity. The investigation of various surface oxides, for example native silicon oxide, thermally-grown dry and wet silicon oxides or atomic layer deposition of aluminium oxide, to determine the optimum surface concentration of P_{b0} centres for maximising the EDMR signal is also important. This will extend previous preliminary work performed that compared native with thermally-grown silicon oxide [95]. A thorough and direct comparison for the different oxides listed above has not been performed with equivalent EDMR device designs and donor concentrations. Fabricating metal-oxide-semiconductor capacitors in parallel on these various oxides would provide information about the density of interface traps and fixed oxide charge to see what effect these have on the strength of the EDMR signals produced by donor spin resonance.

Additionally, the EDMR signal amplitude of some of the donor spin transitions could be increased by increasing the magnetic field strength and microwave frequency at which the transition is excited [239]. This could be achieved by increasing the magnetic field range capable of being swept by increasing the number of turns in the Helmholtz coils. This would also increase the versatility of the EDMR system, enabling the spin transitions from various donor species to be probed. An additional pair of Helmholtz coils could be added to the system in order to explore magnetic field modulation instead of microwave frequency modulation.

The temperature dependence of the amplitude, linewidth and position of the EDMR signal from the spin resonance of P_{b0} centres could be investigated into higher temperatures since the Janis cryostat is capable of maintaining temperatures over a large range from ~ 5 K (whilst the device is illuminated with a laser and irradiated with microwaves) to higher than room temperature. It would also be interesting to fabricate a series of EDMR devices where the P donors are implanted at various energies to investigate the optimum depth below the interface that produces suitable weakly-coupled spin pairs from the P_{b0} centres and the donors, necessary for spin-dependent recombination. This would allow the active thickness of the EDMR device to be determined and would guide the future selection of donor implantation energy.

Spin transitions from alternative donors, such as As and Sb, could be measured by fabricating devices onto Si substrates background-doped with various donor species. These donors

have a greater nuclear spin, I , than P donors with $I = 1/2$ and so a greater number of transitions exist that can be probed. An investigation into how the EDMR signal to noise varies with dopant concentration will also be important to determine the sensitivity of this system. Therefore, EDMR devices could be fabricated on Si substrates with various doping levels.

The fabrication of EDMR devices on both natural and isotopically enriched ^{28}Si substrates ion implanted with donors is required to compare the EDMR signal linewidths produced by donors in these two environments. From this, a lower bound estimate of the coherence time T_2^* can be determined, giving a lower bound for the donor coherence time T_2 . Low microwave powers and modulation amplitudes will be required to avoid the artificial broadening of EDMR signal linewidths produced by donors in ^{28}Si . We have seen in chapter 6 how the decrease in EDMR signal amplitude follows decreasing microwave power and modulation amplitude and therefore it is important to maximise the sensitivity of the system before this experiment is performed. In future, this EDMR system could be used as a quality control to extract the lower limit of coherence times of donors implanted into our isotopically enriched ^{28}Si layers. Integrating this EDMR system with pulsed magnetic resonance techniques would enable the elimination of inhomogeneous broadening by performing a Hahn echo pulse sequence to extract the true coherence time, T_2 , of the donors. This high sensitivity system allows the measurement of transitions from a small number of spins, necessary due to the ~ 100 nm thickness of the ^{28}Si layer and low donor concentration required to limit donor-donor coupling, which cannot be probed with the lower sensitivity technique of conventional ESR. This EDMR method is convenient to test the donor quantum environment provided by the ^{28}Si layer as it avoids the need to produce a single donor qubit device that requires many highly controlled fabrication steps for surface nanocircuitry.

7.4 Ultimate Goal

All of the experimental projects researched in this thesis lead towards the ultimate goal of fabricating a scalable silicon quantum computer using deterministic donor ion implantation. The realisation of the flip-flop qubit architecture [64] is well suited to donor ion implantation

as it relaxes the spatial precision required. In the near term, this realisation would allow for the demonstration of small-scale quantum algorithms and in the far term, the implementation of error correction for a large-scale universal fault-tolerant quantum computer. How much progress did my PhD research contribute towards attaining this ambitious goal?

The investigation of Bi as an alternative donor qubit suggests that the electrical activation yield (maximised at around only 50%) would be a significantly limiting factor for the performance of such quantum computing devices fabricated using ion implantation in silicon. However, quantum memories that use an ensemble of Bi donors could still be a viable option and there still exists many interesting and unexplored physical phenomena with the operation of single Bi donor qubits and their coupling to superconducting flux qubits. Therefore, the optimum implantation and annealing strategy provided by this study will be important for increasing the operational yield of such devices. The measurement of the 10 Bi donor ESR transitions and the agreement of their positions with simulations suggest that the non-activated Bi donors do not significantly influence the quantum environment of the activated Bi donors.

The development of a method for producing single-crystal ^{28}Si layers from natural sources using conventional ion implantation technology shows great promise for increasing the accessibility of isotopically enriched silicon material required for high fidelity quantum computers. This method of high fluence ion implantation is particularly suited to the incorporation into the fabrication process flow for implanted donor qubits, since this can be performed *in-situ* and would increase the placement precision of donor qubits by reducing ion channeling effects. The concentration of residual ^{29}Si spins produced by this method was significantly lower than that found in commercial Isonics ^{28}Si epilayers which could lead to an increase in the already record-breaking solid-state coherence time held by donor qubits.

The design and implementation of a new EDMR system, with promising demonstrations of spin resonance in background-doped Si:P, provides a technique for the low-temperature quantum measurement of donors in Si. This capability opens up many exciting areas of research for our group to determine the magnetic environment of donor electrons bound to group V nuclei in Si. This system is already around 5 orders of magnitude more sensitive than conventional ESR, which enables the measurement of a much smaller number of donor spins. In future, the

measurement of EDMR transitions from donors implanted into Si will be able to confirm the suitability of the implant and annealing strategy used to electrically activate the donors. The measurement of the EDMR signal linewidth will provide information on the lower bound of the coherence time of implanted donors. Upgrading this EDMR system with pulsed microwave capabilities would be particularly important for the assessment of the suitability of our enriched ^{28}Si layers for providing a noise-free quantum environment, in which a low concentration of donors are implanted in the surface ~ 100 nm. This EDMR system could therefore act as a quality control for the materials that are fed into the donor qubit fabrication process.

This research makes progress towards the fabrication of donor qubits in isotopically enriched silicon with exceptionally long coherence times. The method of ion implantation used here shows great promise for the realisation of a large-scale quantum computer due to its scalability and integration with the semiconductor industry. In the future, modern technology is set to be revolutionised by harnessing the vast parameter space of quantum systems. This promises the computation of problems that are currently intractable which could, as a topical example, aid drug discovery in the face of future pandemics.

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Appendices

Appendix A

Unsuitability of Positive ^{28}Si Ion Implantation for Isotopic Enrichment

Presented here are the results of pilot experiments conducted at GNS Science, Lower Hutt to examine the use of positive ion beams for the isotopic enrichment of Si, where it was known that the isobars CO^+ and N_2^+ present in the ion beam were likely to present a significant source of contamination [254].

The 40 kV ion implanter at GNS Science, equipped with a silane gas penning sputter source of positive ^{28}Si ions was used for the Si implants performed on samples C and D. 31 keV $^{28}\text{Si}^+$ was implanted at a fluence of $1 \times 10^{18} \text{ cm}^{-2}$ and $4.5 \times 10^{18} \text{ cm}^{-2}$ into UHPS Topsil $^{\text{nat}}\text{Si}$ with a target chamber vacuum of $< 1 \times 10^{-7}$ Torr to fabricate samples C and D, respectively. Sample C was given a thermal anneal at 650°C for 1 hour in an Ar atmosphere, followed by an RTA at 1050°C for 5 s in an Ar atmosphere. Sample D was given a thermal anneal at 609°C for 15 min in air.

SIMS was performed at the University of Western Sydney on both samples C and D before annealing. The Si isotopes and C, O and N impurities were measured in negative polarity with a Cs^+ beam current of 12 nA, raster size of 160 μm and analysis diameter of 33 μm .

The crystallinity of sample C was measured after annealing using a TEM (JEOL, 2100F) at RMMF, RMIT. Protective layers of Ar sputter deposited Pt, e-beam deposited Pt and then

ion beam deposited Pt were used. A lamella was then extracted and thinned to a thickness of ~ 100 nm, with a final polishing step performed with a 2-5 keV Ga ion beam. High-resolution cross-sectional images were taken in which a 200 keV electron beam was transmitted down the [110] direction through the lamella. Raman spectroscopy with a 532 nm wavelength laser was used to confirm the polycrystalline nature of the enriched surface layer after annealing of sample C.

The concentration of the Si isotopes and the impurities ^{12}C , ^{14}N and ^{16}O in sample D before annealing were measured with SIMS and are displayed as a function of depth below the surface in Fig. A.1. Fig. A.1a shows the high fluence ^{28}Si implantation depleted ^{29}Si and ^{30}Si to concentrations of around 900 ppm and 320 ppm, respectively, in a surface layer of thickness ~ 120 nm. A significantly thicker layer with a lower level of ^{29}Si and ^{30}Si is achieved experimentally with 31 keV $^{28}\text{Si}^+$ implantation than for the TRIDYN simulation for 30 keV ^{28}Si implantation shown in Fig. 5.7a. This is likely due to the high levels of contamination that decrease the sputter yield, shifting the implantation from the erosion to the accumulation regime, as discussed in section 5.4.7.

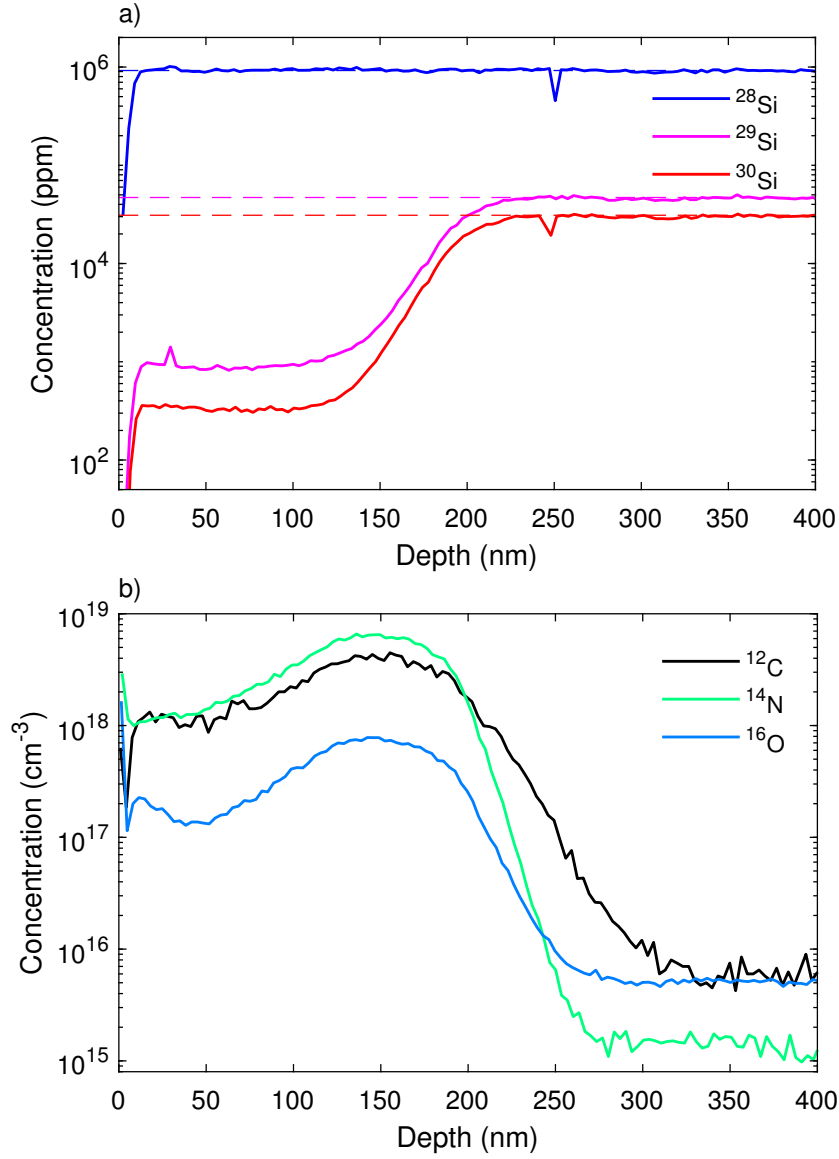


Figure A.1: Experimental SIMS depth profiles for sample D before annealing. a) The concentration of the isotopes of ^{nat}Si as a function of depth below the surface. Natural abundance is indicated with dashed lines. b) The concentration of the impurities ^{12}C , ^{14}N and ^{16}O as a function of depth, calibrated with typical maximum background impurity levels expected in UHPS Topsil.

Fig. A.1b shows the concentrations of ^{12}C , ^{14}N and ^{16}O in the implanted region of sample D before annealing. The concentrations are increased above the background levels to around $4 \times 10^{18} \text{ cm}^{-3}$ for C, $6 \times 10^{18} \text{ cm}^{-3}$ for N and $8 \times 10^{17} \text{ cm}^{-3}$ for O by the process of high fluence implantation of $^{28}\text{Si}^+$ ions. The concentrations of these impurities were calibrated by assuming that the background levels at a depth of $\sim 400 \text{ nm}$ were $5 \times 10^{15} \text{ cm}^{-3}$ for C and O and $1 \times 10^{15} \text{ cm}^{-3}$ for N; the maximum expected background contamination for UHPS Topsil quoted by the supplier. Since the N^- ion is not detectable with SIMS, the presence of N was measured by detecting CN^- ions. The levels of C, N and O impurities introduced here with $^{28}\text{Si}^+$ ions

are much greater than the contamination introduced with negative ions, as revealed in section 5.7.1. The source of this increased contamination is due to the co-implantation of CO^+ and N_2^+ molecular ions that plague positive ^{28}Si ion beams, as discussed in section 5.4.7. These levels of contamination, particularly for N and C, are much higher than those present in Czochralski-grown Si and cannot be tolerated due to the complete impediment of recrystallisation via SPE. No gettering of impurities is observed at sources of vacancy-rich open volume defects in this case as SIMS measurements were performed before annealing. Heavy metal impurities are also likely to be present in this isotopically enriched layer from forward recoils of a metal aperture used to collimate the ion beam since a Si aperture was not used in this implantation.

Raman spectroscopy measurements of the intensity of the reflected laser beam due to inelastic collisions from phonon interactions as a function of wavenumber, $k = 2\pi/\lambda$, were performed in the School of Physics, University of Melbourne. Raman spectra for a non-implanted *c*-Si substrate and sample C after annealing are shown in Fig. A.2, with the first order Raman peak at 521 cm^{-1} characteristic for *c*-Si. The asymmetry of the *c*-Si peak indicates that the isotopically enriched layer of sample C is polycrystalline after annealing, in contrast to the symmetric *c*-Si peak for single crystal Si.

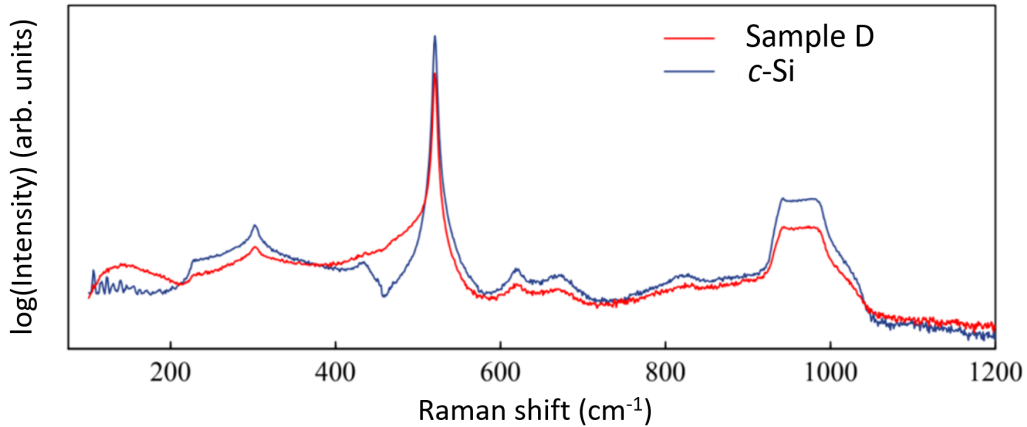


Figure A.2: Raman spectra for non-implanted *c*-Si and sample C after annealing.

The isotopically enriched layer of sample C after annealing was also investigated with TEM and was confirmed to be polycrystalline with a small grain size. This is undesirable for donor spin qubits as they will be ionised with their donor electrons trapped in defects found at the polycrystalline grain boundaries and defects with spin, such as dangling bonds, will perturb the magnetic environment of the donors resulting in reduced coherence times. End of range defects

are visible as a dark band ~ 120 nm below the surface in Fig. A.3a. The interface between *c*-Si and polycrystalline Si is visible between the end of range and the surface, indicating the incomplete recrystallisation via SPE. The increased levels of C, N and O in the implanted layer impeded the progression of the *a/c*-interface and allowed the nucleation of many *c*-Si grains throughout the amorphous layer. The polycrystalline nature of this resulting surface layer is demonstrated by the characteristic ring patterns in the FFT of a high-resolution TEM image taken in the region indicated in red, shown in Fig A.3c.

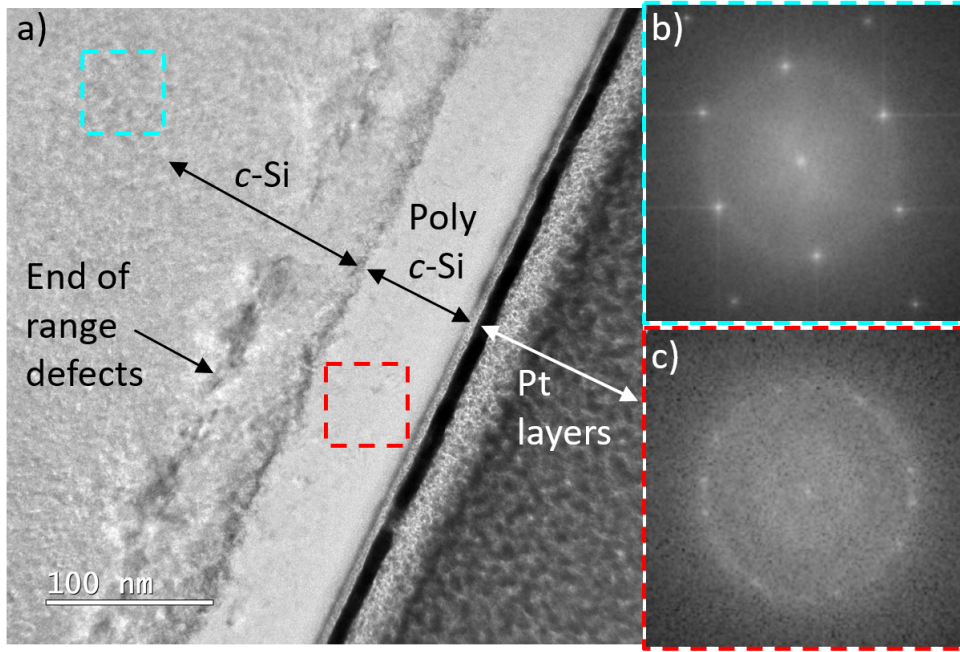


Figure A.3: Cross-sectional TEM images of a lamella of sample C after annealing. a) The end of range defects are visible as a dark band ~ 120 nm below the surface. Incomplete recrystallisation of the enriched surface layer via SPE is observed, with the surface layer being polycrystalline Si. Crystal diffraction patterns of b) the non-implanted region (highlighted in cyan) and c) the implanted region (highlighted in red).

These measurements show that the high fluence implantation of positive ^{28}Si ions performed here results in an unacceptably high level of contamination which prevents the creation of a single crystal ^{28}Si layer upon annealing. This is due to the inadequate control of the ion beam contamination, particularly for the isobars CO^+ and N_2^+ , which can originate from the ion source, implanter components and residual gases in the vacuum chamber. The levels of these contaminants are much more difficult to control with a positive ion beam compared to a negative ion beam, where the CO^- and N_2^- molecule ions are electronically unstable. This highlights the need for a source of negative ions when using a standard ion implanter without

UHV capabilities for the isotopic enrichment of Si.

Appendix B

$^{28}\text{Si}^-$ Implantation at the University of Leipzig

Presented here are the results of pilot experiments conducted at the University of Leipzig to examine the use of negative ion beams for the isotopic enrichment of Si. The cleaning of the $^{\text{nat}}\text{Si}$ substrate before implantation and the vacuum level in the implant chamber were inadequate to limit the incorporation of impurities during implantation and resulted in the impediment of recrystallisation by SPE.

The 100 keV implanter at the University of Leipzig, equipped with a solid $^{\text{nat}}\text{Si}$ SNICS ion source was used to perform the Si implant for sample E. 31 keV $^{28}\text{Si}^-$ was implanted at a fluence of $2.84 \times 10^{18} \text{ cm}^{-2}$ into UHPS Topsil $^{\text{nat}}\text{Si}$ with a target chamber vacuum of around $2 \times 10^{-6} \text{ Torr}$.

The composition with depth of sample E before annealing was obtained with SIMS at the IOM (IONTOF GmbH, TOF.SIMS 5). The Si isotopes and impurities H, C, N and O were measured in negative polarity with a 2 keV Cs^+ beam used for sputtering and a 15 keV Ga^+ beam used for analysis. The sputtered area was $300 \times 300 \mu\text{m}^2$ and the analysed area was $50 \times 50 \mu\text{m}^2$.

The concentration of the Si isotopes and the impurities ^{12}C , ^{14}N and ^{16}O in sample E before annealing were measured with SIMS and are displayed as a function of sputter time in Fig. B.1.

Fig. B.1a appears to show that the 31 keV $^{28}\text{Si}^-$ implantation at a fluence of $2.84 \times 10^{18} \text{ cm}^{-2}$ depleted ^{29}Si and ^{30}Si to concentrations of around 1×10^4 ppm and 100 ppm, respectively, in the surface layer. However, the mass resolving power of the SIMS setup was not large enough to resolve the ^{29}Si ion and ^{28}SiH molecule ion peaks. Since H contamination was measured with SIMS to be high in the surface layer (not shown), the ^{29}Si concentration profile is misleading as it contains a large contribution from ^{28}SiH in the implanted layer. The true depletion of ^{29}Si is likely to be by a factor of around 300 (as for ^{30}Si), resulting in a concentration of around 160 ppm. A significantly lower level of ^{29}Si and ^{30}Si is achieved here with 31 keV $^{28}\text{Si}^-$ implantation than for the TRIDYN simulation for 30 keV ^{28}Si implantation shown in Fig. 5.7a. This is likely due to the high levels of contamination that decrease the sputter yield, shifting the implantation from the erosion to the accumulation regime, as discussed in section 5.4.6.

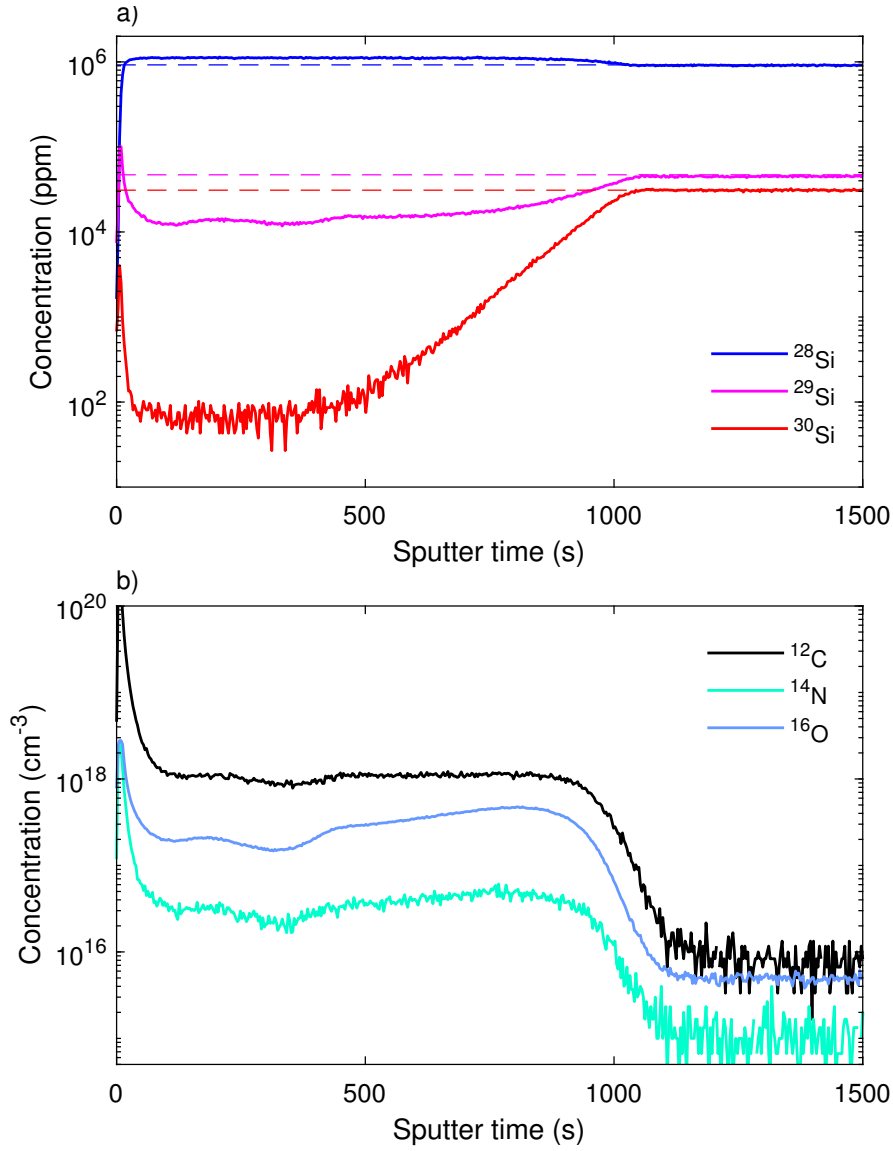


Figure B.1: Experimental SIMS concentration profiles for sample E before annealing. a) The concentration of the isotopes of $^{\text{nat}}\text{Si}$ as a function of sputter time. Natural abundance is indicated with dashed lines. b) The concentration of the impurities ^{12}C , ^{14}N and ^{16}O as a function of sputter time, calibrated with typical maximum background impurity levels expected in UHPS Topsil.

Fig. B.1b shows the concentrations of ^{12}C , ^{14}N and ^{16}O in the implanted region of sample E before annealing. The concentrations are increased above the background levels to around $1 \times 10^{18} \text{ cm}^{-3}$ for C, $5 \times 10^{16} \text{ cm}^{-3}$ for N and $5 \times 10^{17} \text{ cm}^{-3}$ for O by the process of high fluence implantation of $^{28}\text{Si}^-$ ions. The concentrations of these impurities were calibrated by assuming that the background levels at a sputter time of ~ 1500 s were $5 \times 10^{15} \text{ cm}^{-3}$ for C and O and $1 \times 10^{15} \text{ cm}^{-3}$ for N; the maximum expected background contamination for UHPS Topsil quoted by the supplier. Since the N^- ion is not detectable with SIMS, the presence of N was measured by detecting $^{28}\text{SiN}^-$ ions. The levels of C, N and O impurities introduced here with $^{28}\text{Si}^-$ ions are

lower (by more than 2 orders of magnitude in the case of N) than the contamination introduced with positive ions, as discussed in section A, due to less ion beam contamination. However, the concentration of all impurities introduced here is higher than for sample A, shown in section 5.7.1. The source of this increased contamination is likely due to forward recoils from the inferior vacuum and the hydrocarbon surface layer that was not removed before implantation. No gettering of impurities is observed at sources of vacancy-rich open volume defects in this case as SIMS measurements were performed before annealing. Despite the positive side effect of introducing impurities in reducing the sputter yield thereby leading to greater levels of isotopic enrichment, the concentrations of contaminants were too high to allow for successful SPE, as evidenced by Raman spectroscopy which showed the surface layer to be polycrystalline after annealing (not shown). A negative ion beam, sample cleaning prior to implantation and a high vacuum level are therefore all required for successful recrystallisation of the ^{28}Si layer.

Appendix C

EDMR Device Fabrication Process Flow

Table C.1 gives the full fabrication process flow for the EDMR device measured in chapter 6. The substrate of choice was background-doped $^{\text{nat}}\text{Si}$ and ohmic contacts were formed by the drive in diffusion of As donors.

Substrate preparation		
1. Wafer dicing	a. $12 \times 12 \text{ mm}^2$ $0.1\text{-}0.5 \text{ }\Omega\cdot\text{cm}$ $^{\text{nat}}\text{Si:P}$	
	b. Label back	
2. Clean off debris	a. Acetone, 5 min, sonicator	
	b. IPA, 5 min, sonicator	
	c. DI water, 5 min, sonicator	
	d. Piranha, 10 min, 90°C	
	e. RCA, 10 min, 70°C	
	f. DI water rinse, N ₂ blow dry	
Oxide etch mask		
3. Oxide growth	a. Set flow rate: O = 1, N = 30	
	b. Heat furnace: 900°C, N	

	c. Load sample into wait chamber d. Furnace only: O, 10 min e. Purge: N, 20 min f. Load sample into furnace, N g. Purge: N, 5 min h. Oxidation: O, 20 min i. N, 60 min j. Unload (< 1 min) k. Wait 5 min before removing sample	
4. Photoresist	a. Pre-bake: 120°C, 10 min b. Spin on TI 35E: 1 s @ 1000 rpm, 1 s @ 2000 rpm, 40 s @ 4000 rpm c. Soft bake: 95°C, 2 min	
5. Expose etch mask	a. UV exposure: 13.5 s b. Outgas: > 15 min c. Bake: 120°C, 2 min d. UV flood exposure: 50 s	
6. Development	a. Develop: AZ 400K:DI water (1:3), ~ 1 min b. Stop with DI water c. Hard bake: 140°C, 2 min d. O ₂ plasma ash: 2 min	
7. HF etch	a. HF:DI water (1:10), ~ 1.5 min b. Rinse: DI water, 2 min c. Dry: N ₂ gas	
8. Laser cut	a. 2% laser power, 20 passes	

alignment markers	b. Remove resist: acetone, IPA, DI water, N ₂	
Ohmic contacts		
9. Drive in diffusion	a. Pre-bake: 120°C, 10 min b. Spin on As-200: 1 s @ 1000 rpm, 1 s @ 2000 rpm, 40 s @ 7000 rpm c. Bake: 100°C, 15 min d. Diffuse As: 950°C, 10 min, ArH	
10. Photoresist	a. Pre-bake: 120°C, 10 min b. Spin on TI 35E: 1 s @ 1000 rpm, 1 s @ 2000 rpm, 40 s @ 4000 rpm c. Soft bake: 95°C, 2 min	
11. Expose etch mask	a. UV exposure: 13.5 s b. Outgas: > 15 min c. Bake: 120°C, 2 min d. UV flood exposure: 50 s	
12. Development	a. Develop: AZ 400K:DI water (1:3), ~ 1 min b. Stop with DI water c. Hard bake: 140°C, 2 min d. O ₂ plasma ash: 2 min	
13. HF etch	a. HF:DI water (1:10), ~ 3 min b. Rinse: DI water, 2 min c. Dry: N ₂ gas	
14. Clean off resist	a. Acetone, IPA, DI sonicator b. Rinse: fresh DI water	
Metal mask		

15. Photoresist	a. Pre-bake: 120°C, 10 min b. Spin on TI 35E: 1 s @ 1000 rpm, 1 s @ 2000 rpm, 40 s @ 4000 rpm c. Soft bake: 95°C, 2 min	
16. Expose metal mask	a. UV exposure: 14 s b. Outgas: > 15 min c. Bake: 120°C, 2 min d. UV flood exposure: 50 s	
17. Development	a. Develop: AZ 400K:DI water (1:3), ~ 1 min b. Stop with DI water	
18. HF etch	a. Prepare evaporator first b. HF:DI water (1:10), 5 s c. Rinse: DI water, 2 min d. Dry: N ₂ gas	
Metallisation		
19. Metal deposition	a. Vacuum improvement: Ti sublimation 0 nm b. e-beam evaporation: 10 nm Pt, 50 nm Au	
20. Lift-off	a. Acetone soak, 5 min b. Agitate with pipette/sonicator	
21. Laser cut	a. Protect with PMMA resist b. Laser cut with 50% power and 3 passes c. Clean off resist, mount on chip and wirebond	

Table C.1: The full fabrication process flow for EDMR devices.