Bismuth implantation and fabrication routes towards silicon donor based quantum technologies

Tomas Peach
Advanced Technology Institute
University of Surrey

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Abstract

Group V donors in silicon are extremely promising candidates for applications within quantum technologies due to their long spin coherence lifetimes and existing compatibility within the microelectronics industry. However, there are various technical challenges which need to be overcome in order to achieve this potential. This body of work aims to address two such fabrication challenges and attempt to provide solutions which will aid the realisation of silicon and donor based quantum architectures.

Bismuth donors display a vast potential for the implementation as spin qubits however there are limited techniques to controllably fabricate a high quality Si:Bi doped system. Ion implantation is the leading candidate to achieve this although there are concerns that the violent mechanism of Bi\(^{+}\) bombardment into the silicon lattice will significantly degrade the condition of the crystal environment. Therefore, the formation of bismuth donor states in silicon using ion implantation is studied with a specific emphasis on the quality of dopant incorporation. Using a combination of electrical measurements and donor bound exciton spectroscopy it is determined that, under the appropriate annealing conditions, it is possible to produce ion implanted bismuth donors in an environment free from the effects of lattice strain. This therefore motivates the use of ion implanted samples as an alternative to bulk doped Si:Bi for applications within quantum technologies. Implanted samples are then fabricated into simple two–terminal devices and used in electrically detected THz spectroscopy measurements. Using a free electron laser, the resonant excitation of implanted bismuth donors is observed, however the characteristic properties of photoconductivity spectra strongly suggest that devices are being heated significantly.

Finally, an alternative to bulk silicon is studied as a vehicle for quantum technologies. Specifically, the fabrication requirements to controllably align single crystal silicon nanowires is studied using a process known as dielectrophoresis, DEP. Here it is demonstrated that, under the appropriate experimental conditions, it is possible to utilise DEP to manipulate single silicon nanowires to fabricate a wide range of devices. This could prove highly beneficial for the integration of this material within quantum technologies.
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Chapter 1

Introduction

Since the invention of the MOSFET transistor over half a century ago, silicon has been at
the forefront of the technology industry and has led to the invention of numerous staples
of modern day life. However, there is a limit to the capabilities of the classical electronics
industry. In 1965 Gordon Moore published an article in which he theorised that within the
next ten years, the number of individual components on a single computer chip may exceed
65,000 [1]. This was later famously coined as Moores Law which states that with every two
years that pass, the number of transistors per computer chip would double. This prediction
held remarkably true for the next 50 or so years, however in the last decade a saturation point
is beginning to manifest [2]. Simply put, there is a finite limit on how small a transistor
can be before properties such as silicon crystal inhomogeneities significantly effect device
operation. Furthermore, and perhaps more crucially, with the introduction of transistors
as small as 10 nm, node dimensions are approaching the limit where quantum mechanical
effects can no longer be ignored. Rather than seeing this as a detriment, the emergence of
quantum mechanical effects in classical transistors has been embraced as a potential source
for vast new computational power known as quantum computing.

1.1 Quantum computing

Quantum computing is based on the concept of the coherent manipulation of 2 state quantum
mechanical systems in order to fulfill functions that cannot be achieved by classical analogues.
While quantum computers should not be considered a direct replacement for classical sys-
tems, they would allow for the utilisation of various quantum algorithms to accomplish tasks
that are not currently feasible. Foremost examples of this would be the factorisation of extremely large numbers and even the efficient simulation of complex quantum systems [3]. In its purest form, the definition of what a quantum computer would be is actually remarkably broad and as such there are numerous architectures, spanning various material systems, which all are suitable candidates [4]. Therefore there exists a widely followed set of criteria of which any physical implementation of a quantum computer must follow. This is known as the DiVincenzo criteria [5] which specifies, among other things, any practical quantum computer architecture must be scalable, initializable, robust to decoherence, universal and have suitable read-out capabilities. A fair number of infrastructures have been demonstrated to fulfill the majority of this criteria, with the present leading candidates being ion trap qubits [6] and superconducting circuits [7]. Whilst silicon is also a promising candidate, it has not yet met such levels of maturity. One such reason for this is widely accepted to be the sophisticated fabrication requirements for devices that would realise a fully formed silicon based quantum architecture. Although significant steps have been made on this front which will be explored in the next section.

As such, some rather more pragmatic conditions for implementation of quantum computing are that systems should be both practical to fabricate and integratable within classical electronics. It is these latter constraints that provide the general motivation for the line of work presented in this thesis.

1.2 Silicon qubits

Primarily, there exists two different types of silicon qubits: quantum dots [8, 9, 10] (defined either electrostatically by gate electrodes, or physically in a mesa structure) or donor (or acceptor) spin qubits [11, 12]. One of the primary challenges of silicon based quantum systems is the fact that the relatively high electron effective mass, paired with a large silicon dielectric constant, has the result of the electron exchange interaction being of extremely short range. This means that typical donor Bohr radii and quantum dot sizes are on the scale of nanometres which makes device fabrication discernibly more complex. Thus techniques such as electron beam lithography, EBL, are required in the manufacture of devices on this scale as typical photolithography cannot achieve the desired feature resolution. This is not necessarily a tremendous problem as EBL has been used to fabricate some incredibly sophisticated structures that display the potential of silicon quantum dots as a quantum
A recent example would be the extremely high fidelity 2-qubit CNOT gate operation which was exhibited using a coupled silicon quantum dot architecture [13]. This was achieved using a series of 5 lithographically described top gate electrodes which had a cumulative size spanning only $\sim 300$ nm. In this architecture two gates were used to define the dots themselves and the remaining three controlled the source/drain coupling strengths and the inter-dot exchange interaction. In the context of donors in silicon there exists an additional challenge of deterministically positioning impurities within the silicon lattice. This will also require a great deal of precision [14]. The practical implications of this will be discussed in more detail in the next section.

While there are technical challenges facing silicon based quantum computers, there is also no shortage of motivation. Silicon (and germanium) has the significant advantage over alternative semiconductor systems that its nucleus exhibits no spin. The existence of additional atoms with a non-zero nuclear spin in a quantum system has the effect of inducing a magnetic dipole–dipole interaction that can severely reduce electron spin coherence times. This has been demonstrated to limit spin decoherence, $T_2$, times to only a few microseconds [15]. However, while silicon-28 has a nuclear spin $I = 0$, there exists a silicon-29 isotope that is $I = 1/2$, with approximately a 4.7% abundance in natural silicon. While this is a very small percentage of a natural silicon crystal, its significance has been demonstrated such that $T_2$ times achieved in isotopically pure silicon-28 crystals have been measured to exceed 0.6 s [16]. This therefore illustrates that, for a silicon based quantum state, it is hugely beneficial to manufacture a system whereby your donor (or quantum dot) exists in an atomistically perfect lattice with no stray magnetic field lines or additional sources of strain. This sentiment is of great importance to the work presented in this thesis.

1.3 Group V donors in silicon

At low temperatures, group V donors in silicon act as analogues to hydrogen atoms such that they exist as a system in which a single electron is localised to a positively charged nucleus. Therefore, they demonstrate a vast potential for implementation as qubit states through either the spin of the bound electron [17] or the nuclear spin of the donor itself [18]. Electron spin coherence times have been demonstrated to be $> 10$ ms in natural silicon [19] and much longer in isotopically pure silicon-28, whereas donor nuclear coherence times have been demonstrated to be even longer than 3 hours [20]. This is largely down to the reduced mag-
netic moment of the donor nucleus. There are numerous proposals for the implementation of both sets of donor spins within various quantum computation architectures.

1.3.1 The Kane quantum computer

Widely regarded as the foremost architecture for the application of donors in silicon as a quantum computer, the Kane model uses the donor nuclear spin to store quantum information [21]. In this infrastructure individual phosphorus donors would be positioned under a series of alternating gate electrodes labeled as $A$ and $J$ gates. $A$-gates would control the resonant frequencies of the donor nuclear spins through the hyperfine coupling strength while the $J$-gates switch on and off the electron-mediated coupling between the neighbouring nuclear spins. Furthermore a global AC magnetic field would also flip the nuclear spins when at resonance to allow for different operations to be performed on each of the spins simultaneously. This architecture displays vast potential for implementation as a quantum computer however there are significant fabrication challenges that would need to be overcome in order to realise such a scheme. Firstly, a great deal of control would be required over the spatial positioning of phosphorus atoms within the silicon lattice. It is known that the strength of the exchange interaction between a pair of donors decreases exponentially as a function of separation and as such for the Kane scheme donors would need to be positioned within 10–20 nm to one another. Additional considerations must be made to the fact that the donor electron orbital wave function also has a oscillatory term which means that the coupling can dramatically vary over only minute changes in position [14]. Furthermore the requirement would be for there to be three top gate electrodes in the space of only $\sim 15$ nm which, even with the most sophisticated lithographic techniques, would be extremely challenging to realise.

1.3.2 The SFG scheme

It is also possible for the electron exchange interaction to be mediated by donor electrons that are excited into higher lying energy levels. An example of a proposal that would use this phenomena is known as the Stoneham-Fisher-Greenland, SFG, scheme [22]. This architecture would make use of the donor electron optical excitation spectrum and the chemical properties of the different species of nuclei in order to perform quantum operations.

Much like the hydrogen atom, donors in silicon exhibit a bound electron orbital excitation
spectrum. However, while a hydrogen atom exists in free space, the excited energy levels of donor electrons scale by an amount corresponding to the electron effective mass and silicon dielectric constant. This is referred to as effective mass theory, EMT [23]. Although EMT accurately predicts the binding energies of electron states with an even angular momentum quantum number \((l = 2, 4, \ldots)\), it is less successful when \(l\) is odd. In other words, states with an electron wavefunction that has a maxima close to the donor site will experience a shift in binding energy that relates to the chemical nature of the donor species itself [24]. This is often referred to as the central cell correction and has the strongest effect on the 1s state. This therefore means that the groundstate binding energies of donors in silicon will vary strongly from species to species, but the higher lying excited \((l = 2)\) states will not. This phenomena would be utilised in the SFG scheme. Furthermore, it is also noteworthy that the presence of the donor nucleus within the silicon lattice has the effect of breaking the crystals tetrahedral symmetry. This symmetry break has the effect of lifting the 6-fold conduction band degeneracy into 3 different states known as the \(A_1\), \(T_2\) and \(E\) states which are singlet, triplet and doublet levels respectively [25]. Thus the donor groundstate will also be split into 3 different levels with energies that depend on nuclear species [26]. The effects of these split-off grounds states, in the context of spectroscopic measurements, will be discussed at a later point however henceforth in this text the term ‘ground state’ will be used in reference to the 1s\((A_1)\) level. Figure 1.1 presents the electron orbital level schemes for both phosphorus and bismuth donors in silicon. Here it is illustrated that the difference in excited state binding energies is negligible between the two species however bismuth donors have a significantly deeper ground state. This is a direct result of the high mass nature of the bismuth nuclei. Specifically these two species are considered as they are suitable candidates for implementation within the SFG scheme and are of relevance to the work presented in this thesis.

In the SFG scheme for quantum computing, a shallow donor is positioned in between two deeper binding donors such that all three centres are isolated from one another and therefore non-interacting in their groundstates. A good example of a system of this nature would be a phosphorus dopant sandwiched in between two bismuth donors. In this case the spins of the bismuth donor electrons would act as the computation qubits, and the interaction between the two would be mediated by the phosphorus donors which would be acting as a control. Here, the bismuth donor is the preferential spin qubit as its electron is much more tightly bound which means that it has a longer electron spin coherence time and
Figure 1.1: Ground state and excited electron energy levels of phosphorus and bismuth donors in silicon.

a smaller spacial overlap making the system more isolated from its environment (and the other computational qubits). In order to ‘turn on’ the exchange interaction between the two spin qubits the control donor would need to be excited into a higher level such that its, less spatially localised, excited state orbital overlaps with the bismuth donors. Thus allowing for the possibility of a two qubit operation which is gated by an additional control qubit. This control can be achieved optically. The SFG proposal works based on the idea that it is possible to optically and coherently manipulate the control qubit at the desired moment in order to mediate the exchange interaction between the electron spin qubits. This coherent control has been demonstrated on a number different occasions including the observation of a photon echo in a system of Si:P pumped with a free electron laser, FEL, [27] and the coherent excitation, manipulation and destruction of Si:P orbital wavepackets using Ramsey interference [28].

In terms of the fabrication requirements to realise a system of this nature, there are significant positives and negatives when compared other schemes. For example, it would significantly relax the scale related fabrication constrictions as electron exchange interactions would occur over a discernibly larger lengths. Furthermore, it would reduce the dependence on nanoscale lithographic gate electrodes which are both technically difficult to fabricate.
and are likely to have detrimental effects on the environment, and hence lifetimes, of donor systems. However, plainly it does still require a high degree of accuracy over donor placement and with the further complication of two different species of impurity being involved in the fabrication process. Additional consideration must be given to the effect that high intensity THz illumination has on the operation of small scale devices which contain only a small number of donors. At the time of writing, experiments of this nature have largely been focused on the measurement of large scale bulk doped samples.

1.4 Donor incorporation

It is evident that, in any scheme for quantum computing that centres around donors in silicon, a great deal of control is required over where the impurity atoms are positioned within the silicon lattice. At present the two leading candidates to achieve this are hydrogen-resist lithography [29] and ion implantation [30]. Both techniques have their own unique advantages and disadvantages which will be discussed in this section.

1.4.1 Hydrogen resist lithography

Hydrogen-resist lithography is unquestionably at the forefront when it comes to the controlled placement of donors in silicon in terms of spatial resolution. This is such that the positioning of a single phosphorus atom onto the surface of a silicon lattice has been demonstrated with near atomistic precision [31].

The process begins with an atomistically flat silicon surface held within an ultra high vacuum chamber. The entire surface of the silicon is then passivated with hydrogen and using a voltage biased scanning tunneling microscope, STM, tip, individual hydrogen atoms are desorbed from the substrate. Next, the chamber is filled with the dopant precursor gas, which is phosphine, PH$_3$, in the case of phosphorus donors, that then incorporate within the exposed silicon atoms. Thus effectively yielding silicon wafer with a hydrogen mask and a atomistically precise pattern of deposited phosphorus which has been drawn directly with the STM. However, while it is possible to draw the STM structure with atomistic precision, it has been demonstrated that in order to successfully incorporate a single phosphorus donor it is necessary to open at least 3 sets of dimers in the hydrogen mask. Therefore resulting in an effective donor placement resolution of 1 in 6 lattice sites. Furthermore, it has been suggested that the mechanism through which the arsenic precursor gas (arsenine) incorporates onto
the silicon surface requires only one dimer pair [32]. This therefore corresponds to a 1 in 2 lattice site precision and may fuel the speculation that arsenic could prove a more suitable candidate for a silicon donor qubit in terms of fabrication accuracy. Alternatively, by increasing the STM bias voltage and the distance from the surface it is possible to pattern comparatively much larger areas and define more sizeable device regions which can be contacted electrically [33]. The final steps involve annealing the substrate to incorporate the atom and then overgrowing the surface with silicon to fully enclose the donors. This technique has been demonstrated to have vast potential for applications within quantum technologies both in the context of donor and quantum dot qubit fabrication [34] including the particularly impressive single atom transistor [35].

While it is clear that hydrogen resist lithography is an incredibly powerful tool in the fabrication of single to few atom devices, it is not without its shortcomings. For example, at the present time, only phosphorus and arsenic donors have been demonstrated to be incorporated via this technique. Here, the limiting factor is the absence of a suitable gaseous precursor for the other donor species. Furthermore, it is a very time and cost expensive technique so has potential limitations in terms of scalability. Additionally it is not possible to use alternative substrate materials (such as silicon on insulator, SOI) which are commonplace in the current electronics industry.

1.4.2 Ion implantation

An alternative technique for the incorporation of donors in silicon, which has an existing pedigree within the semiconductor electronics industry, is ion implantation. Here, the desired dopant ion is accelerated to high energies (10s to 1000s of keV) and made to collide with a target silicon crystal. Accelerated ions will penetrate the surface of the silicon and, upon thermal annealing, become incorporated within the lattice. The penetration depth and spatial density of implanted atoms can be controlled by tuning the ion beam energy and dose (fluence) respectively.

Inherently, ion implantation is a much less controllable fabrication technique as it involves the incorporation of impurity states via high energy lattice collisions. Two approaches are commonly implemented to combat this limited spacial resolution. The first involves covering the target substrate with a resist and then lithographically opening up small apertures through which incident ions can penetrate into the lattice [36]. While this technique successfully increases the spatial resolution of the implantation, it is limited by the statistical
probability of an ion hitting the uncovered region of the substrate. The second, more control-
larable technique involves using a focused ion beam, FIB, to deterministically implant single
ions into a focused beam spot [37]. Here there is no need for a lithographically determined
mask but instead the limiting factor is the size of the beam spot. Sophisticated FIB setups
can focus a beam spot to as small as 10 nm in diameter [38]. Furthermore, it is also possible
to integrate a secondary electron detector close to the implant region to effectively count the
ions as they are implanted into the substrate [39].

Although there are techniques in place to increase the spacial resolution of the incident
ion beam, there are also factors that will effect the ion position both during and after
the implantation event. One such process is known as range straggling whereby once ions
enter the target lattice they scatter off native silicon atoms. This can result in a final
spatial ion position that is considerably different from the entrance point. Depending on the
implantation energy, the typical straggling ranges of phosphorus ions as they pass through
a the silicon lattice are of the order of 10s of nanometers, however for much heavier atoms
(for example bismuth) the expected deviation will be much less (<10 nm) [40]. Another
consideration is the fact that an implanted ion will not necessarily incorporate into the silicon
lattice at the point where it initially stops. This is because it is required to thermally anneal
the substrate post implantation in order to both repair the lattice damage, and incorporate
the ions. Typically, diffusion takes place as ions couple to defects, interstitial and vacancies
within the silicon lattice and can, to an extent, be mediated by controlling the annealing
temperature and duration [41].

There is a lot of motivation for incorporating ion implantation into the fabrication of
devices for applications with quantum technologies. One of the primary benefits of implant-
ation over alternative donor incorporation techniques is the vast range of ion species which
can be utilised. This allows for the fabrication of substrates doped with any of the group
V donors as well as some more exotic ion species. Furthermore, an additional source of
motivation is the fact that ion implantation is both commonplace in the microelectronics
industry and extremely versatile in terms of the implant medium. For example ion implant-
ation allows for the possibility of quantum donor systems fabricated using SOI and even
more unconventional substrates such as nanowires and pre-existing device structures.

A more in depth look into ion implantation, in the context of bismuth donors in silicon,
can be found in the following chapter of this thesis.
1.5 Summary and thesis outline

The intention of this chapter is to act as a brief introduction into the field of quantum computing with a specific view towards silicon based donor architectures. A particular emphasis was made on the more pragmatic considerations for various silicon donor quantum systems and the associated fabrication techniques that would be required to realise them.

For reasons that will be expanded upon in the next chapter, the donor species that is of specific interest to the work presented in this thesis is bismuth. At present the only fabrication technique by which bismuth donors can be controllably incorporated within a silicon crystal is through ion implantation. However, while phosphorus impurities have been successfully implanted into silicon, and utilised in quantum devices [36], there are questions regarding the compatibility of bismuth ions with this technique. This is largely due to the fact that bismuth is an extremely heavy mass nuclei ($A = 209$) and therefore the target silicon lattice will incur a significant amount of damage during the implantation process. Thus, it would be required that the crystal be greatly repaired post implantation in order to support bismuth donor qubit operation. The primary question that the work presented in this thesis will seek to answer is whether ion implanted bismuth donors in silicon are a suitable platform for integration within quantum technologies. Or alternatively, if the lattice damage caused by the introduction of the high mass Bi$^+$ during this procedure is too severe.

Chapter 2 presents a more detailed literature review of the areas which are specifically relevant to this thesis. For example, the direct motivation for the application bismuth donors in silicon for quantum technologies and an in depth look into ion implantation and the lattice defects that can occur as a result. Information regarding the formation of donor bound excitons, $D^0X_s$, is also provided. The characteristic properties of this complex is the foremost basis by which the quality of ion implanted substrates are judged in this thesis.

This body of work contains a wide range of experimental techniques that are used to measure the characteristic properties of ion implanted bismuth donors in silicon. As such chapter 3 is dedicated to providing an overview of each methodology in the context of the work presented in the subsequent chapters. Chapter 4 contains the first set of results presented in this study. This includes an analysis of various ion implanted Si:Bi samples that have been annealed at different temperatures. The intention here is to distinguish whether post implantation annealing can be implemented to repair the lattice damage incurred by the bismuth ion implantation, such that the donor states are not significantly degraded by their
environmental conditions. In other words, to identify whether it is possible to fabricate a ion implanted Si:Bi sample that is indistinguishable from an equivalent bulk doped substrate. Then the following chapter presents a brief exploration on the effect of implantation dose on the characteristic properties of ion implanted bismuth donors in silicon. This is evaluated both in terms of lattice damage and an increased population of bismuth donors.

Chapter 6 takes the information learned in the previous two chapters and looks to incorporate the ion implantation procedure into the fabrication of a simple device structure. Here two methods of electrically detected THz spectroscopy are used to measure the electron orbital excitation spectra of the implanted bismuth donor states in the high and low illumination regime. In order to realise a quantum computational architecture that relies on the coherent excitation of neutral donors in silicon (the SFG scheme) it is first necessary to verify that the illumination of high power THz radiation will resonantly pump the desired donor transitions without significantly altering the characteristic properties of device operation. This chapter will look to address some of these considerations.

Up until this point, work has revolved around the utilisation of bulk silicon and implantation as a vehicle for quantum technologies. However chapter 7 explores a novel fabrication method revolving around single crystal silicon nanowires as a possible alternative. One of the key motivating factors for this study is the vast potential for pairing with deterministic ion implantation fabrication channels in the future.

Much of the work presented in this thesis has extensive implications for work that could follow on in the future. Therefore chapter 8 contains a summary of the conclusions made in the preceding text and a look forward into the work that may ensue.
Chapter 2

Background & theory

This chapter will provide a more detailed review of some of the areas that are specifically related to the work presented in this thesis.

2.1 Bismuth donors in silicon

The extrinsic doping of semiconductors with group V impurities has been a staple of the technology industry for decades, however typically bismuth donors have been overlooked in favour of more conventional elements such as phosphorus. Primary reasons for this is the relatively low solid solubility limit of bismuth donors in silicon [42] and the fact that the fabrication techniques for phosphorus doped substrates are much more developed.

For example, in the mass production of silicon wafers it is commonplace use phosphine as a process gas to create high quality bulk doped Si:P substrates [43]. Additionally, both arsenic and boron doping can be achieved in the same way using arsine [44] and diborane [45] respectively. Furthermore, the utilisation of dopant precursor gasses also allows for the incorporation of active impurities though various other, more controllable, fabrication techniques such as epitaxially grown silicon layers [46] and hydrogen resist lithography (section 1.4.1). However, in the case of bismuth there exists no equivalent precursor gas and therefore fabrication of doped Si:Bi is much less utilised.

There are a handful of techniques to incorporate bismuth donors into silicon substrates with varying degrees of control. The foremost method of fabricating large scale bismuth doped silicon wafers is known as ‘pill doping’ [47]. A schematic illustration of this process is provided in figure 2.1, however in order to understand pill doping it is first useful to briefly
review how high quality, single crystal, silicon wafers are created using the float-zone growth technique [48]. In short, a polysilicon ingot, known as a ‘feed rod’, is passed through a ‘molten zone’ induced by a RF heating coil. This causes the ingot to transfer from a solid phase into a liquid phase. As the rod travels past the liquid phase, it cools and eventually re-crystallises to form a single crystal silicon ingot. Naturally great care must be taken to ensure that the structural integrity of the molten region is enough to sustain the process. The FZ growth technique produces much higher quality silicon wafers compared to alternative methods such as Czochralski, CZ, growth [48]. This is because the ingot is held in a vacuum and never comes into contact with any contaminating material. While this is not generally too significant for applications within classic microelectronics, for quantum technologies the quality of the crystal lattice is paramount and therefore FZ silicon is the preferred choice.

During pill doping a hole is fashioned into the polysilicon ingot within which a quantity of crystalline bismuth is placed. As the ingot passes through the melting phase the bismuth...
incorporates within the silicon lattice, thus creating a doped Si:Bi crystal. In conventional float zone pulling geometries (as illustrated in figure 2.1), as the dopant pill passes through the melting phase it will abruptly invade the silicon region. This ultimately results in most of the impurity material being wasted and only a small region of the crystalline silicon being doped. Therefore the ‘pedestal pulling’ geometry is favoured to allow the dopant pill to gradually and steadily incorporate into the crystal. Using this technique it is possible to fabricate very high quality bulk bismuth doped silicon wafers, however the control over the active donor concentration is less than would be ultimately desirable.

While pill doping is a perfectly suitable fabrication technique for the production of bulk doped Si:Bi substrates, eventually it will be required that donors will be incorporated with a much higher degree of control. As such the fabrication of bespoke, high quality, Si:Bi substrates suitable for applications within quantum technologies is not practical using this technique. Alternatively, ion implantation provides a much more versatile platform for the fabrication of bismuth doped silicon crystals however questions remain over the quality of incorporation and the detrimental effects that heavy ion bombardment has on the resultant lattice quality. The work presented in this thesis aims to demonstrate whether ion implantation is a suitable alternative to bulk bismuth pill doping for applications within quantum technologies.

2.1.1 Bismuth donors in quantum technologies

For many of the same reasons that bismuth was left largely unused in the classical microelectronics industry, when the transition to quantum architectures began to develop they were again mostly overlooked in favour of phosphorus based donor spin qubits. This is largely due to the high degree of control that can be achieved over the donor placement and the fact that its nuclear mass is very comparable to silicon which leads to an unobtrusive crystal incorporation. Conversely, the large mass nuclei of bismuth, and its much lower solubility in silicon lead to concerns that associated defect states and lattice strain local to the incorporation site could lead to spin decoherence that would be too significant to allow for optimal qubit operation.

However, there is a great deal of motivation to incorporate bismuth donor states as spin qubits. Like phosphorus, bismuth atoms are able to become interstitial within a silicon lattice and, at low temperatures, produce a bound electron with spin $S=\frac{1}{2}$ however, while phosphorus atoms also have a nuclear spin $I=\frac{1}{2}$, bismuth nuclei have a much higher spin
of $I=^9/2$. This leads to what is known as a 20-dimensional nuclear spin Hilbert space where quantum information can be stored which is significantly larger than the 4-dimensional phosphorus equivalent. Moreover, this corresponds to a hyperfine interaction of 1475.4 MHz compared to 117.53 MHz for phosphorus. This strong hyperfine interaction manifests itself in a large splitting of the donor groundstate into to two hyperfine states, with spins $F = 4$ and $F = 5$, which are separated by 7377 MHz (30.51 µeV). This separation is large enough to be resolved in natural silicon using various common spectroscopic techniques, without the requirement of an external magnetic field. Additionally, bismuth has a deep groundstate binding energy of 70.98 meV which means bound electrons are less liable to be affected by localised crystal imperfections. These properties therefore make bismuth a strong potential candidate for implementation as a qubit, either through their nuclear spin and strong hyperfine coupling or their electron spin along side a different species of donor in a quantum gate geometry. Examples of architectures that could utilise either property are discussed in section 1.3.

In light of this vast potential, a sharp increase research publications pertaining to the application of bulk doped bismuth donors within quantum technologies has occurred over the last decade. In 2010 two articles were published that eased some of the concerns regarding the practical implementation of bismuth donors as spin qubits [49, 50]. A combination of electron spin resonance, ESR, and pulsed electron nuclear double resonances, ENDOR, measurements were used to evaluate the bismuth donor electron and nuclear spin decoherence times respectively. In either cases it was found that the limiting factor was actually the magnetic dipole interaction of neighbouring $^{29}$Si nuclei and as such the performance of bismuth donors was very comparable to equivalent Si:P systems. This therefore led to the conclusion that incorporating bismuth in conjunction with phosphorus would not significantly degrade the coherence time of the system. In fact, because bismuth donors have a higher binding energy, bound electrons have a correspondingly smaller Bohr radii which leads to the environmental effects being less significant and electron decoherence times being longer. Although, again, an emphasis was made on the benefit of using isotopically pure silicon-28 irrespective of donor species.

The effect of the strong hyperfine interaction of the Si:Bi complex has been demonstrated by way of donor bound exciton, $D^0X$, spectroscopy. In these studies the zero field hyperfine splitting of the bismuth donor groundstates were resolved, in natural silicon, through photoluminescence, PL, and photoconductivity, PC, measurements. In [51], additional measure-
ments with an applied external magnetic field demonstrated a Zeeman split spectrum with 6 broad components that have a structure indicating a strong nuclear hyperpolarisation of the bismuth donor nuclei into the $I = -9/2$ state at low temperatures. Comparatively [52] shows that by resonantly pumping a given hyperfine state through a $D^0X$ transition, it is possible to polarise the donor nuclear spin without the requirement of a magnetic field. In this measurement the THz electron absorption spectrum was used to illustrate this spectroscopically. Both results are of significance as they demonstrate the possibility of polarising the hyperfine states of the bismuth donor nucleus either resonantly through optical pumping and non-resonantly with an external magnetic field. Using resonant $D^0X$ transitions to observe the bismuth donor zero-field hyperfine structure is of great importance to the work presented in this thesis and as such is discussed in more detail in section 2.3.4. Furthermore, it was shown in [19] that by utilising a phenomena known as clock transitions, where the electron spin resonance is protected from magnetic field noise from the environment, it is possible to dramatically improve electron spin coherence times. This is such that samples of natural Si:Bi achieved $T_2$ times of 93 ms and up to 2.7 s in isotopically pure substrates.

It is therefore clear that bismuth has vast potential for integration within quantum technologies. However it is also noteworthy that every study that was discussed here used bulk doped Si:Bi substrates which were fabricated using the pill doping technique discussed in the previous section. In order to fully utilise the potential of bismuth within quantum computing architectures, it is necessary to have a much greater degree of control over the placement of donors than what is achievable with bulk substrates. At present the only technique for incorporating bismuth donors into silicon with any significant degree of control is through ion implantation.

2.2 Ion implanted bismuth donors

It is clear that bismuth donors in silicon are strong candidates for application as spin qubits, however there are significant practical challenges that need to be solved in order to fulfill this potential. The foremost challenge being the mechanism by which bismuth nuclei will be integrated within the silicon lattice. For reasons that were discussed in the previous section, ion implantation is currently the leading fabrication technique through which the controlled doping of silicon with bismuth can be achieved. Although broad area ion implantation is a non-deterministic method of depositing dopants in silicon, there is a large degree of
control over the depth and spatial density of implanted donors. This is achieved through
careful selection of the implantation energy and beam fluence respectively. Furthermore, by
utilising FIB technology it is possible to improve the spatial resolution of the implantation
area. However, questions remain over whether the violent nature through which bismuth
ions are integrated within the silicon crystal will prove damaging to the coherence of any
potential qubit operation. Therefore, this thesis presents a study of ion implanted bismuth
donors in silicon, with a specific emphasis on applications within quantum technologies.

Bismuth has the largest atomic mass number of all the group V donors in silicon and
as such it displays the lowest ion straggling range after implantation. In one respect this is
beneficial as it increases the spatial precision of the final ion stopping position, compared
with lighter group V elements. However, a much less desirable effect of the high mass nature
of bismuth ions is that, during implantation, a significant amount of damage is incurred by
the silicon lattice. Therefore it is required that post implantation annealing is implemented
to both repair the native lattice and also to incorporate the bismuth nuclei within the crystal
structure. This section will provide an overview of the current understanding of ion implanted
bismuth donors in silicon and the annealing procedures which follow. In the first instance
the discussion will focus primarily on maximising the electrical activation yield, EAY, of
bismuth donors in silicon through careful selection of annealing recipes. Following this, the
topic will concentrate on the lattice damage caused by the implantation of high mass ions
into silicon and the defects that may be formed during heat treatment.

2.2.1 Bismuth donor electrical activation yield

After the ion implantation has taken place it is necessary to anneal the substrate in order
to ensure the electrical activation of implanted ions into the target lattice. However, a
great deal of care must be taken in order to select the appropriate thermal conditions to
ensure the maximum donor EAY is achieved. As such the thermal annealing of implanted
substrates can take various forms depending on the ion beam dose, energy and even species.
The heating of samples can be implemented through numerous methods, from conventional
furnace annealing to quicker heating techniques such as high intensity lasers [53], electron
beams [54] or flash lamps [55]. These various techniques are capable of treating substrates
on timescales ranging from hours to as short as milliseconds. One example of a common fast
heat treatment is known as rapid thermal annealing, RTA, whereby samples are heated to
high temperatures over short timescales. This is often utilised during low density, shallow
implants that are close to the surface of the substrate in an effort to reduce the effects of thermal diffusion. Additionally, it is common to control the atmosphere of the chamber in which the substrate is being annealed in order to avoid contamination from unwanted impurities. Frequently used atmospheres are nitrogen, forming gasses, or even annealing under vacuum.

Historically, studies of bismuth ion implantation into silicon have been in the context of applications within classical microelectronics. Therefore the intention generally was to introduce an extremely high density layer of bismuth doping that is above the metal insulator transition [56]. To achieve this, very high implant fluences ($\sim 1 \times 10^{14}$ cm$^{-2}$) are implemented which will often result in the formation of an amorphous lattice region that coincides with the implanted layer. In this case an effective annealing method is known as solid phase epitaxial regrowth, SPER, [57]. During SPER samples are heated at relatively low temperatures (600 °C) for tens of minutes. This allows for a bottom up, full recrystallisation of the amorphous layer that is created during implantation. Using this technique it has been reported that bismuth donor electrical activation yields of up to 90% can be achieved with minimal diffusion [58]. In fact higher temperatures were found to be less successful and resulted in lower EAYs. The effectiveness of SPER has been reported on many occasions [59, 60] including a very recent study of high density bismuth implantation into SOI [61].

However, for devices designed with quantum technology applications in mind, it is desirable for donor densities to be much lower in order to preserve long spin coherence times. Therefore it is expected SPER will not be as effective due to the fact that limited silicon lattice amorphisation occurs for these implant doses. This was demonstrated using room temperature Hall measurements of substrates implanted with various Bismuth ion densities [62]. For the highest ion doses it was found that the lowest temperature annealing ($\sim 600$ °C ) achieved the maximum EAY, whereas the opposite was true for the lower dose (non-amorphising) implants. Furthermore, it has also been shown that while SPER allows for a near perfect silicon recrystallisation in amorphising Bi$^+$ implants, if the crystal is not fully amorphised then a significant amount of lattice disorder remains in the crystal post annealing [63]. This therefore raises the question of what the optimum annealing conditions are in order to achieve the highest EAY and crystal recovery in low density Bi$^+$ implants. There have been limited studies regarding the optimum post implantation annealing of bismuth donors specifically for applications within quantum technologies. One article reports on bismuth implantation into enriched silicon-28 with a ion dose of $1.1 \times 10^{12}$ cm$^{-3}$. Here
annealing temperatures ranging from 600 °C to 900 °C were used which achieved a maximum EAY of 67% corresponding to an annealing temperature of 900°C for 15 minutes [64]. In addition, ESR measurements were implemented to display an electron spin $T_2$ time of (0.71±0.08) ms in an implanted sample. While this value is is lower than the measured bulk Si:Bi value (discussed previously [49]) it is a reasonable value and thus provides a indication that lattice defects were largely repaired during the anneal.

2.2.2 Implantation defects and annealing

In addition to considering the electrical activation of bismuth donors, it is also beneficial to understand the formation of lattice damage caused by the implanted ions. It is well understood that as ions travel through the target crystal they will collide with lattice sites and transfer energy into the native silicon. If the energy transferred is greater than the lattices displacement energy, $E_{\text{disp}}$, a vacancy will be created (for silicon $E_{\text{disp}} = 15$ eV [65]). Furthermore, the liberated silicon atom will now have its own kinetic energy and can create additional vacancies through further collisions with lattice sites. This is known as a recoil cascade and only occurs as a result of high energy collisions. The Monte Carlo simulation software SRIM [66] has been used to simulate the damage path caused by the implantation of bismuth ions into a silicon target lattice. Figure 2.2 provides a cross sectional view of the damage caused by Bi$^+$ ions with an energy of 2000 keV. (a) displays the damage from a single bismuth ion whereas (b) corresponds to 100 implanted ions. Figures (c) and (d) are equivalent simulations for a 300 keV phosphorus ion implantation as a comparison. Simulated implant energies were selected to achieve an implanted ion depth of approximately 500 nm. Black lines indicate the path of ions through the substrate whereas red lines represent silicon atoms that have been dislodged from the lattice via a collision with an implanted ion. Blue dots are lattice vacancies caused by collisions with liberated silicon atoms.

By comparing (a) and (c) it becomes immediately clear that a single bismuth ion implantation creates far more lattice damage than an equivalent phosphorus ion. One of the primary reasons for this is the generation of many more high energy recoil cascades, which has the effect of creating clusters of vacancies far away from the path of the ion itself. Comparatively the damage caused by the phosphorus implant is local to the motion of the ion. The SRIM simulation calculates the creation of vacancies purely by the kinetics of collision events, however in a real system thermal effects, such as spontaneous annealing, will also play a significant role. This is in reference to the fact that (at ~300 K) the silicon lattice
Figure 2.2: SRIM simulated damage cascades corresponding to the implantation of, a) a single Bi$^+$ ion, b) 100 Bi$^+$ ions, c) a single P$^+$ ion, d) 100 P$^+$ ions. Black lines indicate the path of the implanted ion whereas red lines are the paths of liberated Si ions, blue marks indicate secondary vacancy events. Bismuth and phosphorus ions were simulated to using energies of 2000 keV and 300 keV respectively to achieve an approximate ion depth of 500 nm.

has enough thermal energy to repair a exceedingly high fraction of vacancies (up to 98%) instantaneously [67]. The efficiency of spontaneous annealing does however depend on various properties of the system, including the structural integrity of the lattice surrounding the vacancy site. Therefore areas with a highly concentrated population of vacancies it is expected that this effect is much less functional in repairing crystal damage as compared to dilute regions. Thus it is reasonable to expect that spontaneous annealing will less efficient during the implantation of a heavy bismuth ion compared to a lighter phosphorus. Therefore, high mass implants such as bismuth will likely result in highly disordered regions of lattice damage and even local amorphicity caused by recoil collisions. Comparatively, phosphorus ions will create a more dilute population of vacancies and is very unlikely to cause more
Figure 2.3: a) The evolution of extended defects in non-amorphising implants into silicon as a function of both annealing temperature and duration. b) Various types of extended defects after annealing at a temperature of 750 °C for 400s, clusters, \{113\}s, FDLs and PDLs are all observable. Taken from [68]

significant damage.

For low mass ions such as phosphorus, boron or even silicon, it is well understood how lattice vacancies respond to thermal annealing. Upon heating, lattice vacancies and silicon interstitials migrate to from larger extended defects such as \{113\} ‘rod defects’ or dislocation loops, DL [68]. The exact nature of defect formation depends strongly on the both the implantation dose and energy, as well as the annealing temperature. For example, if the implant is shallow then the population of defect states will be low as vacancies will ‘dissolve’ at the surface of the silicon [69]. By comparison, for higher implant energies the majority of vacancies will be created deeper into the substrate and consequently the number of defects will be much higher. Additionally, it has been demonstrated that the species of defect that are formed will evolve as annealing temperature is varied [70]. For lower temperatures (\sim 700 °C ) \{113\} defects will be majoritively present however as annealing temperatures increase above 900 °C , loop defects will begin to dominate. Simply put, the extra thermal budget transferred into the lattice by the higher annealing temperature is enough to break apart the \{113\} defects however loop defects tend to be much more stable. Furthermore, there exists two main types of dislocation loops known as prefect dislocation loops, PDLs, and faulted dislocation loops, FDLs with the latter being observed to survive annealing temperatures above 1000 °C [68]. It has also been reported that as annealing temperatures
increase, the density of DLs decreases however those that remain remaining are much greater in size, this is referred to as Ostwald ripening [71].

It is not clear whether the more dense clusters of lattice damage caused by bismuth ion implantation will result in the formation of similar extended defects upon annealing. However it has been reported that the presence of simple vacancy related point defects were observed to persist in Bi⁺ implanted silicon up to annealing temperatures of 500 °C [72]. Comparatively, after implants with lighter ions, ~350 °C is often quoted as being sufficient to remove the vast majority of vacancies [73] in favour of extended defects. This was attributed to the presence vacancy clusters caused by an increase in recoil cascade events. Furthermore, it has been suggested that donor-vacancy complexes may be formed to reduce lattice strain caused by the incorporation of a heavy bismuth ion. This has been reported to explain the observation of ambipolar properties of incorporated bismuth ions at the surface of the substrate. Here it is suggested that incorporated bismuth donors can contribute to the formation of either a negatively charged hydrogenic donor or a positively charged donor–vacancy complex [74]. The suggestion that bismuth ion implantation can result in the formation of positively charged defects was actually speculated upon previously [75]. Here, Rutherford scattering measurements indicated a bismuth active donor yield of approximately 80 % however only around 20 % were active electrically. It was speculated that this discrepancy was caused by a population compensating acceptor centres near the surface of the sample. Moreover He⁺ channeling measurements were used to study the lattice location of ion implanted bismuth in silicon, whereby it was concluded that approximately 50 % were displaced from a lattice site by 0.45 Å [76]. The remaining ions were incorporated within the lattice substitutionally. Plainly it is of great importance for any potential application within quantum technologies to ensure that both lattice strain is minimised and the quality of donor incorporation is high.

2.3 Donor bound excitons (D₀X)

Having established the challenges that are associated with implementing ion implanted bismuth donors in silicon as spin qubits, the discussion now switches to the primary mechanism by which the quality of donor incorporation is evaluated in this study.

The energy scales of electron orbital transitions of group V donors in silicon are known to be in a notoriously challenging region of the electromagnetic spectrum known as the terahertz [77]. This corresponds to electron state transition energies ranging from approximately 30
to 70 meV (7 to 16 THz)[78]. Therefore a mechanism for interacting with group V donors in silicon that does not rely on pumping in the terahertz region would be extremely useful in the characterisation of doped substrates. Fortunately such complexes exists and are known as donor bound excitons [79].

2.3.1 Free excitons (X)

Before considering the properties of donor bound excitons, it is necessary to first understand the formation and characteristics of their precursor complexes which are known as free excitons, X. Free excitons are quasi-particles comprising of an electron and a hole bound together via Coulomb forces [80]. Primarily associated with semiconductors, free excitons are highly delocalised systems with electron-hole separations much larger than the silicon lattice constant. This therefore allows the exciton to move freely throughout the crystal. Due to the nature of the complex, parallels have been drawn between free excitons and the hydrogen atom where the positively charged hole is acting in place of a proton. Therefore, it stands to reason that the Bohr model can be applied to this system to calculate its characteristic properties. In fact it has been shown that this modified Bohr model provides a suitable representation of free excitons in various semiconductor systems [79]. There are two significant differences between a free exciton and a hydrogen atom, firstly the ratio of masses between the two constituent quasi-particles is much more even in the exciton complex. This will have the effect of reducing the stability of the particle and hence result in a larger orbital radius. The second effect is that, while the exciton is free to move, it is still bound to be contained within the silicon crystal and as such it will feel an increased dielectric constant, $\varepsilon$, as compared to a hydrogen atom in free space. Therefore the attractive potential felt by the electron from the hole (and vice versa) will be correspondingly reduced. The modified exciton Bohr radius, $r_X$, can be expressed as,

$$r_X = \frac{\varepsilon}{m_r/m_0}n^2a_B$$

(2.1)

where $a_B$ Bohr radius of hydrogen and $m_r = m_em_h/(m_e + m_h)$ is the reduced mass of the exciton. $n$ corresponds to the principle quantum number of the exciton however in this body work only the groundstate is considered so $n$ will always be equal to 1. Similarly, the binding
energy of the free exciton, $E_X$, can be written as,

$$E_X = \left(\frac{m_r}{m_0}\right)\frac{\varepsilon^2}{\alpha^2}Ry(H)$$

(2.2)

where $Ry(H)$ is the Rydberg energy of the hydrogen atom. For free excitons in silicon, which are of interest in this thesis, $r_X = 4.9$ nm and $E_X = 14.7$ meV [81]. Therefore the energy required to promote an electron from the valence band and form a free exciton can be defined as,

$$h\nu_X = E_g - E_X$$

(2.3)

where $E_g$ is the bandgap energy of the semiconductor. In indirect semiconductors (e.g. silicon) an additional phonon term must be included to form a free exciton due to the conservation of crystal momentum. A further discussion of this, in the context of the work presented in this thesis, can be found in section 3.2.1.

2.3.2 Bound excitons

As previously discussed, free excitons are delocalised and are as such able to propagate freely throughout the crystal lattice. However, active impurity centres serve as very efficient traps for free excitons which result in delocalisation and the formation of complexes known as donor bound excitons, $D^0X$. First identified in photoluminescence measurements of arsenic doped silicon [82] (and comprehensively studied subsequently [83, 84, 85]), $D^0X$s consist of four constituent elements and can be considered as a single hole bound to a positively charged donor through a covalent bond. In that sense they are analogous to a hydrogen molecule. The formation energy of this complex corresponds to the energy cost required bring an electron from the valence band to form an exciton, and then bind it to a neutral donor site [79]. This process can be written as,

$$D^0 + X \rightarrow D^0X + E_{D^0X}$$

(2.4)

where $E_{D^0X}$ is the binding energy of the $D^0X$ complex. The radiative decay caused by the annihilation of the exciton can therefore be expressed as,

$$D^0X \rightarrow D^0 + h\nu_{D^0X}$$

(2.5)
leaving the constituent donor in a neutral state and emitting a phonon of energy $h\nu_{D^0X}$ which corresponds to the formation energy of the bound exciton state. Thus, by comparing equations 2.4 and 2.5, and knowing the free exciton energy given by equation 2.3, it is possible to express the energy of a $D^0X$ using equation 2.6.

$$h\nu_{D^0X} = h\nu_X - E_{D^0X} = (E_g - E_X) - E_{D^0X}$$

The low temperature (<20 K) band gap energy of silicon is known to be $\sim 1.17$ eV [86] and the binding energy of a free exciton in silicon has previously shown to be 14.7 meV. Therefore, in order to determine the energy level of a donor bound exciton the only remaining term in equation 2.6 to be understood is the binding energy of the donor bound exciton, $E_{D^0X}$.

Haynes [82] showed, using photoluminescence measurements, that the binding energy of the $D^0X$ complex scales linearly with the groundstate ionisation energy of the constituent donor species. This relationship for various group V donors (and group III acceptors) in silicon is displayed in figure 2.4. This lead to the determination of the relation often referred
to as ‘Haynes rule’ which states,

\[ E_{D^0X} = a + bE_D \]  

(2.7)

where \( a \) and \( b \) are constants specific to the semiconductor material (\( a = 0 \) and \( b = 0.124 \) for donors in silicon) and \( E_D \) is the groundstate binding energy of the appropriate donor (or acceptor) species. This simple empirical relation is remarkably representative of a wide variety of semiconductor systems and was later theoretically explained in relation to the species specific chemical shift seen by the groundstate of group V donors in silicon known as the ‘central cell correction’ [87].

It is now possible to calculate the formation energy of \( D^0X \) complexes for various doping species using equation 2.6. Of specific interest to the work in this thesis are both bismuth and phosphorus donors in silicon which have ground state binding energies of \( E_D = 70.98 \text{ meV} \) and \( E_D = 45.59 \text{ meV} \) respectively. Therefore the \( D^0X \) formation energies are predicted to be 1.147 eV for bismuth donors and 1.150 eV for phosphorus [84]. The fact that \( D^0X \) states for different species of donors are not degenerate is of great convenience as it allows for the characterisation of various systems non destructively through techniques such as photoluminescence and photoconductivity. Furthermore, the energy region at which these complexes exist is of the order of eVs rather than tens of meVs (group V donor electron transition energies). This is of significance as it means that experimentally they are much more accessible as table-top \( \sim 1 \text{ eV} \) laser sources are commercially available.

2.3.3 \( D^0X \) recombination

As previously discussed, donor bound excitons are an extremely useful tool in the characterisation of doped semiconductors. One primary reason for this is the fact that they recombine both radiatively through the emission of a photon [82] and nonradiatively through the promotion of an electron into the conduction band [88]. This therefore allows for the possibility of both optical and electrical experimental techniques to measure these systems.

The mechanism of radiative recombination manifests in such a way that when the electron and hole annihilate, energy is emitted optically which leaves the bismuth donor in a neutral state. Silicon is an indirect band gap medium and as such when the exciton recombines it is required that momentum, \( k \), is conserved during the process. This therefore leads to two primary mechanisms of luminescence [83]. The first corresponds to the exciton trans-
ferring momentum into the donor during the recombination. This is known as a no-phonon transition where only a negligible amount of energy is spent in the momentum conservation and the emitted photon has an energy corresponding to the level of the \( D^0X \) complex as described by equation 2.6. The second mechanism is referred to as a phonon assisted transition, whereby the \( k \)-vector is conserved via the generation of an accompanying lattice phonon. In this case the energy of the emitted radiation will be red-shifted by an amount equalling the phonon energy. The relative probability of each mechanism depends strongly on the chemical nature of the donor species. In the case of no-phonon luminescence, the efficiency of transferring momentum into the donor scales positively with its ground state binding energy. Whereas phonon assisted transitions have the same probability irrespective of donor species. Both of these channels are used in the characterisation of samples through photoluminescence measurements, of which an overview is provided in section 3.2.1.

Non-radiative recombination is known as the Auger process [89]. This corresponds to when, upon exciton recombination, energy is transmitted into the donor which causes it to ionise by ejecting the second electron far into the conduction band. In this case both energy and momentum are transferred into the ionised donor. Auger recombination of \( D^0X \)s is utilised in this study using photoconductivity measurements as illustrated in section 3.2.2. In the case of phosphorus and arsenic donors in silicon, the experimental \( D^0X \) lifetimes, \( \tau_{\text{exp}} \), were measured to be 272 ns and 183 ns respectively [90]. This is much shorter than the radiative lifetimes predicted by the known transition oscillator strengths for the formation of \( D^0X \)s with either of these donor species. This therefore indicates that the non-radiative Auger process massively dominates over \( D^0X \) luminescence. In fact, subsequent measurements of Si:Bi \( D^0X \) transitions found a \( \tau_{\text{exp}} \) value of only 8.6 ns [91] which is approximately an order of magnitude less than what was predicted by extrapolation from the other shallow donor lifetimes. Therefore it is clear that the non-radiative Auger process is significantly stronger than the radiative luminescence of \( D^0X \) complexes for all species of donors, but this particularly true in the case of bismuth. However, both recombination mechanisms are sufficiently strong to be utilised as a readout in a wide range of spectroscopic measurements.

2.3.4 Hyperfine spectroscopy

A significant source of motivation for implementing bismuth donors in silicon as qubits is the large hyperfine interaction between the high mass Bi nuclei and the bound electron. This interaction manifests as a splitting in the \( 1s(A_1) \) ground state which has a magnitude of
30.51 $\mu$eV, the largest of all group V donors in silicon. The size of this splitting is such that it is resolvable using various common spectroscopic techniques without the need for an external magnetic field. Techniques that have been shown to successfully resolve the hyperfine structure of bismuth donors in silicon include THz spectroscopy (using FTIR) [52] and the resonant pumping of donor bound exciton transitions [51]. As discussed in section 2.1.1, the large hyperfine splitting of bismuth donors in silicon allows for vast opportunities within quantum technologies. One such application is the ability to control the spin of the donor through optical pumping. Known as hyperpolarisation, this involves emptying a given spin state via photoexcitation of an appropriate resonant transition thus leaving the donor species largely in the un-pumped groundstate. FTIR is not a suitable experimental technique to achieve this as it does not use a coherent, monochromatic light source so is not able to pump a specific transition. Therefore the resonant formation of donor bound excitons is the only candidate for optical pumping.

While the groundstate of the $D^0X$ itself is not subject to hyperfine coupling, due to the formation of a $S=0$ electron spin singlet, the hyperfine structure of the bismuth donor is still reflected in the formation energy required to create a $D^0X$ complex. This due to
the fact that the energy cost to bind a free exciton to a donor in the $F = 4$ or $F = 5$ groundstate differs by an amount equal to the energy separation between the two split spin states. Figure 2.5 displays an illustration of the level schemes involved in the formation of $D^0X$ states corresponding to both $F = 4$ and $F = 5$ bismuth donors. There is a certain amount of debate regarding an appropriate level scheme to represent the formation of the $D^0X$ complex that satisfactorily incorporates the hyperfine splitting of the ground state nucleus. With this in mind, figure 2.5 provides two different schemes that employ different energy scales to illustrate the manifestation of this splitting in the formation of donor bound excitons, (a) and (b) respectively. In figure 2.5(a) the zero energy point is set to be the silicon valance band in an effort to represent the binding energies of the donor complexes relative to the conduction band. The hyperfine splitting of the groundstate bismuth donor is illustrated and the two different channels of $D^0X$ formation are indicated as dashed arrows labeled 1 and 2 which represent the capture of an exciton by a neutral donor in the $F=4$ and $F=5$ spin states respectively. Alternatively, figure 2.5(b) provides a somewhat simplified picture,
the conduction and valance band energy levels have been omitted and the formation of the 
$D^0X$ is purely represented as the energy required to be introduced into the system in order  
to transition a neutral donor into a bound exciton. Here the hyperfine splitting of the donor 
groundstate is clearly indicated and the $D^0X$ is represented as a single fixed energy level. The 
drawback with this representation is that the energy scale is misleading as it suggests that 
the binding energy of the $D^0X$ is more than 1 eV greater than the donor level. Plainly this  
is not the case and the 1 eV energy scale is largeley due to the cost of promoting an electron  
from the valance band during the initial formation of the exciton itself. However this scheme  
is commonly used research articles reporting on the utilisation of $D^0X$s in the readout of  
Si:Bi hyperfine structure [52]. In both cases the outcome is the same, that is two available  
transition energies corresponding to the formation of a $D^0X$ complex from an exciton binding  
to a active bismuth donor in either the $F = 4$ or $F = 5$ groundstate. This corresponds to an  
energy requirement of 1146.947 meV and 1146.916 meV respectively. Moving forward figure  
2.5(a) will be used in the remainder of this thesis to illustrate the various channels of $D^0X$  
formation and recombination that have been utilised in this work.

Under the appropriate experimental conditions the bismuth ground state hyperfine split- 
ting is observable in both $D^0X$ photoluminescence, PL, and photoconductivity, PC, measure- 
ments. Figure 2.6(a) displays the repeatability of hyperfine structure in both PL and PC  
spectroscopy techniques, taken from Saeedi et al [52]. A full overview of the experimental  
procedure required in a PC measurement of the Si:Bi hyperfine structure using $D^0X$ spec- 
troscopy can be found in section 3.2.2. Taken from the same study, and presented in figure  
2.6(b), is an example of the hyperpolarisation of the bismuth donor groundstate using $D^0X$  
optical pumping. The effect of this polarisation is observed in the $1s(A1) \rightarrow 3p_{\pm}$ Rydberg  
transition as measured using THz FTIR.

At the time that the work in this thesis was being done there had been no reports in  
literature of bismuth zero field $D^0X$ spectroscopy using an implanted Si:Bi sample. Thus  
one of the primary motivations of this body of work is to determine whether it is possible  
to resolve the hyperfine structure of implanted bismuth donors in silicon or if implantation  
damage and the resulting lattice disorder will inhibit this feature. Being able to observe  
this splitting in an implanted substrate would be of great significance in determining the  
suitability implantation as a fabrication technique for devices in quantum technologies.
Chapter 3

Experimental techniques

In this body of work numerous experimental procedures have been implemented in both the fabrication and characterisation of ion implanted Si:Bi substrates. This section will provide an overview of the various techniques used in this study to characterise samples.

Spreading resistance profiling measurements were performed by Solecon Laboratories, an external company specialising in semiconductor characterisation. The photoluminescence spectra of implanted samples was measured in a collaboration with Prof. Kevin Homewood at the University of Surrey under the experimental guidance of Dr Manon Lourenco. Electrically detected FTIR measurements were performed at the London Centre for Nanotechnology, based at University College London, under the supervision of Dr Guy Matmon. Finally, THz photoconductivity spectra of implanted devices using a free electron laser were measured at the FELIX Laboratory, an international laser facility based at Radboud University in the Netherlands. These experiments were performed with the assistance of Dr Kamyar Saeedi and Dr Viktoria Eless. All other experimental techniques discussed in this chapter were undertaken at the University of Surrey under the guidance of Dr Steve Clowes.

3.1 Spreading resistance profiling

Before considering any effects related to implantation damage or lattice strain, it is first necessary to simply determine whether any bismuth ions have successfully integrated within the silicon crystal. Furthermore, it is useful to identify the depth of active donor centres in order to discern whether any diffusion has taken place during annealing. It is therefore beneficial to include a measurement that allows for the determination of both the electrical
activation of donors, and their incorporation position within the silicon crystal. Fortunately, there are various experimental techniques from which this information can be extracted. A common example, which has been used in this study, is known as spreading resistance profiling, SRP, [92]. SRP is a process where the implanted sample is beveled such that the entirety of the implantation profile is exposed down an angled surface. The two terminal resistivity is then measured across the face in order to evaluate the electrical properties of the substrate as a function of surface depth. SRP analysis takes advantage of the well defined room temperature relationship between dopant concentration, \( N \), and resistivity, \( \rho \),

\[
\rho = (N e \mu)^{-1} \tag{3.1}
\]

where \( e \) and \( \mu \) are the electron charge and mobility respectively. By identifying the two terminal resistivity of the substrate at iterative steps down the beveled surface, it is possible to infer the active donor concentration as a function of depth and hence quantify the position of implanted impurity centres. SRP measurements work under the assumption that the dominating source of electrons in the conduction band are directly from implanted donors, which are all ionised at 300 K.

Therefore it is necessary that the density of implanted bismuth ions is significantly greater than any bulk doped impurities in the substrate. Additionally, it is possible that free electrons can be compensated for by the presence of anomalous positive charges, which may be
caused by lattice defects, and would thus yield misleading results. However, even with these limitations, SRP remains an extremely useful characterisation techniques that is commonly used in the semiconductor industry. In this study bismuth ions have been implanted into substrates that contain a bulk concentration of phosphorus donors. An illustration of the SRP procedure, with a specific relation to these samples, is displayed in figure 3.1. The co-doped implant region of the substrate is indicated as shaded purple whereas the single phosphorus bulk doped substrate is shown as grey. The path of the two terminal resistivity measurement down the substrate face, beveled at an angle \( \phi \), is denoted by a dotted line. SPR measurements in this study use a beveling angle of 0.005 \( ^\circ \) and 4 \( \mu \)m iterative steps to evaluate depth down the substrate and at each probe position resistivity values are measured using tungsten carbide probes with a bias voltage of 5 mV to quantify active donor concentration.

3.2 \( D^0X \) spectroscopy

As discussed previously, \( D^0X \)s are a powerful tool in the characterisation of group V donors in silicon. A full overview of the formation and characteristic properties of the \( D^0X \) complex can be found in section 2.3 however, in short, donor bound excitons are formed when an electron-hole pair, \( X \), becomes bound to a neutral donor. As a result of the chemical shift in the groundstate donor binding energy, known as the central cell correction, both the binding energy and subsequent recombination energies of \( D^0X \)s have a strong dependence on the species of the donor itself. Therefore observation of both the radiative and non-radiative emissions of donor bound excitons can reveal much about the species of donors in a given system and their properties.

In this section a summary of two different \( D^0X \) spectroscopic techniques is provided, both methodologies are utilised in the succeeding results chapters.

3.2.1 Above bandgap \( D^0X \) photoluminescence

Above bandgap photoluminescence, PL, is a spectroscopic technique that is widely used in the characterisation of various semiconductor systems [93]. It is favored as it is a non destructive mechanism that allows for the identification of properties of both intrinsic semiconductors and extrinsic impurity states. In the context of this body of work, above bandgap PL measurements have been used as a tool to both identify the presence of electrically active
bismuth donors and uncover some information regarding the quality of incorporation into the silicon lattice.

In intrinsic semiconductors, under illumination from above bandgap light, valance band electrons are photoexcited into the conduction band and subsequently form free excitons, $X$. Upon recombination the exciton self-annihilates and a photon is emitted that matches the semiconductor band gap energy. The luminescence is then measured spectroscopically to allow for an identification of the exciton binding energy. The luminescence energy of a free exciton complex is discussed in section 2.3. However, in the case of silicon, which is an indirect bandgap material, emission from direct electron relaxation is heavily suppressed as it is required that crystal momentum be conserved. Therefore recombination events of free excitons in silicon must be accompanied by the formation of an appropriate recoil phonon to compensate for the momentum mismatch. Consequently in luminescence measurements spectral features corresponding to free exciton recombination are heavily suppressed and instead phonon assisted transitions are observed. Figure 3.2 displays a measured above bandgap luminescence spectra of intrinsic silicon measured at 20 K. The luminescence spectra contains two significant peaks at 1.098 eV and 1.138 eV. Using equation 2.2 the binding energy of a free exciton is calculated to be 14.7 meV and knowing the low temperature silicon bandgap energy to be 1.17 eV the free exciton luminescence is expected to be at approximately 1.155 eV. However, for the reasons discussed, that transition is not present in figure 3.2, instead luminescence corresponding to phonon assisted recombination are measured. It is well known that significant phonon modes exist at energies of $18.4\pm0.2$ meV and $58.0\pm1$ meV [94] which are referred to as the transverse acoustic, TA, and transverse optical, TO, phonons respectively. Therefore, it stands to reason that phonon assisted recombination of free excitons in silicon will be shifted down in energy by an amount equal to the corresponding phonon energies. Thus the high and low energy peaks in figure 3.2 can be identified as the silicon BG(TO) and BG(TA) phonon transitions.

Above bandgap photoluminescence is also an extremely effective technique for characterising extrinsically doped semiconductors. The introduction of donors (and acceptors) into silicon has a significant affect on the luminescence properties of the substrate such that additional channels of emission become available. These transitions arise from the creation and subsequent recombination of donor (or acceptor) bound exciton complexes. This study will concentrate on the characteristics of $D^0X$ complexes in ion implanted Si:Bi which have a well established recombination energy of 1.147 meV.
Similarly to intrinsic band gap transitions, luminescence from the recombination of $D^0X$ states can also be assisted by the creation of a phonon. However unlike intrinsic transitions no-phonon, NP, recombination is also allowed whereby excess crystal momentum is transferred into the silicon lattice via the impurity center itself. Therefore multiple peaks corresponding to the emission of $D^0X$ states are present in luminescence spectra. This is useful as certain $D^0X$ energy transitions are known to be in close proximity to silicon bandgap transitions and therefore it can be difficult to resolve the specific features of the PL strength. Furthermore the intensity ratios of corresponding no-phonon and phonon assisted luminescence centres are well understood which allows for the evaluation of various material properties [83]. An additional benefit of a measurement of this nature is the fact that the $D^0X$ binding energy scales with the donor binding energy. This therefore means that each species of dopant will have different $D^0X$ transition energies that are easily identifiable.

Figure 3.3 displays the experimental layout implemented in this study and a level scheme illustrating the formation, and subsequent recombination, of $D^0X$s utilised in this measurement. Both no-phonon and phonon assisted luminescence is represented in figure 3.3 (b) and (c) respectively. For the measurements in this study, above band gap excitation was provided by a 200mW, 532nm laser which was incident on the sample contained within a liquid helium cooled HV chamber held at a temperature of 10K. The incident laser was modulated using a
Figure 3.3: a) Schematic diagram of experimental setup for above bandgap photoluminescence measurement. b & c) Level schemes illustrating the formation and radiative recombination of $D^0 X$ states during above bandgap photoluminescence measurements, without and with the formation of an accompanying phonon respectively. For simplicity the hyperfine structure of the donor groundstate is not include in the level schemes.
optical beam chopper which, used in conjunction with a 5209 single phase lock-in amplifier, was used to filter out any signal from background noise. The emitted luminescence signal was analysed using a 1 m SPEX spectrometer using a slit width of 1mm and measured using a germanium detector with a diameter of 5mm and a sensitivity of 1 mV. This corresponds to a spectral resolution of approximately 0.5 meV and a resolving power of 2000.

### 3.2.2 Resonant $D^0X$ photoconductivity

In the context of this study, above bandgap photoluminescence is utilised primarily as a technique to identify the global properties of our substrates and further confirm of the presence of active bismuth donors. However, to fully evaluate the quality of incorporated bismuth impurities, the implementation of a more specialised methodology is necessary. In this section a measurement technique, henceforth referred to as resonant $D^0X$ photoconductivity, is introduced as a method to directly interact with implanted bismuth donors.

The formation energy of the Si:Bi $D^0X$ complex is known to be 1147meV (1081nm) and therefore, by optically pumping bismuth donors resonantly at this energy, it is possible to directly form $D^0X$ states. While photoluminescence measurements utilise the optical emission channel of $D^0X$ recombination, photoconductivity employs the much stronger Auger process. This corresponds to, upon exciton self-annihilation, the donor electron gaining enough energy to be promoted far into the conduction band and hence be measured electrically. Therefore, a large population of $D^0X$s being resonantly formed will cause a significant change in the electrical properties of the silicon which can be measured. Furthermore, due to the extremely large groundstate hyperfine splitting of bismuth donors, it is possible to differentiate between forming $D^0X$ states using $F = 4$ or $F = 5$ bismuth nuclei. Of course, this is provided that the pump laser has a line width that is much smaller than the separation between the two states that are attempting to be resolved. Therefore, by scanning the pump laser over the energy range of the Si:Bi $D^0X$ formation, and measuring the electrical response of the substrate, it is possible to spectroscopically resolve the two spin states of the ground state bismuth donors. This is a extremely useful technique as the properties of this phenomena have been very well characterised in bulk doped Si:Bi substrates and therefore a comparison with an equivalent implanted sample will be a strong indication of the quality of implanted donor incorporation. Furthermore, the quality of extracted spectra would allow for the inference of any sources of strain that remain the implantation procedure. Figure 3.4(c & d) provides level schemes depicting the photoexcitation and subsequent Auger re-
Figure 3.4: (a) Schematic diagram of experimental setup for resonant $D^0X$ photoconductivity measurement. (b) Illustration of ‘wrap around’ capacitor plate substrate contacting. (c & d) Level schemes illustrating the resonant formation and Auger recombination of $D^0X$ states during photoconductivity measurements. A & B display $D^0X$ formation for bismuth donors in spin up and spin down hyperfine states respectively.
combination of $D^0X$'s formed using bismuth donors in the $F = 4$ and $F = 5$ spin states respectively.

Figure 3.4 also displays a schematic illustration of the $D^0X$ experimental setup and sample contacting technique (a & b respectively). The pump laser was provided by an amplified, tunable external cavity infra-red diode laser source with an output power of 80 mW. The wavelength of the emitted light is swept by applying a tunable voltage bias across a piezo controlled cavity mirror. Prior to amplification, a small fraction of coherent light is split off from the main path using a pick-off beamsplitter and subsequently analysed using a wavemeter for the purposes of calibration. Crucially the laser has a linewidth of less than 1 µeV which is small compared to both the splitting and linewidths of the spectral features that are of interest in this measurement. Samples were held in a liquid helium cooled bath cryostat at a temperature of 10K and electrical signal was recorded using an AC biased lock in technique. While the ground state hyperfine splitting of bismuth donors in silicon is comparatively much larger than any other group V donor, it is still an exceedingly sensitive measurement and therefore is very much subject to strain. In order to be able to resolve the individual spin states, it is necessary to contact the substrate in such a way that induces as little strain as possible. For this reason the non-intrusive ‘wrap around’ capacitor plate contact geometry has been developed (figure 3.4(b)) [20]. This consists of implementing two pieces of copper foil and wrapping them around either side of the substrate to act as capacitor plates. It is important for this detection technique that even an uniform coverage of the substrate is achieved for each plate electrode whilst also leaving a suitably sized gap between the two to allow for optical illumination. Additional care is also taken during measurements to avoid introducing mechanical strain to the substrate during the mounting procedure. The dielectric change of the substrate caused by a change in conduction band population caused by $D^0X$ recombination is clearly detectable capacitively and hence $D^0X$ photoconductivity spectra can be extracted without introducing strain to the substrate.

3.3 Low temperature Hall measurements

The next experimental technique used in this study is low temperature Hall measurements which are implemented in an effort to extract information regarding the defect population incorporated into ion implanted Si:Bi samples. Understanding the transport properties of a semiconductor under an applied external magnetic field is an extremely powerful charac-
terisation tool that has various applications from uncovering its basic material properties to deciphering information regarding lattice defect states and strain. The most widely used of such techniques is known as the Hall effect whereby, in a four terminal contact geometry, current, \( I \), is drawn across a substrate with an applied magnetic field, \( B \), acting perpendicular to the plane of the sample. This field has the effect of inducing a voltage drop, \( V_H \), across the sample perpendicular to the direction of current which allows for the determination of a material parameter known as the Hall resistivity, \( R_H \). Figure 3.5(a) provides an illustration of the Hall terminal geometry and the corresponding relation is expressed in equation 3.2, where \( d \) is the thickness of the sample.

\[
V_H = R_H \frac{IB}{d}
\]  

(3.2)

Here \( R_H = (ne)^{-1} \) where \( n \) is the charge carrier density and \( e \) is charge. As equation 3.2 illustrates, the simple one carrier Hall model describes a relationship between applied magnetic field and induced voltage drop that is linear in nature. However, in this study it is found that in order to sufficiently represent measured data it is necessary implement the 2-carrier Hall model. As a consequence of an additional population of charge carriers within
the system, the Hall resistivity is no longer described by equation 3.2 and rather has a more complex relationship with applied magnetic field. In order fully extract the contribution of each individual charge type within the material, it is first necessary to understand the conductivity tensor, \( \sigma \). During a Hall measurement it is clear that the conductivity of the material is anisotropic in nature, with components both parallel and perpendicular to the direction of applied current. The separate constituent elements of \( \sigma \) are expressed in equation 3.3.

\[
\begin{pmatrix}
\sigma_{xx} & \sigma_{xy} \\
\sigma_{yx} & \sigma_{yy}
\end{pmatrix} = \frac{\sigma_0}{1 + \mu^2 B^2} \begin{pmatrix} 1 & -\mu B \\ \mu B & 1 \end{pmatrix}
\]

(3.3)

Where \( \sigma_{xx} = \sigma_{yy} \) and \( \sigma_{xy} = -\sigma_{yx} \) and \( \sigma_0 = n e \mu \) represents the conductivity at \( B = 0 \). To represent the contributions of both types of charge carriers in the transport measurement it is necessary to sum the individual conductivity terms of \( \sigma_{xx} \) and \( \sigma_{xy} \) such that,

\[
\sigma_{xy} = \sigma_{xy,1} + \sigma_{xy,2} = \pm \frac{n_1 e \mu_1^2 B}{1 + \mu_1^2 B^2} \pm \frac{n_2 e \mu_2^2 B}{1 + \mu_2^2 B^2}
\]

(3.4)

\[
\sigma_{xx} = \sigma_{xx,1} + \sigma_{xx,2} = \frac{n_1 e \mu_1}{1 + \mu_1^2 B^2} + \frac{n_2 e \mu_2}{1 + \mu_2^2 B^2}
\]

(3.5)

where the subscripts 1 and 2 indicate the different charge carrier populations. The sign of the terms in \( \sigma_{xy} \) depend on the sign of the charge carriers, positive for electrons and negative for holes. Finally, in the context of a Hall measurement the physical quantity that is measured is the voltage drop across the sample, \( V_y \), therefore it is useful to represent equations 3.4 and 3.5 in terms of the resistivity tensor, \( \rho \), where \( \rho = 1/\sigma \). It is therefore possible to express the physical quantities \( \sigma_{xx} \) and \( \sigma_{xy} \) in terms of elements of the resistivity tensor, \( \rho_{xx} \) and \( \rho_{xy} \).

\[
\rho_{xy} = \frac{\sigma_{xy}}{\sigma_{xy}^2 + \sigma_{xx}^2}
\]

(3.6)

\[
\rho_{xx} = \frac{\sigma_{xx}}{\sigma_{xy}^2 + \sigma_{xx}^2}
\]

(3.7)

Where \( \rho_{xy} \) is resistivity in the direction perpendicular to the applied flow of current (known as the Hall resistivity) and \( \rho_{xx} \) is the resistivity parallel to the current which is related to the Van Der Pauw resistance. The latter term (expressed in equation 3.7) is utilised later in this section. Therefore, using equations 3.4, 3.5 and 3.6 it is possible to generate a fit to measured
\( \rho_{xy} \) data and extract parameters corresponding to the sheet density, \( n \) and mobility, \( \mu \) of each charge carrier type.

In an effort to reduce the dimension of the fitting parameter space, \( n_1 \) was calculated using \( n_2, \mu_1 \) and \( \mu_2 \) in conjunction with the zero field Van der Pauw resistivity which was measured at each temperature iteration. The van der Pauw contact geometry is illustrated in figure 3.5(b) where current is passed through one side of the contact and the voltage drop is measured across the opposite edge of the sample. The resistance measured from this voltage is known as the van der Pauw resistance, \( R_{vdP} \), which is related to the resistivity parameter, \( \rho_{xx} \) using equation 3.8.

\[
\rho_{xx} = \frac{\pi R_{vdP}}{\ln 2} \quad (3.8)
\]

By considering equations 3.4 and 3.5 at the limit where \( B = 0 \) it becomes clear that, under this condition, equation 3.7 reduces to \( \rho_{xx} = 1/\sigma_{xx}(B = 0) \). Moreover equation 3.5 becomes \( \sigma_{xx}(B = 0) = n_1 \mu_1 + n_2 \mu_2 \). Therefore it becomes possible to express one of the four fitting parameters in terms of the remaining three and \( R_{vdP} \), which is measured, thus reducing the parameter space to three. In the context of this work the sheet density of the first charge carrier, \( n_1 \), was eliminated from the fitting procedure using this technique.

Experimentally Hall measurements in this study were performed using magnetic fields up to \( \pm 2 \) T at temperatures ranging from 10 K to 24 K. Samples were fashioned into a square geometry and silver contacts were deposited at each corner onto the surface of the substrate to allow for resistivity values to be measured using both standard Hall and Van der Pauw orientations [95]. Contacts were deposited onto the surface of the silicon substrate to specifically address the transport properties of charge carriers within the implanted bismuth layer region. A low temperature measurement of the free charges within implanted samples will allow for a better understanding of the effectiveness of thermal annealing and hence identify any regions of charged implantation defects.

## 3.4 THz spectroscopy

Analogous to the Rydberg electron transitions in hydrogen, donors in silicon are also known exhibit similar spectral transitions under optical illumination [78]. However, while hydrogen transitions are largely confined to the ultraviolet part of the electromagnetic spectrum, donors in silicon find themselves in the more technically onerous 9 to 18 THz (37 to 74 meV) region [11]. The challenges in experimentally generating coherent light sources of this en-
Figure 3.6: The Rydberg absorption spectrum of Si:Bi at a temperature of 1.5 K, measured using transmission FTIR spectroscopy. Taken from [52].

Energy are well established [77] however there are two techniques that are commonly used to measure the excitation spectra of these systems. These techniques are Fourier-transform infrared spectroscopy, FTIR, [96] and using a free electron laser, FEL, [97] which overcome these technical challenges using different methodologies. Figure 3.6 displays an extremely high quality THz absorption spectrum of bismuth donors in silicon, measured using FTIR. Notably, the resolution of this measurement is high enough that it was possible to observe transitions from each of the hyperfine split bismuth groundstates. Typically measurements of bulk doped substrates excitation spectra are recorded by measuring the transmission of light passing through the substrate. However, as the absolute number of donors decreases, an optical measurement of this nature becomes more and more challenging. Therefore, for measuring implanted samples, it is necessary to utilise their electrical response to THz illumination.

FTIR and FEL spectroscopy have been used in this body of work to measure the orbital excitation spectrum of implanted bismuth donors in silicon. Therefore this section will provide an overview of each experimental procedure.
3.4.1 Electrically detected FTIR

FTIR is a spectroscopic technique that is commonly used as a characterisation measurement of various different material systems including group V donors in silicon \(^{[96]}\). Analysis involves generating an absorption spectrum using a combination of a broadband infrared light source and a Michelson interferometer. A schematic diagram illustrating the FTIR setup used in this study is provided in figure 3.7(a). As light is emitted from the infrared source, it passes a beam splitter such that 50% propagates through towards a reciprocating mirror and the other half is reflected towards a mirror that is fixed in place. Once both beams are reflected back they meet at the beamsplitter at which point they recombine and interfere either constructively or destructively depending on the optical path difference between the two arms of the interferometer. However, as the infrared source is broadband, each frequency of light will undergo a different degree of interference. Therefore, as the position of the moving mirror is changed, the light reaching the substrate will have a different spectrum and will induce a different excitation spectrum in the silicon accordingly.

Typically, in a measurement of this nature, the excitation spectrum would be measured by detecting the amount of light transmitted through the sample as a function of the mirror position. This would generate an interferogram which can be Fourier transformed to extract spectral information regarding the light absorbed by the sample. However, as the number of donors decreases, the strength of this signal becomes challenging to measure because the required detection sensitivity becomes unfeasibly high. Therefore, for a FTIR measurement of implanted bismuth donors in silicon, a more sensitive detection mechanism is required. In this study electrical detection of FTIR interferograms has been implemented such that interactions of the substrate impurities with the infrared light are interpreted as changes in the conduction band population of the silicon within the region of the implanted bismuth donors. In effect, the sample itself is now acting as the detector during this measurement and, by recording the device photocurrent as a function of mirror position, an interferogram can be generated which is analogous to an optically detected equivalent. Naturally, for this technique to be effective, it is required that the interaction of the substrate with the incident light corresponds to a change in conduction band population. As such, the various mechanisms through which electron orbital transitions can contribute to donor ionisation are discussed in section 3.5. An example of a typical interferogram generated by a measurement of this nature is presented in figure 3.7(b). Fourier transform photocurrent spectroscopy is
Figure 3.7: a) Schematic illustration of the electrically detected FTIR experimental infrastructure used in this study. b) A typical example of an interferogram measured using this technique. c) Electrically detected FTIR measurements of the silicon bandgap at a temperature of 10 K. Indicated as a dotted blue line is the expected bandgap energy at that temperature (1.17 eV).
a extremely useful technique for measuring small numbers of donors in silicon and also has been used in the characterisation of various thin film materials and also silicon solar cells [98, 99]. A more thorough review of this technique can also be found in reference [100].

Interferograms record data in the time domain and therefore, in order to extract spectral information about the sample in frequency space, it is necessary to mathematically process the information using a Fourier Transform [101]. The Fourier Transform, \( G(f) \), of a given interference pattern defined by the function \( g(t) \) can be evaluated using the following equation.

\[
G(f) = \int_{-\infty}^{\infty} g(t)e^{-2\pi ift} dt
\] (3.9)

However, due to the fact that interferograms are recorded as a set of discretised data points equation 3.9 is not practical to use during FTIR measurements. Therefore fast Fourier Transform, FFT, algorithms are typically utilised whereby the frequency domain spectra is calculated from an interferogram defined by an experimentally measured data set [102]. FFTs also have the benefit of being much quicker and less computationally exhaustive than alternative discrete Fourier Transform algorithms, DFTs [103]. Figure 3.7(c) displays an example measurement of the silicon bandgap at a temperature of 10 K using this technique. The presented spectrum was measured with an experimental setup as described in figure 3.7(a) using a halogen lamp as a source of polychromatic black body infrared radiation. Also included as a dotted line superimposed onto the spectrum is the expected bandgap energy of silicon at 10 K which is known to be 1.17 eV [86].

In the characterisation of group V dopants in silicon the FTIR light source that is used emits a range of photons in the mid-infrared region to encapsulate the donor orbital transition energies. Additionally, as the transitions of interest are in the same spectroscopic region as numerous water absorption lines, the whole system is kept under vacuum to remove the moisture in the air. A spectral range of approximately 9 to 17 THz (37 to 70 meV) was measured to interact with both bismuth and phosphorous donors. The mirror modulation was set to 10 kHz and each spectrum was averaged 100 times to increase signal to noise. Chapter 6 includes a full discussion of the results from electrically detected FTIR measurements using the implanted Si:Bi devices fabricated in this work.
3.4.2 FEL photoconductivity

While FTIR has significant benefits in terms of versatility and spectral resolution, it is limited in terms of power. Additionally, the fact that it uses a non–monochromatic light source means it can not be used to directly pump a single optical transition. There are a handful of light sources that emit coherent radiation in the 10s of THz spectral region, including methanol gas lasers [104], quantum cascade lasers [105] and even donors in silicon themselves [106], although many such regimes suffer in terms of output power or tunability. However one source that excels in both of these areas are known as free electron lasers, FELs [107].

Free electron lasers use electrons to generate a coherent source of THz radiation. Accelerated electrons are passed through a pair of arrays containing a series of alternating magnets known as an undulator. As they propagate they are forced by the alternating field profiles to oscillate in the plane of the undulator, and perpendicular to the direction of electron motion. This sinusoidal motion causes the electrons to emit photons in the direction that the electron is traveling with an energy defined by the frequency of oscillation. This is called as synchrotron or Bremsstrahlung radiation. The transverse electric field of the emitted radiation interacts with the transverse current generated by the electrons via a phenomena known as the ponderomotive force. This results an increase in the amplitude of oscillation for electrons that gain energy from the photons which contributes to a modulation in the longitudinal electron velocity and causes a bunching in the beam. Electrons within each bunch radiate coherently which contributes to further bunching until the electron beam is completely micro-bunched. This results in an exponential growth in radiation power. As a consequence of this process the light emitted from a FEL is a series of intense pulses of photons. The wavelength of the emitted radiation can be changed by either altering the energy of the electron beam or, more commonly, by adjusting the strength of the magnetic field through adjusting the magnet separation. Therefore the emission of a FEL is a short burst of coherent, extremely tunable, high power light which is arguably the best suited source for interacting with the orbital states of group V donors in silicon. Moreover, the extreme short pulses that are typical of these systems are ideal of the study of the electron dynamics within the donor systems relavient to this discussion. However it must be stated that the practical implications and running costs of a FEL are vast and therefore for any practical application within quantum technologies a suitable ‘table top’ alternative would be
Figure 3.8: a) A schematic illustration of the experimental implementation used in the spectroscopy of implanted devices using FELIX. b) The signal response of the MCT detector over the duration of the FELIX macropulse.
The free electron laser that has been used in this work is called FELIX (Free Electron Laser for Infrared experiments) which is based at Radboud University in the Netherlands. In this study FELIX has been used to resonantly pump the electron orbital transitions of implanted bismuth donors in silicon. The purpose of this measurement was to evaluate the effect that the FEL has on the electrical measurement of a device with a relatively small number of donors. Typically measurements of this nature at the FELIX facility have focused on optical detection of bulk doped substrates with a large number of donors. Therefore it is important to identify the practical differences when measuring a much smaller implanted device. Furthermore, spectroscopically measuring the devices in this study with FELIX allows for a direct comparison with FTIR as a technique and an evaluation of whether ion implanted Si:Bi devices are potential candidates for further experimentation using this technique.

Figure 3.8(a) provides an illustration of the experimental setup utilised in this study. Initially the FELIX beam is passed through a 90 degree beamsplitter with a transmission : reflection ratio of 98 : 2. The reflected beam is then focused using a parabolic mirror onto a mercury cadmium telluride, MCT, detector. This is measured because the power output of FELIX varies as a function of radiation wavelength and therefore calibration is required. The remaining fraction of transmitted light is focused onto the device which is mounted on a cold finger cryostat. As with the FTIR experimental setup, the system is contained within a vacuum chamber to eliminate the effect of absorption from moisture in the air. Light can be globally attenuated by a series of wire mesh filters that are contained within the FELIX beamline.

Optical radiation arrives in a series of macropulses with a duty cycle of approximately 10 µs/100 ms, within each macropulse light is further broken up into a series of bursts referred to as micropulses. These micropulses are of the order of ps in length with a repetition rate of around 25 MHz. Figure 3.8(b) provides the measured response of the MCT detector over the duration of the FELIX macropulse. The electrical response of the device is only measured when the sample is illuminated by the light. Spectra of donor states within the device region were measured by applying a voltage bias across the two contacts and measuring the electrical response as the wavelength of the THz illumination is swept. A full discussion of the mechanism by which THz illumination alters the electrical properties can be found in the following section.
Figure 3.9: An optical level scheme of a bismuth donor in silicon. Indicated are various electron transitions including the optical excitation of a ground state electron into a higher lying orbital state (1), the ionisation of an excited electron into the conduction band through interaction with a thermal phonon (2) and an impact event with an already free charge carrier (3). Ionisation of a bound electron via interaction with multiple photons is indicted (4).

3.5 Electrical detection of Rydberg transitions

The previous section provides an overview of the spectroscopic aspects of both electrically detected FTIR and FEL photoconductivity. However one thing remains to be considered is the mechanism through which pumping electron orbital transitions results in a measurable effect on the electrical properties of the substrate. In the FTIR example provided in figure 3.9 it is clear how the mechanism being studied, silicon inter-band transitions, has a significant effect on the conduction band population and hence can be detected electrically. However, when considering the spectroscopy of group V donor transitions it is less obvious as to how electrical measurements are possible. Therefore, it is useful to provide a discussion of the various mechanisms by which electron can be liberated into the conduction band from an excited state bound level.

Figure 3.9 provides an illustration of the various processes that can contribute to the promotion of a bound electron into the conduction band. This discussion will focus on 3 mechanisms, henceforth referred to as photothermal ionisation, PTI, impact ionisation, II, and multi-photon interactions. Firstly, PTI can be expressed as a two step process involving an electron being excited into a higher lying orbital state through the absorption of a THz
photon, then liberation into the conduction band via interaction with a thermal phonon (transitions 1 and 2 in figure 3.9). Similarly, II begins with the absorption of a photon to pump the electron into an excited state however the second step, that releases the bound electron into the continuum, occurs through a collision with an already free charge carrier (transitions 1 and 3). Finally, it is possible for the donor to be ionised through interaction with multiple photons. This can manifest either through the sequential absorption of two photons or through a coherent ionisation by two photons simultaneously. In the non resonant case the excited states is used as an intermediate. Although multi-photon processes have been demonstrated to have an effect on the ionisation of neutral donors in silicon [108], the mechanism is not very well understood in terms of the effect it has on the electrical measurements of devices under these experimental conditions. Therefore this will not be focused on in the discussion presented in this thesis. However, both photothermal ionisation and impact ionisation are of specific interest to this work and therefore will be explored in more detail in the following sections.

3.5.1 Photothermal ionisation spectroscopy

Photothermal ionisation corresponds to the ionisation of an excited electron through the interaction with a thermal phonon. This two step process is displayed diagrammatically in figure 3.9 (transitions 1 and 2) and can be expressed using equation 3.10,

\[ \sigma_f(\omega) = \sigma(\omega) I^{(n)}; \quad \omega = \omega_n \]  

(3.10)

where \( \sigma(\omega) \) is the absorption cross-section of the transition and \( I^{(n)} \) is the probability of thermal ionisation into the conduction band from the \( n \)th excited level. By comparison, an optical measurement based on the transmission/absorbance of incident radiation (as in figure 3.6) would depend solely on \( \sigma(\omega) \). Therefore the spectral intensities of a given transition will differ between an electrical an optical measurement by an amount proportional to \( I^{(n)} \). For thermal ionisation, \( I^{(n)} \) has been demonstrated to be,

\[ I^{(n)} \approx \exp \left( -\frac{E_n}{k_B T} \right) \]  

(3.11)

where \( E_n \) is the state binding energy [109]. Therefore equation 3.11 displays that there is an intimate relationship between the ionisation probability and the temperature of the system,
Moreover, it is clear that, for a fixed temperature, $I^{(n)}$ will be increased for bound states that are closer to the conduction band. Therefore, when compared to equivalent optical measurements, PTIS spectra will be weighted in favour of higher excitation levels as they are easier to ionise.

### 3.5.2 Impact ionisation

As illustrated in figure 3.9, ionisation of a bound electron can also occur through a collision with an already free electron in the conduction band. This is known as impact ionisation and has been reported in a handful of publications in relation to various material systems [110, 111] as a sudden increase of device current as the voltage bias is increased. In the context of phosphorus donors in silicon this threshold bias has been reported to occur at electric field values in the region of $0.5 \times 10^5 \text{ Vm}^{-1}$ to $1.2 \times 10^5 \text{ Vm}^{-1}$. This corresponds to the electric field required to accelerate electrons with enough energy to ionise neutral phosphorus donors through impact collisions. The average energy of free electrons in the conduction band, $E_0$, is given by,

$$E_0 = \frac{1}{2} m^* v_d^2 + \frac{3}{2} k_B T_e$$  \hspace{1cm} (3.12)

where $v_d$ is the electron drift velocity, and $T_e$ is the effective electron temperature. Typically the magnitude of $T_e$ depends on the number of electrons in the conduction band. For example if the population is high, then the electron–electron, $ee$, interaction will dominate over dopant or phonon scattering. This means that energy will be transferred between electrons and not lost to the environment which will result in $T_e$ being very high. This is known as the ‘hot electron’ regime which can dramatically increase the average energy of free charge carriers. However, in practice $T_e$ is a difficult parameter to define analytically and rather empirical values are often used [112]. Therefore for the purposes of this work the lattice temperature will be used in place of $T_e$ with the understanding that in practice the electron energy may be higher. However this will serve to demonstrate the minimum effect of impact ionisation on the systems that are of interest.

The number of ionisation events can be broken down as the product of three terms that are illustrated in equation 3.13

$$n A_{ii} N^0$$  \hspace{1cm} (3.13)
Figure 3.10: Calculated impact ionisation rates, $A_{ii}$, for a system of bismuth doped silicon as a function of applied electric field, $F$. Indicated are neural donors in either the $1s(A_1)$, $2p_\pm$ or $3p_\pm$ states.

where $n$ is the number of free charge carriers in the conduction band, $A_{ii}$ is the rate of impact ionisation events and $N^0$ is the number of neutral donors in a given state. Plainly $N^0$ is dictated by the device doping conditions and donor excitation/relaxation rate, while $n$ is related to the current density flowing through the device. $A_{ii}$ on the other hand is dependent of a range of system conditions. The formalism used in the context of this work follows the analytic solution first presented in Dierickx et al [113]. Here the average electron energy is defined using equation 3.12, with a probability distribution that is defined using Boltzmann statistics such that $f(E) = \exp \left( -E/E_0 \right)$. Next the cross-section of a ionisation event between an electron and a neutral donor, $\sigma_{ii}(E)$, is considered where the typical approach of electron collisions with a hydrogen atom is implemented. This is such that $\sigma_{ii}(E)$ is maximised when $E = 2E_n$ where $E_n$ is the donor electron binding energy. Finally the electron velocity, $v(E)$, is defined using the effective mass approximation such that $v(E) = \sqrt{(2e/m^*)}$. The average impact ionisation rate is then defined as follows.

$$A_{ii}(F) = \frac{\int_0^\infty f(E)\sqrt{E}v(E)\sigma_{ii}(E)dE}{\int_0^\infty f(E)\sqrt{E}dE} \approx a_{ii} \left( \frac{\mathcal{E}}{E_n} \right)^{-3/2} \exp \left( -\frac{E_n}{\mathcal{E}} \right)$$ (3.14)
Where \( a_{ii} \) is a constant pertaining to the donor state interaction cross-section and \( \varepsilon \) is a variable representing the average drift energy gained by the carrier. A full derivation of this expression can be found in reference [113]. Using equation 3.14, \( A_{ii} \) has been evaluated for a system of bismuth donors in silicon in the \( 1s(A_1) \) ground state and both the \( 2p_{\pm} \) and \( 3p_{\pm} \) excited levels. The distinction between states has been made by incorporating the various donor state binding energies and Bohr radii. Figure 3.10 indicates that an electric field of \( \sim 10^4 \text{ Vm}^{-1} \) is required to maximise \( A_{ii} \) for the excited Si:Bi donor levels whereas \( F > 10^5 \text{ Vm}^{-1} \) is required for the \( 1s(A_1) \) state. Additionally an overall reduction of \( A_{ii} \) is observed in the \( 1s(A_1) \) which is a manifestation of its lower interaction cross-section due to a smaller electron Bohr radius.

Plainly this is a very broad estimation but it does serve the purpose of demonstrating that there is a strong relationship between applied electric field and the rate of impact ionisation events. This is such that there is a extremely sharp increase in \( A_{ii} \) over only a moderate variation in \( F \). Furthermore it does also display that the field required to cause this onset decreases with increasing state binding energy. Therefore it is expected that impact ionisation is more significant for donors in higher orbital excited states. This feature will prove useful in the discussion of experimental results contained within chapter 6.
Chapter 4

Post implantation treatment of ion implanted Si:Bi

This chapter will focus on evaluating the optimum annealing treatment of implanted bismuth donors in silicon with a particular emphasis on applications within quantum technologies. Numerous characterisation techniques have been used to uncover the suitability of various annealing temperatures both in terms of maximizing the electrical activation yield and ensuring a quality of bismuth incorporation that supports quantum phenomena.

Initial characterisation will focus on evaluating various annealing temperatures purely in terms of the fraction of implanted bismuth ions that become substitutional within the silicon lattice and hence act as extrinsic donor centres. Spreading resistance profiling measurements have been used to identify the apparent implanted bismuth donor density profiles as a function of depth for each of the annealed samples in this study. This allows for an identification of both the EAY achieved for each treatment temperature and an inference on ion diffusion during annealing. Having established that bismuth donors have successfully been introduced into silicon lattice sites, the bulk of this chapter discusses the quality of said incorporation in terms of both spectroscopic and transport measurements. Donor bound exciton spectroscopy has been used as a tool for identifying the presence and characteristic properties of donors with regards to their post implantation annealing conditions. This has been achieved through an initial study of above bandgap $D^0X$ photoluminescence and ultimately by probing the zero field hyperfine structure of the Si:Bi groundstate using resonant $D^0X$ photoconductivity. Additionally, low temperature Hall measurements have been implemented in an effort to identify some of the sources of lattice defects introduced to the
silicon substrate during the implantation procedure.

This chapter is intended to act as an overview on the suitability of ion implantation as a fabrication technique of introducing bismuth donors in silicon for applications within quantum technologies.

### 4.1 Implanted Si:Bi samples

The samples in this study were fabricated using a chain of 5 high energy Bi\(^+\) implantation steps to introduce a large scale layer of bismuth donors that are well separated from the surface of the substrate. This regime was selected to produce samples with a large number of active bismuth donor centers that can be measured using conventional experimental techniques designed for the characterisation of bulk doped silicon wafers. A full overview of the experimental procedures used in this chapter can be found in chapter 3. Detection mechanisms include optical photoluminescence and non-intrusive electrical contacting. This allows for a direct comparison with bulk doped bismuth donors in silicon which have been very well characterised in literature.

Every substrate in this study was implanted using the same 5 energies and beam fluences unless otherwise stated. Table 4.1 provides the experimental bismuth ion implant energies and fluences used in the fabrication of samples. Ion beams used a tilt angle of 7\(^\circ\) to encourage channelling effects.

<table>
<thead>
<tr>
<th>Implant #</th>
<th>Energy (keV)</th>
<th>Fluence (10^{12}\text{cm}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2000</td>
<td>6.12</td>
</tr>
<tr>
<td>2</td>
<td>1400</td>
<td>2.40</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>2.40</td>
</tr>
<tr>
<td>4</td>
<td>700</td>
<td>1.38</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Table 4.1: Bi\(^+\) implantation energies and fluences used in the fabrication of samples in this study.
Figure 4.1: SRIM Monte Carlo simulation of Bi⁺ ion implantation into silicon using beam energies and fluences as specified in table 4.1. Filled distributions indicate individual implantation steps whereas the solid black line is the cumulative bismuth ion density profile.

Figure 4.1 displays a calculated depth profile corresponding to the bismuth ion implantation, including each of the 5 implantation steps and a cumulative implanted ion profile. Density distributions were calculated the Monte Carlo simulation software SRIM, which takes into account the ion straggling ranges and interactions with the target lattice during the implantation procedure. Figure 4.1 illustrates that using a series of implantations with energies and fluences as specified in table 4.1 corresponds to a broad distribution of bismuth ions with a flat top structure spanning approximately 100 nm to 600 nm below the surface of the target silicon lattice. The peak bismuth ion concentration has been estimated to be $3 \times 10^{17} \text{cm}^{-3}$ over the flat top region.

The silicon substrates used as the handle for ion implantation were 300 µm thick, ⟨111⟩ oriented and float-zone grown with a substrate resistivity of 7-8 Ωm from bulk doped phosphorus impurities. This corresponds to a volume phosphorus donor density of $6 \times 10^{14} \text{cm}^{-3}$. To repair crystal damage and incorporate bismuth atoms into lattice sites, substrates were annealed using a RTA temperatures of either 700 °C, 800 °C or 900 °C for 300 s. An atmosphere of N₂ was used to inhibit contamination.
4.2 Implanted Si:Bi depth profiles

Before considering the suitability of implanted bismuth donors as possible qubit states, it is first necessary to evaluate annealing temperatures purely in terms of the fraction of ions that successfully incorporate into the silicon crystal. This section will focus on maximizing the EAY of bismuth ions by varying the post implantation annealing temperatures and measuring the active bismuth donor concentration as a function of depth from the surface of the substrate.

As described in the previous section, the samples used in this study have been fabricated using a chain of 5 individual implantation steps with varying ion energies and fluences. Post implantation, substrates were furnace annealed at temperatures of either 700 °C, 800 °C or 900 °C for a duration of 5 minutes in an effort to both incorporate bismuth ions and repair silicon lattice damage incurred during the ion bombardment. Figure 4.1 displays a SRIM Monte Carlo simulation of a bismuth ion depth profile for an identical implantation chain to that which has been used to fabricate samples in this study. The simulation does not take into account what happens to implanted ions during the annealing procedure and therefore provides a useful reference of the location of bismuth ions immediately after the implant has taken place. Furthermore, it can be used as an indicator of an ‘ideal’ annealed substrate that has achieved a 100 % ion activation yield and undergone zero thermal diffusion of ions during heat treatment.

Spreading resistance profiling measurements have been used to evaluate the depth profiles for each of the annealed substrates in this study, the experimental procedure for a measurement of this nature is outlined in section 3.1. Figure 4.2 displays the measured charge carrier concentrations as a function of depth for each annealing temperature. For the sake of comparison the SRIM calculation has also been included in the plot. Figure 4.2 indicates that every sample fabricated in this study has successfully introduced a layer of electrically active bismuth donors in the region predicted by the SRIM calculation. However, it is clear that the achieved bismuth donor depth profiles vary significantly for certain annealing temperatures. To more fully compare each temperature, table 4.2 provides values for both the peak active bismuth donor density and EAY corresponding to each depth profile. Values for the peak donor density were evaluated by taking the statistical average of each distribution over their corresponding flat top regions while the EAY was determined by comparing the total integrated area of each profile and comparing with the known implant fluences.
Figure 4.2: Measured SRP depth profiles for substrates annealed at various temperatures (as indicated). Also included, as a solid black line, is a SRIM Monte Carlo simulation that illustrates the depth profile of a ‘perfect’ implanted sample with 100% EAY and zero thermal diffusion.

It is clear that there is a sizable reduction in both the peak bismuth donor density and EAY in the substrate annealed at 700 °C as compared to the other samples. This therefore suggests that the thermal budget provided by the annealing procedure at 700 °C is not sufficient to incorporate a higher fraction of implanted bismuth ions. However only a small difference is observed between samples annealed at 800 °C and 900 °C. It is found that annealing at 900 °C does correspond to an increased EAY however the value is not significantly more than the corresponding 800 °C sample. In fact the peak bismuth donor densities achieved are also very comparable, with the 800 °C substrate slightly higher. This

<table>
<thead>
<tr>
<th>Anneal Temp (°C)</th>
<th>Peak Bismuth Density (10^{17} \text{cm}^{-3})</th>
<th>EAY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>$1.33 \pm 0.04$</td>
<td>$59 \pm 3$</td>
</tr>
<tr>
<td>800</td>
<td>$1.42 \pm 0.06$</td>
<td>$53 \pm 2$</td>
</tr>
<tr>
<td>700</td>
<td>$1.07 \pm 0.03$</td>
<td>$41 \pm 2$</td>
</tr>
</tbody>
</table>

Table 4.2: Electrical activation yield of implanted bismuth donors in silicon with various annealing temperatures for 300 s.
therefore suggest that there is a mechanism limiting the incorporation of bismuth donors in these substrates that simply increasing the annealing temperature does not significantly improve. It is noteworthy that the donor concentrations used in these samples approaches the solid solubility limit of bismuth donors in silicon (\(2.3 \times 10^{17} \text{ cm}^{-3}\) [42]) and it is likely that this is effecting the activation yield. A further discussion of this phenomenon is included in a later chapter however this observation is consistent with other studies using similar implant densities [64].

It is also notable that, in all samples, a significant amount of active centres are measured to be at depths greater than 600 nm below the surface of the substrate, this therefore indicates that thermal diffusion of implanted bismuth ions has occurred before incorporation into the silicon lattice. However, while this observation is consistent between all samples, the number of donors measured at surface of the substrate appears to have a dependence on annealing temperature. This is such that a higher population of active bismuth donors is measured to be at the surface of the substrate in the 900 °C sample compared to the lower annealing temperatures. A possible explanation for this will be provided in this section and this feature will also be expanded upon further in the next chapter.

4.3 Above bandgap \(D^0X\) spectroscopy

The previous section has confirmed that ion implanted bismuth donors have successfully been incorporated into silicon and furthermore it has been established that there is a correlation between substrate annealing temperature and apparent bismuth donor electrical activation yield. While this is a useful statement, the utilised SRP measurements purely provide evidence for extrinsic doping of the silicon crystal through room temperature conductivity measurements, from which the location of active bismuth donor centres can be inferred. Therefore it would be beneficial to interact directly with the implanted donor states in order to both verify their existence and further understand their properties. In an effort to achieve this, above bandgap photoluminescence measurements have been implemented to identify the prescience of active bismuth impurity centres through the formation, and subsequent recombination, of Si:Bi donor bound exciton complexes. An overview of both the \(D^0X\) complex and the above bandgap photoluminescence experimental procedure can be found in sections 2.3 and 3.2.1 respectively. Figure 4.3 displays the measured PL spectra for each of the implanted Si:Bi samples in this study. Also included is the spectrum from a
Figure 4.3: Above bandgap photoluminescence spectra of ion implanted Si:Bi substrates annealed at 700 °C, 800 °C and 900 °C, illustrated as solid red, green and blue lines respectively. Dashed lines represent indicated transition energies. Substrates were measured at 10K.

non-implanted control substrate.

Figure 4.3 presents luminescence spectra measured over two different energy ranges, both contain features indicating the presence of electrically active implanted bismuth impurities and bulk doped phosphorus donors. Firstly, figure 4.3(a) displays that in every sample measured a small energy peak at 1150 meV is present, this aligns with the recombination energy of a Si:P $D^0X$ without the assistance of a phonon. This feature is observed in every spectrum (including the control) as all measured samples contained a fixed bulk phosphorus density of $6\times10^{14}$ cm$^{-3}$. The equivalent Si:Bi no-phonon $D^0X$ recombination peak is expected to be at an energy of 1147 meV and is clearly observable in spectra taken from the 900 °C and 800 °C annealed samples. While there is no significant spectral feature at this energy
in the substrate annealed at 700 °C, a small low energy shoulder is observed next to the Si:P $D^0X$(NP) transition which could be the result of a very low population of electrically active Si:Bi. However the EAY of implanted bismuth donors presented in figure 4.2 and table 4.2 would suggest that this feature should be much stronger and more comparable with the peaks from the 800 °C and 900 °C samples.

In figure 4.3(b) transverse optical phonon replicas of both the phosphorus and bismuth $D^0X$ transitions are presented. Broadly speaking, the spectral features observed in figure 4.3(b) are consistent with what is displayed in (a). This is such that every spectra contains a peak at 1092 meV corresponding to the Si:P $D^0X$(TO) transition however the equivalent bismuth line (expected at 1089 meV) is only present in the samples annealed at either 800 °C or 900 °C. As with figure 4.3(a) there is no reasonable indication of active bismuth donors in the substrate annealed at 700 °C. TO phonon replica peaks are observed to be 58 meV lower in energy than their no-phonon equivalent, this is consistent with the known energy of the silicon transverse optical phonon [94].

It is also apparent that the relative intensities of the $D^0X$ spectral peaks, for the two different species of donors, changes significantly between the no-phonon and transverse optical phonon assisted mechanisms. This is such that the Si:Bi $D^0X$(NP) peak is considerably stronger than the equivalent no-phonon phosphorus line whereas in the TO assisted spectra, both transitions are of much more comparable intensities. This is consistent with literature, where it has been reported that the relative strengths of no-phonon $D^0X$ transitions are 0.35 : 2.2 for phosphorus and bismuth impurities respectively. This relationship is attributed to the fact that $D^0X$ transitions take place through the coupling of a free exciton with a spatially fixed impurity centre. This coupling has been shown to scale with the ionisation energy of the donor species, therefore the no-phonon strength of a Si:P $D^0X$ is much less than an equivalent Si:Bi complex. However, the relative TO assisted $D^0X$ transitions were shown to be consistent between species. Knowing these characteristics, and using the phosphorus spectra as a control, it is possible to extract some useful information regarding the properties of the implanted bismuth donors in the samples. Table 4.3 provides measured values for the ratio of peak intensities between the two donor species for both the no-phonon and TO assisted transitions. Also included are literature values for the relative transition intensity ratios and the predicted TO transition ratios for each of the samples.

Table 4.3 displays that, for both annealing temperatures, the ratio of no-phonon $D^0X$ peak intensities is weighted heavily in favour of the bismuth donors. This is to be expected,
<table>
<thead>
<tr>
<th>Sample Temperature</th>
<th>$I_{P(NO)} : I_{Bi(NO)}$ (Measured)</th>
<th>$I_{P(TO)} : I_{Bi(TO)}$ (Measured)</th>
<th>$I_{P(TO)} : I_{Bi(TO)}$ (Predicted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>1 : 9.01</td>
<td>1 : 1.40</td>
<td>1 : 1.43</td>
</tr>
<tr>
<td>800</td>
<td>1 : 8.38</td>
<td>1 : 0.60</td>
<td>1 : 1.33</td>
</tr>
<tr>
<td>Literature*</td>
<td>0.35 : 2.2</td>
<td>1 : 1</td>
<td></td>
</tr>
</tbody>
</table>

* Literature transition intensity ratios [83].

Table 4.3: Relative peak intensities of no-phonon and TO phonon assisted $D^0X$ transitions between bulk phosphorus and implanted bismuth donors in silicon. Taken from figure 4.3.

However, it is also apparent that the relative bismuth signal strength is higher in the 900 °C substrate than in the 800 °C annealed sample. Using the fact that the concentration of bulk doped phosphorus donors is consistent between samples, this corresponds to an increase in active bismuth donor population of approximately 11%. This observation is in agreement with the EAY values provided by SRP measurements and displayed in table 4.2. Using the literature intensity ratios, and assuming a constant phosphorus density, it is possible to use the relative strength of the Si:Bi $D^0X(NP)$ transitions to estimate the expected strength of the equivalent TO phonon replica for each sample. Evaluation of this yields a predicted $I_{P(TO)} : I_{Bi(TO)}$ ratio of approximately 1 : 1.43 for the 900 °C sample and 1 : 1.33 in the 800 °C sample. By inspecting table 4.3 it is found the sample annealed at 900 °C is in good agreement with this prediction whereas Si:Bi $D^0X(TO)$ transition in the sample annealed at 800 °C is significantly weaker. In fact the experimental peak intensity is only ~45% of what would be expected given the equivalent no-phonon transition strength. This therefore indicates that there is a correlation between substrate annealing temperature and the strength of the Si:Bi $D^0X(TO)$ transition. One such explanation for this is that lower annealing temperatures are less successful in repairing the crystal damage incurred by the silicon lattice during the bismuth ion implantation procedure. A higher population of lattice dislocations and defects would have a significant effect on the rate of phonon scattering within the substrate [114, 115] and therefore it stands to reason that the $D^0X(TO)$ phonon replica transition will be weakened. This would also be compatible with the observation that the no-phonon transitions are consistent in the 900 °C and 800 °C samples given their associated bismuth donor EAY and it is only the TO transition that is affected.
4.4 Si:Bi implantation defects

The previous section illustrates a correlation between lower annealing temperatures and a suppression of the transverse optical phonon assisted \( D^0X \) transition of implanted bismuth donors in silicon. It is speculated that this behaviour is linked to an increase in silicon crystal inhomogeneities within samples annealed at lower temperatures. In an effort to better understand the nature and formation of implantation defects in ion implanted Si:Bi samples, low temperature Hall measurements have been implemented for each of the annealed substrates in this study. A full description of the experimental technique, and the proceeding analysis, can be found in section 3.3. Measured Hall resistivities for each of the annealed samples in this study, at various temperatures ranging from 10 K to 24 K, are presented in figure 4.4. This temperature range was selected to explore the free charge population at temperatures corresponding to the previous measurements and other techniques in this study.

The only channel of conduction in a typical sample of extrinsically doped n-type silicon (of non-degenerate doping concentrations) is the conduction band, therefore it is expected that a measurement of this nature should yield a linear Hall resistivity, as a function of magnetic field. Furthermore, by evaluating the gradient of this signal it is possible to extract information regarding both the conduction band population and free electron mobility. However, figure 4.4 displays that the Hall resistivities, \( \rho_{xy} \), measured in this study differ significantly from that which would be expected from a typical sample of extrinsically doped silicon. Moreover, the measured signal strongly indicates that there are multiple channels of transport within each of the implanted samples. This is such that, \( \rho_{xy} \) appears to vary approximately linearly for low magnetic field values however as \( B \) increases the signal undergoes a turning point indicating that a second free charge carrier is dominating the transport through the sample at higher magnetic field values. Furthermore, it is observable that the magnetic field value at which this turning point occurs increases when the substrate temperature rises. This therefore suggests that, as temperature is increased, the relative population of the two free charge channels also varies.

To more appropriately interpret this dataset the two carrier Hall model, as described in section 3.3, has been used to fit the signal presented in figure 4.4. Typical fits to each dataset at various temperatures are also presented in figure 4.5. The model for the two carrier Hall resistivity is described more fully in section 3.3 however for reference the expression for \( \rho_{xy} \)
Figure 4.4: Low temperature Hall resistivity measured as a function of applied magnetic field for ion implanted Si:Bi samples annealed at either 700 °C, 800 °C or 900 °C, (a), (b) & (c) respectively. Samples were measured at temperatures ranging from 10 K to 24K (as indicated in the figure).
Figure 4.5: Typical fits to low temperature Hall resistivity measured as a function of applied magnetic for ion implanted Si:Bi samples annealed at either 700 °C, 800 °C or 900 °C, (a–d), (e–h) & (i–l) respectively, at various temperatures. Distributions have been fit using the two carrier Hall model as described by equations 3.6-3.5.
in terms of $\sigma_{xy}$ and $\sigma_{xx}$ is stated again below.

$$\rho_{xy} = \frac{\sigma_{xy}}{\sigma_{xy}^2 + \sigma_{xx}^2} \quad (4.1)$$

$\sigma_{xy}$ and $\sigma_{xx}$ are the Hall conductivity values perpendicular and parallel to the direction of applied current as defined by,

$$\sigma_{xy} = \pm \frac{n_1 e \mu_1 B}{1 + \mu_1^2 B^2} \pm \frac{n_2 e \mu_2 B}{1 + \mu_2^2 B^2} \quad (4.2)$$

$$\sigma_{xx} = \frac{n_1 e \mu_1}{1 + \mu_1^2 B^2} + \frac{n_2 e \mu_2}{1 + \mu_2^2 B^2} \quad (4.3)$$

where $n_1$ and $\mu_1$ are the carrier sheet density and mobility values corresponding to charge type 1 and $n_2$ and $\mu_2$ are equivalent parameters for charge type 2. By fitting each of the measured Hall resistivities using equations 4.1 - 4.3 it is possible to extract values for the charge carrier densities and mobilities for each sample at a given temperature. Furthermore, by identifying the sign of each term in equation 4.2, it is also possible to differentiate between contributions from electrons and holes. Figure 4.6 displays extracted sheet density and mobility parameters for each of the annealed samples at temperature setpoints ranging from 10 K to 24 K.

Figure 4.6 presents that, at low temperatures, the Hall resistivity for each sample contains contributions from the conduction of both electrons and holes. It is observed that the population of holes in each of the samples is relatively consistent as a function of measurement temperature but differs significantly between each of the samples annealed at a different temperatures. Conversely, the sheet density of electrons is more consistent as the annealing temperature of the substrate is changed but increases strongly as the temperature of the measurement rises. However it is apparent that the measured charge carrier densities far exceed that which would be allowed at 10 K by the law of mass action [116]. Therefore it must be inferred that the origin of these differing carriers are spatially separated into two distinct population regions between which there is limited charge recombination. Furthermore, it is apparent that annealing the implanted substrate at higher temperatures corresponds to a decrease in p-type charge carrier density which suggests that the mechanism of which holes are being created is directly related to damage incurred by the lattice during ion implantation. However it is also notable that even for samples annealed at the highest
Figure 4.6: (a-c) Charge carrier sheet densities as a function of temperature for ion implanted Si:Bi substrates annealed at 700 °C 800 °C or 900 °C. (d-f) Charge carrier mobilities as a function of temperature for corresponding samples. Markers displayed as + indicate holes whereas – are electrons.

At higher temperature, a significant proportion of p-type carriers remain active.

There is some precedent in literature that relates ion implanted Si:Bi substrates with the observation of positively charged defect states. For example, [74] reports on ambipolar charge behaviour of activated bismuth ions at the surface of the silicon lattice using STM measurements. Here it is postulated that the positive charge originates from bismuth ions that incorporate into the lattice with a alongside a crystal vacancy. Additionally, [75] observed a difference in bismuth donor activation yields between electrical and Rutherford back scattering measurement techniques. This discrepancy was attributed to a population of positive charge defects that exist at the surface of the silicon crystal and act as a source of compensation for ionised bismuth donors. Furthermore, it has been shown using RBS
that during ion implantation a thin, heavily damaged layer is generated at the surface of the substrate with an amorphisation rate that is proportional to the nuclear energy deposition at the interface [117]. Therefore it can be reasoned that the origin of measured p-type charge transport is a high density surface layer of lattice defects which act as acceptor centres that are caused by the implantation. Conversely, the measured electron signal can be attributed to the bulk doped phosphorus donors of which a very small fraction be ionised at 10 K through black body radiation.

Furthermore, the behaviour of the extracted electron mobility values are relatively consistent between each of the annealing temperatures in this study. It is observed that for each sample at 10 K, $\mu_1$ (electrons) is approximately $10^5$ cm$^2$V$^{-1}$s$^{-1}$ and subsequently decreases with increasing temperature. A reduction of mobility of increasing temperatures can be attributed to an increase in electron scattering caused by a higher population of phonons and ionised donors [118]. Additionally shown in figure 4.6 is that the mobility of p-type carriers also depends strongly on annealing temperature. It is clear that for samples annealed at 700 °C, $\mu_2$ (holes) is greatly reduced when compared to the corresponding 900 °C annealed value. This can be accounted for considering that as the density of p-type lattice defects decreases, the number of hole scattering events also decreases and corresponding mobility values increase.

Therefore, low temperature Hall measurements indicate that, in each of the samples fabricated in this study, there exists a dense population of defects that manifest as a surface layer of acceptor states. The population of defects within this layer has been identified to have a strong correlation with annealing temperature and therefore must be linked to damage incurred by the silicon crystal during the implantation procedure. Furthermore, by revisiting figure 3.1, it is possible that the surface layer of acceptor states observed in this section provides a justification for the absence of active bismuth donors being measured close to the surface of the substrate in the 800 °C annealed substrate, as compared to the 900 °C sample. This could be a result of acceptors acting as a source of charge compensation for active bismuth centres close to the surface of the substrate during spreading resistance profiling measurements. This effect is discussed further in the following chapter.
4.5 Hyperfine structure of ion implanted Si:Bi

In an effort to more fully evaluate the candidacy of ion implanted bismuth donors in silicon as spin qubits, it is useful to explore the effect that the implantation procedure has on the nature of the zero-field hyperfine spin splitting. Moreover, it is essential to determine the optimum annealing conditions to promote bismuth incorporation such that donor states are unaffected by implant strain. Resonant Si:Bi $D^0X$ photoconductivity measurements are used to probe into the zero-field hyperfine structure of the implanted donors and serve as a indicator of the quality of bismuth incorporation through the characteristic properties of extracted spectra. Samples used in this measurement have depth profiles identical to those discussed previously in this study however use a slightly reduced peak active bismuth donor concentration of $6 \times 10^{16}$ cm$^{-3}$ to eliminate any potential concentration broadening effects.

Figure 4.7 displays the measured photoconductivity signal as a function of pump laser energy. There is a clear correlation between the quality of observed $D^0X$ spectra and substrate annealing temperature. This is such that samples annealed at 700 °C provide no signal corresponding to bismuth impurities whatsoever. This observation is consistent with the absence of PL spectra observed in figure 4.3 for the corresponding 700 °C annealed sample, and potentially can be related to the abundance of implant related defect states. As annealing temperature increases the bismuth donor spin states begin to emerge. However the spectra taken from samples annealed at 800 °C differs significantly from that which would be expected in bulk Si:Bi. Additional structure within the $D^0X$ spectrum is measured such that a further splitting within the hyperfine states are observed. While the exact mechanism creating this strain is not very well understood, it is clear that there is a correlation between the post implantation annealing conditions and the ‘quality’ of $D^0X$ spectra generated. It is therefore infered that the channel through which these additional undesirable features are formed is related to strain generated during the implantation procedure and is linked to the presence of acceptor defect states presented in figure 4.6. Finally, using an annealing temperature of 900 °C the zero-field hyperfine doublet that is associated with bismuth donors in silicon is clearly resolved.

This therefore identifies that, while a significant amount of implantation related damage remains within the substrate, a 900 °C annealing treatment is sufficient to resolve the zero field hyperfine structure of bismuth donors in silicon. Furthermore, the hyperfine structure presented in figure 4.7 for the 800 °C and 900 °C annealed substrates have been fit using a
Figure 4.7: Resonant $D^0X$ photoconductivity spectra of ion implanted Si:Bi. Samples annealed at 700 °C, 800 °C and 900 °C are displayed in a), b), and c) respectively. Gaussian fits to 900 °C and 800 °C data are indicated as solid lines, dashed lines represent overlapping fits. Measured at 10 K.
Gaussian distribution. Corresponding fits have been included in figure 4.7 and fitting parameters are displayed in tables 4.4 and 4.5 for the 900 °C and 800 °C samples respectively. An energy splitting of (29.77±0.06) µeV is extracted for the two hyperfine spin states measured using the 900 °C sample. The corresponding linewidths of each peak is (8.94±0.09) µeV and (7.68±0.08) µeV FWHM for the low and high energy states respectively. These values are in very good agreement with equivalent parameters extracted from bulk doped Si:Bi substrates; 30.51 µeV and 7.9 µeV for spacing and linewidths respectively [51]. This suggests that, while implantation defects remain present in this substrate, the applied annealing regime is sufficient to both encourage bismuth incorporation and reduce implantation strain such that the groundstate hyperfine doublet is resolvable and comparable to equivalent bulk doped Si:Bi samples.

Extracted fitting parameters to the sample annealed at 800 °C indicate that the energy spacing between peaks 1 and 3 is (30.7±0.1) µeV and peaks 2 and 4 is (30.1±0.1) µeV. Both of these values are in good agreement with the expected energy spacing between the groundstate hyperfine energy levels. Furthermore, by comparing the peak positions of the

<table>
<thead>
<tr>
<th>Peak #</th>
<th>$E_c$ (meV)</th>
<th>FWHM (µeV)</th>
<th>$A$ (µeV²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1146.9050 ± 0.0004</td>
<td>8.94 ± 0.09</td>
<td>0.061 ± 0.005</td>
</tr>
<tr>
<td>2</td>
<td>1146.9348 ± 0.0004</td>
<td>7.68 ± 0.08</td>
<td>0.056 ± 0.006</td>
</tr>
</tbody>
</table>

Table 4.4: Fitting parameters of measured hyperfine structure from ion implanted Si:Bi sample annealed at 900 °C, corresponding data is presented in figure 4.7(a)

<table>
<thead>
<tr>
<th>Peak #</th>
<th>$E_c$ (meV)</th>
<th>FWHM (µeV)</th>
<th>$A$ (µeV²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1146.8988 ± 0.0008</td>
<td>7.2 ± 0.5</td>
<td>0.038 ± 0.003</td>
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<tr>
<td>2</td>
<td>1146.9093 ± 0.0008</td>
<td>8.3 ± 0.6</td>
<td>0.046 ± 0.003</td>
</tr>
<tr>
<td>3</td>
<td>1146.9296 ± 0.0008</td>
<td>6.9 ± 0.4</td>
<td>0.039 ± 0.002</td>
</tr>
<tr>
<td>4</td>
<td>1146.9394 ± 0.0009</td>
<td>8.1 ± 0.6</td>
<td>0.041 ± 0.036</td>
</tr>
</tbody>
</table>

Table 4.5: Fitting parameters of measured hyperfine structure from ion implanted Si:Bi sample annealed at 800 °C, corresponding data is presented in figure 4.7(b)
800 °C and 900 °C samples it is determined that the observed splitting in the 800 °C spectra, from both the high and low energy states observed in the 900 °C sample, is approximately ±5 µeV. There have been a handful of instances reported in literature whereby similar effects are observed in resonant $D^0X$ spectroscopy of phosphorus doped epitaxially grown layers of $^{28}$Si [119, 120]. In these cases a splitting in the zero field Si:P $D^0X$ photoconductivity spectra was observed and is attributed to the biaxial strain incurred by the slight lattice mismatch between the natural silicon substrate and the isotopically pure epitaxially grown layer. It is well understood that in the presence of strain, the valance band degeneracy of the light and heavy holes can be lifted which will have a direct response on the formation of the $D^0X$ complex. While these systems are plainly different to the one presented in this work, it is known that the presence of extended defects (such as dislocation loops and \{133\} defects [68]) are known to induce local strain fields within the silicon lattice [121, 122, 123]. Therefore one possible explanation for the splitting observed in the Si:Bi $D^0X$ photoconductivity spectra of the sample annealed at 800 °C is the presence of extended defects within the implanted region that are inducing strain fields which lift the valence band degeneracy. While it is unlikely that annealing the substrate at 900 °C will completely eradicate the population of extended defects, it has been reported that a higher thermal budget will effect the defect evolution and result in defects with a higher degree of stability.

### 4.6 Temperature dependence of Si:Bi $D^0X$

The previous section in this chapter has illustrated that annealing temperatures of 900 °C are sufficient to incorporate ion implanted bismuth donors in silicon such that their groundstate hyperfine structure is resolvable unperturbed without the requirement of a magnetic field. Furthermore, it was demonstrated that the doublet spacing and line-widths are extremely comparable with equivalent bulk silicon samples. It is reasonable to suggest that in this sample active bismuth donors exist in an environment free of implantation strain. However, it noticeable that the formation energy of both hyperfine $D^0X$ transitions is approximately 10 µeV below the expected literature values (expressed in figure 2.5). This was attributed to a temperature effect reducing the size of the silicon bandgap and thus effecting $D^0X$ formation energy. However there is a possibility that this discrepancy could also be a result of lingering implantation strain within the substrate. Therefore in order to definitively evaluate the quality of implanted bismuth donor incorporation, the temperature dependence
of the $D^0X$ photoconductivity spectra must be evaluated.

It is important to note that the samples discussed in this section differ from those used in the experimentation of this chapter up to this point. Rather the samples in this measurement were fabricated for the purpose of contacted device fabrication and THz spectroscopy outlined in chapter 6. For consistency, the implantation of these substrates consisted of a chain of 5 steps with energies matching the previous samples. However, a lower dose was used to define a peak bismuth ion density of approximately $3\times10^{16}\text{cm}^{-3}$. Having been informed by the previous results in this chapter, implanted samples in this study were annealed at 1000 °C for 300 s to incorporate Bi$^+$ ions and repair lattice damage. A full breakdown of the samples in this section can be found in section 6.1.1.

The $D^0X$ photoconductivity experimental procedure in this measurement is the same as was used in the previous section. The temperature was varied between 8 K and 19 K and at each set-point the $D^0X$ photoconductivity was recorded as a function of pump laser energy. Measured spectra are displayed in figure 4.8. Firstly, it is clear that every measured spectrum displays the characteristic zero-field hyperfine structure of bismuth donors in silicon such that there is no observation of additional strained features. This therefore is a positive initial suggestion that the implanted bismuth donors in this substrate are in a suitable defect-free environment. Moreover, it is observed that as the temperature set-point increases up to 19 K, the measured $D^0X$ transition energies shift to lower energies. For most applications the energy shift of the silicon bandgap between the temperatures of 0 to 20 K is thought to be so small that it can be assumed to be constant. However, in the context of resonant $D^0X$ spectroscopy this energy shift is quite noticeable. Commonly the temperature dependence of the bandgap is described using the empirical relationship derived by Varshni [124], however it has been found to be a poor model in the limit of $T \rightarrow 0$ [125]. It has been shown that in this temperature region the bandgap energy, $E_g(T)$, is of the form,

$$E_g(T) = E_0 - AT^P$$  \hspace{1cm} (4.4)\\

where $E_0$ is the 0 K energy and $A$ and $P$ are fitting parameters to be determined. As discussed in section 2.3 the formation energy of a $D^0X$ complex, $h\nu_{D^0X}(T)$, can be expressed by the following relationship.

$$h\nu_{D^0X}(T) = E_g(T) - E_X - E_{D^0X}$$  \hspace{1cm} (4.5)\\

Where $E_X$ and $E_{D^0X}$ are the binding energies of a free exciton and donor bound exciton
Figure 4.8: Resonant $D^0X$ photoconductivity spectra of ion implanted Si:Bi at various temperature set-points ranging from 8 K to 19 K, as indicated.
respectively. Thus the only term in equation 4.5 that has a dependence on temperature is the silicon bandgap energy. Therefore, by combining equations 4.4 and 4.5, the formation energy of the $D^0X$ state can be expressed as,

$$h\nu_{D^0X}(T) = E_0 - AT^p - E_X - E_{D^0X} = h\nu_{D^0X}(0) - AT^p$$

(4.6)

where $h\nu_{D^0X}(0)$ is the 0 K $D^0X$ energy. For bulk doped bismuth donors in silicon $h\nu_{D^0X}(0)$ has been well characterised and is known to exist at an energy of 1146.947 meV [51].

Figure 4.9(a) presents a plot of peak energy against temperature for each of the measured $D^0X$ spectra displayed in figure 4.8 where P1 and P2 correspond to the low and high energy hyperfine spin states respectively. Additionally, equivalent measurements of a bulk doped Si:Bi sample are presented as triangular points. This sample is $<110>$ float-zone natural silicon with a pill-doped bismuth donor concentration $\sim 10^{14}$cm$^{-3}$. The bulk sample data presented in this figure was measured by Dr Kamyar Saeedi at the FELIX Laboratory, Radboud University. It is clear that there is an excellent agreement between the $D^0X$ state energies as a function of sample temperature. Using equation 4.6, data presented in figure 4.9 has been fit and values for $h\nu_{D^0X}(0)$ can be extracted for $D^0X$ corresponding to each of the hyperfine states. Fitting parameters are displayed in table 4.6. The fitted 0 K $D^0X$ formation energies of samples in this study are observed to be in very good agreement with the established literature values.

The transition energies of the peak P2 corresponds to the formation energy of a $D^0X$ from a bismuth donor in the lower energy $F=4$ hyperfine spin state whereas P1 pertains to a exciton binding to a donor in the $F=5$ state. Therefore the quoted 1146.947 meV $D^0X$ formation energy refers to the transition energy P2, whereas P1 is at an energy cost reduced by an amount equal to the hyperfine splitting of the groudstate bismuth donor. It is clear that the extracted P2 $h\nu_{D^0X}(0)$ matches the literature value to an extremely high degree. By taking the difference in 0 K formation energy between P1 and P2 the 0 K hyperfine splitting can be found to be $31 \pm 3 \mu$eV.

Furthermore, it is useful to evaluate the mannifestation of this splitting as the substrate temperature is varied. Figure 4.9(b) displays the measured zero-field hyperfine splitting $(P2 - P1)$ for the implanted sample over the different temperature set-points. Once again equivalent values for the bulk doped substrate are also provided as triangular markers. As the temperature of the sample is varied there is no observed correlation with hyperfine splitting.
Figure 4.9: (a) Temperature dependence of measured $D^0X$ transitions as displayed in figure 4.8, where P1 and P2 represent the low and high energy hyperfine spin states respectively. Dotted lines are fits to data using equation 4.6. (b) Measured hyperfine splitting of as a function of temperature. The dashed grey line illustrates the average energy spacing. In both (a) and (b) circular markers represent the implanted Si:Bi sample where as triangles are equivalent bulk doped substrates.
Rather, measured values appear to fluctuate stochastically about a central energy which, through taking an average, is calculated to be $30.56 \pm 0.07 \, \mu\text{eV}$. This is to be expected as the electron state binding energies of group V donors in silicon are known to be temperature independent. Moreover, the energy splitting extracted from figure 4.9(b) is consistent with the equivalent 0 K value predicted by the fitting parameters presented in table 4.6 and the literature value which is known to be $30.51 \, \mu\text{eV}$.

This result is of great significance as it demonstrates that, in the context of $D^0X$ spectroscopy, there is no difference between the quality of spectra from the implanted sample and an equivalent bulk sample. Furthermore, the extracted 0 K $D^0X$ formation energy of the implanted sample ($1146.947\pm0.002$ meV) matches very well the known literature value for bulk doped substrates. This therefore demonstrates that the measured Si:Bi $D^0X$ transition energies can be accounted for by considering nothing more than just the temperature dependence of the silicon bandgap energy. Consequently, this observed lack of strain serves as an appreciable illustration of the quality of the environment in which the active bismuth donors are situated. The zero field groundstate hyperfine structure of the implanted bismuth donors was also observed to be clearly resolvable and with an energy splitting of $30.56 \pm 0.07 \, \mu\text{eV}$ between the F=4 and F=5 states. This is also in excellent agreement with literature and further illustrates that the implanted bismuth ions within this sample have been incorporated substitutionally into the silicon lattice with an extremely high degree of quality and within an environment free from implantation damage or strain.

### 4.7 Summary

This chapter has focused on optimising the post implantation annealing temperature of ion implanted bismuth donors in silicon with a specific emphasis on the quality of ion incorporation for applications within quantum technologies.

In the first instance, the focus of this chapter was on determining the optimum annealing
treatment purely in terms of maximising the EAY of implanted bismuth donors in silicon. Spreading resistance profiling was used to indicate the active bismuth donor concentration as a function of depth for each of the samples in this study. Using this technique the apparent donor yield was found to be $(41 \pm 2)\%$, $(53 \pm 2)\%$ and $(59 \pm 3)\%$ for samples annealed at $700\degree C$, $800\degree C$ and $900\degree C$ respectively. This therefore indicates that there is sizeable reduction in Bi$^{+}$ ions that are converted into active donor centres during heat treatment at $700\degree C$ whereas $800\degree C$ and $900\degree C$ appear to be relatively comparable. These observations were also consistent when considering the peak active bismuth donor concentration of each implanted sample.

In order to definitively verify the presence of electrically active implanted bismuth impurity centres, above bandgap photoluminescence measurements were used to probe into the Si:Bi $D^{0}X$ complex. Spectroscopic bismuth donor bound exciton lines were measured in luminescence spectra taken using samples annealed at both $800\degree C$ and $900\degree C$ however there was no evidence to support the presence of electrically active bismuth donors in the sample annealed at $700\degree C$. This directly contradicts the SRP data which suggests after annealing at $700\degree C$ approximately $41\%$ ions should be activated into donor sites. Furthermore, by comparing the no-phonon and transverse optical phonon assisted donor bound exciton spectra, it was made apparent that the Si:Bi $D^{0}X$(TO) transition in the $800\degree C$ annealed substrate was only $\sim 45\%$ of that expected given the equivalent NP peak height. This suggests that there is a suppression in the phonon population in the $800\degree C$ sample. Conversely the measured $D^{0}X$ excitation spectra taken from the $900\degree C$ annealed substrate matched up well to what was predicted using literature of equivalent measurements from bulk doped silicon. Therefore this result indicates that, while the activation yield is approximately consistent between the two samples annealed at $900\degree C$ and $800\degree C$, there is a significant difference in the quality of incorporation of bismuth ions and lattice condition.

In an effort to uncover the extent of the damage incurred by the silicon lattice during the bismuth ion implantation, low temperature Hall measurements were implemented. This measurement yielded the information that there exists a dense population of implantation related defects that act as acceptors at low temperatures and are situated at the surface of substrate. Furthermore, it was observed that there is a strong correlation between the sheet concentration of these states and annealing temperature such that in the $900\degree C$ sample the population was greatly reduced. However, it is notable that even though higher annealing temperatures correspond to fewer surface defects, a significant amount remained present. It
is also likely that these acceptor states act a source of annihilation for extrinsically doped electrons from ionised bismuth donors at room temperature. Therefore, this provides a justification for the absence of bismuth donors close to the surface of the substrate as indicated in the depth profiles yielded from the previously discussed SRP measurements.

The final characterisation technique utilised in this study was \( D^0X \) photoconductivity. A measurement of this nature was intended to resonantly interact with implanted bismuth donors in order to directly probe their groundstate hyperfine structure and therefore evaluate whether the applied annealing treatment is sufficient to incorporate bismuth donors into an environment that supports quantum phenomena. It was observed that an annealing temperature of 900 °C was required to fully resolve the characteristic zero field hyperfine spin splitting that is associated with bulk doped bismuth donors in silicon. The extracted splitting between the high and low energy states was found to be \((29.77 \pm 0.06) \, \mu\text{eV} \) with corresponding linewidths of \((8.94 \pm 0.09) \, \mu\text{eV} \) and \((7.68 \pm 0.08) \, \mu\text{eV} \) respectively. These values are very comparable with equivalent bulk doped substrates. Conversely, while it was found that in the sample annealed at 800 °C the hyperfine structure was resolvable, transition lines appeared to be strained significantly. This once again indicates that there is a disparity between the quality of bismuth ion incorporation in samples annealed at 800 °C and 900 °C that is more significant than solely considering the EAY.

To conclude this series of measurements, the temperature dependence of the measured \( D^0X \) spectra was investigated in an effort to identify any additional sources of strain caused by implantation damage. It was found that the spectra measured using the implanted sample were an excellent match to equivalent bulk substrates. Furthermore, using the temperature dependence of the silicon band gap, the \( D^0X \) formation energy at 0 K was extracted for the implanted samples and found to be a good match to the known literature value. This observation is of great significance as it identifies that the dominating property in determining the energy of the \( D^0X \) transition is solely the temperature of the substrate and there appear to be no additional sources of strain. Considering that over the temperature range of 0 to 20 K the change in silicon band gap energy is only \(~70 \, \mu\text{eV} \) this is a clear indication of the quality of the implanted substrate. Additionally, the zero-field hyperfine splitting of the implanted bismuth donor groundstate energies were measured to be temperature independent and on average have a magnitude of \(30.56 \pm 0.07 \, \mu\text{eV} \). This is also in excellent agreement with the known literature value and further illustrates that the quality of incorporation of the implanted Bi\(^+\) ions is extremely high and there are no remaining sources of implantation
strain present in the sample after annealing.

The conclusion that should be drawn from this chapter is that, although a population of implantation defects remains present at the surface of the sample, annealing at a temperature of at least 900 °C was sufficient to incorporate (59 ± 3) % Bi⁺ ions into donor sites such that various $D^0X$ spectroscopic measurements are consistent with bulk samples. This therefore indicates that, provided the post implantation heat treatment is sufficient, implanted bismuth donors in silicon are highly comparable to equivalent bulk samples and as such should be considered candidates for implementation as qubit states in silicon.
Chapter 5

Dependence of dose on ion implanted Si:Bi

In this chapter the effect of increasing the bismuth ion fluence is explored in relation to the characteristic properties of implanted Si:Bi samples. Substrates have been fabricated using a range of implantation doses culminating in an active donor concentration that exceed the solid solubility limit of bismuth donors in silicon. A combination of spreading resistance profiling measurements and above bandgap photoluminescence have been implemented in an effort to both uncover the fraction of ions that are incorporated into the lattice and furthermore examine their spectroscopic properties. In addition, the amount of damage incurred by the lattice during the implantation procedure is explored in relation to observations from these measurements and conclusions drawn from the previous annealing study.

5.1 Implanted samples

The samples used in this investigation are of the same nature of those used in the previous annealing study. This is such that they were fabricated using a chain of 5 high energy implantation steps at various fluences. While the ion dose was varied between samples, for the sake of consistency the energy of each implantation step was kept constant. Figure 5.1(a) displays a breakdown of the implant energies and fluences used in the fabrication of each of the 4 samples. SRIM simulations have also been used to calculate the expected ion density distributions for each sample. As the energies of each of the implantation steps is consistent between samples, calculated ion profiles have an identical shape, however the peak ‘flat top’
bismuth ion density varies. This is reflected in figure 5.1(b) where, for clarity, the bismuth ion density distributions have been plotted logarithmically. Samples have been labeled from A to D in order of increasing fluence and will be referred to as such for the duration of this chapter. The implant fluences were chosen such that the peak bismuth donor density would increase by approximately a factor of 3 between each sample. Consequently, implant chains A, B, C and D are designed to achieve peak bismuth ion concentrations of $3 \times 10^{16} \text{cm}^{-3}$, $1 \times 10^{17} \text{cm}^{-3}$, $3 \times 10^{17} \text{cm}^{-3}$ and $1 \times 10^{18} \text{cm}^{-3}$ respectively. These concentrations are of interest as they are in the region where bismuth donors go from being completely isolated (in their groundstates) to being close enough to interact with one another. Furthermore, sample D would correspond to a peak dopant density that exceeds the solid solubility limit of bismuth donors in silicon.

The SRIM software that has been used for these simulations is purely designed to predict the final stopping depths of ions immediately after the implantation procedure. Therefore it is useful as a depiction of a ‘perfect’ annealed sample with 100 % EAY and zero diffusion during heat treatment. In the previous chapter it was established that the optimal samples fabricated in this study were annealed at a temperature of 900 °C for 300 s and therefore this treatment has been used for all substrates in this study. Silicon handle substrates are
identical to those in the previous chapter, with a peak bulk doped phosphorus density of $6 \times 10^{14} \text{cm}^{-3}$.

5.2 Bismuth active donor depth profiles

It has previously been established (in section 3.1) that spreading resistance profiling measurements are a useful tool for identifying the presence and location of electrically active implanted bismuth donor states. In this section the same measurement technique has been implemented to compare the bismuth donor depth profiles of substrates implanted with various fluences of bismuth ions. For each of the samples outlined in figure 5.1, the active donor concentrations a function of depth have been measured and are presented in figure 5.2. Also included, for each implant fluence profile, is the corresponding SRIM Monte Carlo simulation illustrating the predicted location and densities of implanted bismuth ions immediately after implantation. Figure 5.2 displays that for every sample fabricated in this study a broad implanted donor layer has successfully been introduced in the region predicted by the SRIM calculation. However, as discussed previously, SRP measures the electrical properties of the samples as a function of depth through which the active donor density profiles can be inferred. Therefore it is beneficial to consider the effect that the bulk doped phosphorus donors have on the measured density profiles. As a reference the constant background phosphorus donor concentration ($6 \times 10^{14} \text{cm}^{-3}$) is indicated in figure 5.2 as a dashed grey line. For each of the four samples it is clear that in the depth region of 0.1 to 0.7 µm the measured charge profile is dominated by the implanted bismuth donors, however as the depth from the surface of the substrate increases, the apparent bismuth donor population decreases and the charge concentration asymptotically approaches the known phosphorus density. Therefore in this region is useful to decompose the extent of the bismuth donor population. Fortunately, knowing the constant background density of phosphorus, it is relatively straight forward to implement a fitting routine which separates the contribution of each donor species. By assuming an exponential decrease in bismuth donor population in the ‘tail’ region of the profile it is possible to use a least squares model to fit to the measured charge profiles and approximate the bismuth density. Fits to data are illustrated in figure 5.2 as solid coloured lines and extracted bismuth concentrations are coloured dashed lines. This will prove useful later in this chapter when considering the bismuth ion diffusion.

To to fully compare the density profiles corresponding to each implant fluence chain,
Figure 5.2: Measured SRP donor depth profiles for substrates implanted with various fluences of bismuth ions (A to D as indicated). Also included for each density, as a solid black line, are SRIM Monte Carlo simulations that illustrate the depth profiles of a ‘perfect’ implanted sample with 100 % EAY and zero thermal diffusion. Dashed grey lines indicate the known concentration of bulk doped phosphorus donors whereas coloured dashed lines are diffused bismuth donors which are approximated by fitting to the SRP data. Corresponding fits are presented as solid coloured lines.

Table 5.1 provides values for both the peak active bismuth donor density and EAY for each depth profile presented in figure 5.2. Values for the peak donor density were calculated by taking the statistical average of each distribution over their corresponding flat top regions while the EAY was evaluated by comparing the total integrated area of each profile and comparing with the known implant fluences, as illustrated by the SRIM calculation. This line of analysis uses the assumption that the increase in conduction measured during SRP is a direct result of active bismuth impurities and that there are no significant additional sources of free charge within the substrate.

Table 5.1 indicates that there is an inverse correlation between bismuth implantation dose and fractional EAY. It is observed that substrates corresponding to implant profiles C and D both achieve an EAY of approximately 60% of the implant dose, this is consistent with
Table 5.1: Electrical activation yield of implanted bismuth donors in silicon with implant densities and various annealing temperatures for 300s.

<table>
<thead>
<tr>
<th>Implant Profile</th>
<th>Peak Bismuth Density $\left(10^{17}\text{cm}^{-3}\right)$</th>
<th>EAY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$0.17 \pm 0.01$</td>
<td>74 ± 3</td>
</tr>
<tr>
<td>B</td>
<td>$0.55 \pm 0.03$</td>
<td>67 ± 3</td>
</tr>
<tr>
<td>C</td>
<td>$1.33 \pm 0.04$</td>
<td>59 ± 3</td>
</tr>
<tr>
<td>D</td>
<td>$4.5 \pm 0.4$</td>
<td>61 ± 4</td>
</tr>
</tbody>
</table>

yield values reported for similar density implants [64]. Significantly, both implant chains correspond to peak active densities that are in close proximity to the solid solubility limit of bismuth donors in silicon. This value is known to be $2.3 \times 10^{17} \text{cm}^{-3}$ [42], as measured for bulk grown Si:Bi substrates, however it has been surpassed various times in implanted Si:Bi samples [58, 126]. Implant profile D is also observed to contain a peak active bismuth impurity concentration greater than the solubility limit. Conversely the donor density profile corresponding to implant chain A is considerably below the solid solubility limit of bismuth donors in silicon and an EAY of 74 ± 3% is achieved. It is also apparent that the peak bismuth donor density of each sample is only approximately 50% of that predicted by the SRIM simulation. Although it is observed that the maximum concentration of the lower dose implants sample A & B is slightly closer to the simulated value than samples C & D. It is found that the sample implanted using chain A has a peak concentration 57 ± 3% of that simulated using SRIM. Conversely the equivalent samples using chains B, C and D achieve peak densities of 55 ± 3%, 44 ± 3% and 45 ± 4% respectively.

An additional source of interest presented in figure 5.2 is the shape of the measured depth profiles for each the various samples. As the energies of each implantation step are consistent between samples it is predicted that shape of each distribution should be identical. This is reflected in the SRIM simulations presented for each sample. However clearly this appears not to be the case. Rather, as the ion implantation dose increases, the measured donor concentration profile becomes noticeably more asymmetric in structure. This is particularly evident when considering sample D where there appears to be both an enhanced diffusion of donors deeper into the substrate and a distinct absence of donors measured at the surface. The asymmetry of each measured concentration profile can be evaluated statistically by introducing a parameter known as the Pearsons skewness coefficient, $Sk$, which is given by...
the equation,

\[ Sk = \frac{3(\mu - M)}{\sigma} \]  

(5.1)

where \( \mu \), \( M \) and \( \sigma \) are the mean, median and standard deviation of each of the distributions. Evaluation of equation 5.1 yields \( Sk \) coefficients of 0.11, 0.16, 0.19 and 0.20 for substrates A, B, C and D respectively. Naturally, all depth profiles have positive \( Sk \) values as, irrespective of implant fluence, thermal diffusion of implanted bismuth ions will be limited by the surface of the substrate. This will therefore result in an asymmetric diffusion with a larger tail of donors at depths greater than 0.6 \( \mu m \) below the surface of the substrate.

A significant contributor to the observed increase in dopant profile ‘skewness’ is the fact that bismuth is measured to be at greater depths from the surface within higher dose samples. This strongly indicates that bismuth ions have diffused further away from the original implant stopping position (as indicated by SRIM). During the Bi\(^+\) implantation procedure, traveling ions will create an abundance of vacancies and interstitials through collisions with lattice sites. It is known that these point defects are extremely mobile and, upon thermal annealing, have been observed to coalesce to form extended defects [68]. This has the additional effect of dramatically enhancing the movement of implanted ions which diffuse through interactions with vacancy sites. This phenomenon is known as transient enhanced diffusion, TED, and can significantly increase the movement of implanted ions from their original stopping position [41, 127]. It is evident that an implantation scheme with a higher ion fluence will result in a larger population of point defects and therefore be more subject to the effects of TED. As discussed previously, the point at which the density of active bismuth donors drops below the concentration of bulk doped phosphorus has been evaluated for each of the samples by way of fitting the tails of the measured SRP distributions. This is illustrated in figure 5.2 where it is found that for samples A & B, the bismuth concentration drops below \( 6 \times 10^{14} \) cm\(^{-3} \) at respective depths of \( \sim 0.9 \) \( \mu m \) and \( \sim 1.0 \) \( \mu m \) whereas for C & D it is observed that bismuth ions diffuse much deeper. Particularly in the case of sample D, bismuth donors are observed to dominate the measurement up to approximately 1.45 \( \mu m \). This is more than double the maximum stopping ion depth that was predicted by the SRIM simulation. Furthermore, TED has the additional effect of reducing the peak donor concentration as the bismuth population will be spread out over a wider area. It is also notable that even though the effects of diffusion appear to be less significant in the lower dose samples, it is clear that ion movement has occurred to some extent. While this is
not a big problem for these samples specifically, it does raise the question of what effect TED will have on small scale implantation schemes designed specifically for applications within quantum technologies. It is reasonable to speculate that it will be necessary to transition over to much quicker heat treatments, such as shorter RTAs or laser annealing, in order to combat ion diffusion.

An additional reason for the asymmetry of profile D is the lack of charge carriers measured at the surface of the substrate. This therefore suggests that there is a mechanism inhibiting either the formation, or measurement of bismuth donors close to the surface in higher doped sample. In the previous chapter it was identified that in every sample measured there existed a dense population of positively charged implantation defects which were speculated to exist at the surface of the substrates. While ultimately it was found that this feature did not have a detrimental effect on the observation of the hyperfine structure in the sample annealed at 900 °C, none of the applied heat treatments were able to completely eliminate these defects. Therefore it is possible that this layer of acceptors is acting as a source of compensation for bismuth donors close to the surface.

5.3 $D^0 X$ luminescence concentration effects

In the previous chapter, above bandgap photoluminescence was demonstrated to be a powerful experimental technique for the characterisation of implanted bismuth donors in silicon. In the first instance it is a convenient measurement for the identification of implanted bismuth donors, and any other donor species, through the observation of $D^0 X$ emission. Furthermore, by drawing comparison between the corresponding no-phonon and phonon replica $D^0 X$ luminescence, it is possible to uncover information regarding the quality of bismuth donor incorporation and hence the environment within which they are contained.

As previously, information regarding the experimental procedure and underlying $D^0 X$ theory can be found in sections 3.2.1 and 2.3 respectively. Each of the samples A to D have been measured using this technique at a temperature of 10 K and corresponding spectra can be seen in figure 5.3. Measured luminescence spectra display characteristic peaks from both implanted bismuth and bulk doped phosphorus donor bound excitons. Figure 5.3(a) displays the spectra taken from every sample in this study contain features corresponding to the luminescence of both species of $D^0 X$ without the formation of a phonon at 1147 meV and 1150 meV for bismuth and phosphorus respectively. This therefore confirms that every
Figure 5.3: Above bandgap photoluminescence spectra of ion implanted Si:Bi substrates with a range of Bi\(^{+}\) ion doses labeled from A to D in order of increasing density. Dashed lines represent indicated transition energies. Substrates were measured at 10K.

The sample fabricated in this study has successfully achieved a population of active bismuth donors. Furthermore, while the intensity of the Si:P \(D^0X(\text{NP})\) transition appears to remain relatively constant, the strength of the Si:Bi \(D^0X(\text{NP})\) varies throughout the different samples. This is such that from sample A to C the strength of this peak increases, which corresponds to the increase in Bi\(^{+}\) ion fluence used in the fabrication of each sample, however in sample D the peak is much weaker than would be predicted. This feature is considered later on in the text but first it is useful to explore the transverse optical phonon assisted \(D^0X\) luminescence spectra displayed in figure 5.3(b).

The spectral features of the bismuth and phosphorus \(D^0X(\text{TO})\) luminescence appear to be consistent with the corresponding no-phonon transitions. This is in reference to the fact that the Si:P \(D^0X(\text{TO})\) peak is constant for each sample whereas the Si:Bi \(D^0X(\text{TO})\) transition intensity increases up to sample C and then drops down in D. In the previous
\[
\begin{array}{cccc}
\text{Sample} & I_{P(NP)} : I_{Bi(NP)} & I_{P(TO)} : I_{Bi(TO)} & I_{P(TO)} : I_{Bi(TO)} \\
\# & \text{(Measured)} & \text{(Measured)} & \text{(Predicted)} \\
A & 1 : 0.94 & 1 : 0.15 & 1 : 0.15 \\
B & 1 : 4.49 & 1 : 0.75 & 1 : 0.71 \\
C & 1 : 9.01 & 1 : 1.40 & 1 : 1.43 \\
D & 1 : 2.43 & 1 : 0.40 & 1 : 0.39 \\
\text{Literature*} & 0.35 : 2.2 & 1 : 1 & \\
\end{array}
\]

* Literature transition intensity ratios [83].

Table 5.2: Relative peak intensities of no-phonon and TO phonon assisted $D^0X$ transitions between bulk phosphorus and implanted bismuth donors in silicon. Measured values are taken directly from figure 5.3 whereas predicted $I_{P(TO)} : I_{Bi(TO)}$ use the provided literature ratio and the measured $I_{P(NP)} : I_{Bi(NP)}$.

In chapter the relative strengths of the bismuth and phosphorus NP and TO $D^0X$ luminescence were used as a metric to uncover the quality of the crystal environment that the donors were situated in. This is because the relative strengths of phonon assisted and no phonon $D^0X$ luminescence are very well understood for a range of donors and acceptors in bulk silicon. Therefore by making the assumption that the phosphorus $D^0X$ luminescence follows the known $I_{P(NP)} : I_{P(TO)}$ intensity ratio (0.35 : 1), it is possible to predict the expected Si:Bi $D^0X(TO)$ luminescence strength using the measured no-phonon transition. Table 5.2 contains the relative $I_P : I_{Bi}$ intensity ratios for both the no-phonon and transverse optical phonon $D^0X$ luminescence centres. Also included for reference is the known literature transition strength ratios. The final column of table 5.2 provides values for the predicted $I_{P(TO)} : I_{Bi(TO)}$ ratios.

It is therefore apparent that for every sample in this study, the predicted $D^0X(TO)$ luminescence intensity ratio matches well the corresponding measured value. Significantly, this is even true for sample D where the measured luminescence is significantly lower than what would be expected given the spectra of A, B and C. This indicates that the quality of the crystal environment that the implanted bismuth donors are situated within is reasonably high such that their characteristic $D^0X$ photoluminescence match well what is expected from equivalent bulk doped samples. Furthermore, it appears that this feature is irrespective of implant density as every sample in this study behaves in the same manner.
However, while the continuity between the phonon assisted and no-phonon transitions is observed for each sample, there is a clear suppression in $D^0X$ luminescence in the highest doped substrate. Additionally, accompanying the suppression of the expected $D^0X$ luminescence, the introduction of a completely new channel of emission is observed at an energy of $\sim 1083$ meV in the TO phonon assisted spectrum. It is difficult to comment on whether this feature is also observable in the no-phonon spectrum as the TO silicon band gap transition is in approximately the same position. An observation similar to this has been made previously in the photoluminescence measurements of a series of bulk doped Si:P samples with increasing donor densities [128]. Here the $D^0X$ TO luminescence transition was measured in a range of samples with phosphorus concentrations spanning $7 \times 10^{15}$ cm$^{-3}$ to $3 \times 10^{18}$ cm$^{-3}$. It was found that, as the sample density increased, the $D^0X$ TO transition shifted lower in energy. This effect was attributed to the interaction of an exciton with a cluster of donors. Specifically, the observed shift in energy was credited to the cost of transferring a bound exciton between two localised donor sites. An accompanying theoretical paper [129] was also published that offered a mathematical formalism to explain this energy shift. Here the cost of transferring an exciton from one donor another was expressed as,

$$\Delta E = \int \psi_1(r)U_1(r)\psi_2(r)d\tau$$ (5.2)

where $\psi_i(r)$ ($i = 1, 2$) is the wave function of an exciton that is bound to the $i$th donor and $U(r)$ is the binding potential of the exciton to the initial donor ($i = 1$). Under the consideration that a donor bound exciton is effectively a donor and a hole paired together by a covalent bond, then the wave function was assumed to extend over a sphere of radius, $r_0$, and decay outside of it. Where $r_0$ is the sum of the donor and exciton Bohr radii. Using this assumption the change in luminescence energy due to this process was approximated as,

$$\Delta E(R) \sim -2\epsilon_0 \exp^{-R/r_0}$$ (5.3)

where $\epsilon_0$ is the $D^0X$ binding energy and $R$ is the separation between two neighbouring bismuth donors. In order to test this formalism with the luminescence data from the samples in this study, it is first necessary to understand the average donor separation for each of the implanted bismuth profiles.

The bismuth – bismuth nearest neighbour probability density distributions can be evaluated using the measured SRP concentration profiles and a Poisson point process. The
Figure 5.4: Probability density distributions of bismuth donor separations as a function of depth for each of the samples in this study (labeled A to D). Dotted lines indicate the expected donor separation as a function given depth.

The probability density of a given donor separation can be calculated by defining a sphere of radius \( r \) which is centred around the site of an active bismuth donor at a given depth, \( z \), with an infinitesimally small shell of thickness \( \delta r \) surrounding it. The probability of finding a nearest neighbour bismuth donor within that volume is defined by the product of the probabilities of there being exactly zero additional donors within the sphere, \( P_0(r, z) \), and exactly one within the shell, \( \delta N = \delta r \frac{d}{dr} N(r, z) \) [130]. The nearest neighbour probability density can therefore be defined as,

\[
P_{z\rightarrow Bi}(r, z) = P_0(r, z) \frac{dN(r, z)}{dr} P_{Bi}(z)
\]

where \( N(r, z) \) is the expected number of bismuth atoms found within the sphere and \( P_0(r, z) \) is defined by the Poisson probability mass function \( (P_0(r, z) = \exp[-N(r, z)]) \). \( P_{Bi}(z) \) is the
Figure 5.5: a) Si:Bi $D^0X$ energy shift as a function of bismuth separation. The dashed line displays the energy shift predicted by equation 5.3 whereas data points are measured shifts corresponding to implanted samples C and D, as indicated. b) PL spectrum for sample C in the region of the Si:Bi $D^0X$ TO-replica, with Gaussian fits. c) Same as b) but for sample D.

probability density function of finding a bismuth donor at a given $z$, this is extracted from the measured SRP distributions and is used to normalise the probability density surfaces. For this calculation complete spatial randomness was assumed within the plane perpendicular to the ion beam direction. However the measured SRP data and Poisson point process statistics were used to take into account the 1D density inhomogeneity in $z$ [131]. Figure 5.4 displays, for each of the implanted samples in this study, the probability density surface of finding a bismuth donor with a nearest neighbour at a given radial distance. As to be expected, the probability density of each sample is such that a dense population of donors with a global minimum separation is found between depths of approximately 0.1 and 0.6 $\mu$m below the surface, with lower density tails at either side. Given its unusual luminescence spectrum, sample D is of specific interest and figure 5.4 indicates that within this ‘flat top’ region the nearest neighbour expectation value is $7.8\pm0.2$ nm. Samples A, B and C have corresponding expectation values of $21.8\pm0.4$ nm, $15.0\pm0.3$ nm and $11.4\pm0.2$ nm respectively.

Having evaluated the nearest neighbour donor distance of sample D, it is now possible to compare the model presented in equation 5.3 with the luminescence data measured in this study. Figure 5.5(a) presents the calculated theoretical energy shift in luminescence as
Table 5.3: Fitting parameters corresponding to figure 5.5 where $E_0$ and $dE$ the peak energy centroid and width respectively.

<table>
<thead>
<tr>
<th>Substrate (Fit)</th>
<th>$E_0$ (meV)</th>
<th>$dE$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>1088.7±0.1</td>
<td>0.87±0.09</td>
</tr>
<tr>
<td>$C_2$</td>
<td>1087.4±0.1</td>
<td>1.6±0.1</td>
</tr>
<tr>
<td>$D_1$</td>
<td>1088.41±0.09</td>
<td>1.4±0.1</td>
</tr>
<tr>
<td>$D_2$</td>
<td>1083.57±0.09</td>
<td>1.3±0.1</td>
</tr>
</tbody>
</table>

a function of donor separation (dashed grey line) with the measured shift between the two peaks observed in the $D^0X$ spectrum of sample D (purple circle). In addition to the clear energy shift in sample D, it is also observable in figure 5.3 that there is a distinct asymmetry in the Si:Bi $D^0X$ (TO) luminescence peak from sample C. Therefore this shift has been evaluated and also included in figure 5.5(a) (blue square). Gaussian fits to the luminescence spectra of samples C and D are included in figure 5.5(b & c) with corresponding fitting parameters contained within table 5.3 for reference. Here it is apparent that the formalism presented in equation 5.3 (taken from [129]) does a reasonable job in representing the energy shift observed in the luminescence spectra of sample D. However the asymmetry observed in the $D^0X$ (TO) transition for sample C is less well accounted for. This could be an indication that the theoretical model is not sophisticated enough to appropriately explain the observed concentration effect. It is also plausible that the resolution of the luminescence measurement was not high enough to sufficiently resolve the true structure of the transitions in this spectra. This is also supported by the fact that it could be argued the equivalent Si:P transition (displayed in figure 5.3(b)) for sample C also has a similar asymmetric structure.

There is also significance in the fact that, while a clear shift is observed in the $D^0X$ (TO) luminescence in sample D, some transition strength still remains at the expected energy value of $\sim 1089$ meV. This can be accounted for by considering the fact that, although the peak bismuth donor concentration in this sample is very high, there was a significant amount of bismuth ion diffusion observed in its measured donor density profile (figure 5.2(d)). Therefore it stands to reason that electrically active donors in this diffusion tail will see a larger nearest neighbour separation and will not be subjected to the same concentration effects. This observation is of note because it indicates that the diffused bismuth donors situated within this region are luminescing regularly. Moreover, the observation made previously, that the
measured ratio between the no-phonon and TO replica peaks are consistent with the well known literature values, indicates that the donor incorporation is of a relatively high quality. This is interesting because primary mechanism by which implanted bismuth atoms diffuse is through interaction with silicon lattice vacancies, which are a direct result of the damage caused by ion bombardment. This therefore suggests that an annealing treatment of 900 °C for 300 s is sufficient to incorporate implanted bismuth ions with a relatively high degree of environmental quality, even in the highest doped sample of this study.

5.4 Summary

The aim of this chapter was to provide a brief exploration into the effect of increasing the Bi\(^+\) ion dose on the characteristic properties of implanted bismuth donors in silicon. As such a set of four samples were fabricated with increasing implantation fluences that resulted in implanted bismuth layers ranging from 3\(\times\)10\(^{16}\) cm\(^{-3}\) to 1\(\times\)10\(^{18}\) cm\(^{-3}\). In chapter 4 it was determined that a post implantation annealing of 900 °C for 300 s was sufficient in order to incorporate the majority of bismuth donors and eliminate the effects of implantation strain. Therefore, this same heat treatment was utilised in the fabrication of samples in this study.

In the first instance, spreading resistance profiling measurements were used to measure the active bismuth donor density profile for each of the implanted substrates. Through this it was possible to estimate the fraction of implanted bismuth ions that became substitutions within the native silicon lattice. Here EAY values ranging 59±3% from to 74±3 % were achieved, with the latter corresponding to the sample with the lowest implant fluence. Additionally, it was found that the peak donor concentration for each of the substrates also differed from both the intended values with the maximum fractional donor density being only 57±3 % of the intended SRIM prediction. This also corresponded to the sample with the lowest implantation dose. The discrepancy between EAY and peak donor concentration was attributed to the diffusion of implanted ions during annealing which causes a ‘flattening’ of the dopant profile and an overall reduction of the peak dopant density. This is supported by the observation of active bismuth donors at much greater depths than predicted by the SRIM calculated ion stopping range. This was particularly significant in the highest density sample where a large number of bismuth donors were measured at depths of up to 1.45 \(\mu\)m below the surface of the substrate. This lends itself to the ion diffusion mechanism known as transient enhanced diffusion whereby implanted atoms diffuse via interactions with the
lattice vacancies and interstitials which are generated by implantation damage. Therefore it stands to reason that this effect will be the strongest in the sample with the highest beam fluence as the population of vacancies will scale proportionally with the number of implanted ions. SRP measurements also indicated a noticeable absence of bismuth donors at the surface of the substrate in samples with the highest densities. The resulted in a more skewed, asymmetric dopant profile which was attributed to a population of positively charged defects that exist at the surface of the substrate. This is consistent with the conclusions drawn from chapter 4 where low temperature Hall measurements indicated the presence of this defect layer. This therefore raises a degree of ambiguity in regards to the EAY values extracted from the SRP measurements. This is because there is very likely active bismuth donors in the surface region of the high density samples, however the positively charged defects act as a source of charge compensation.

The focus of the second part of this chapter then switched to above bandgap photoluminescence measurements of the various samples in this study. Here the luminescence channels of specific interest were the no-phonon and TO phonon replicas of Si:Bi $D^0X$ transitions and additionally the equivalent peaks from the phosphorus donors in the bulk of the substrate. It was found that spectra from each of the implanted samples in this measurement included spectral features from active bismuth donors however the luminescence of the highest doped sample was much weaker than its measured dopant profile would suggest. Moreover, an additional transition peak was observed at an energy of $(1083.57 \pm 0.09)$ meV in the spectra of this sample. This corresponds to approximately 8 meV below the known Si:Bi $D^0X$ (TO) transition and was attributed to a concentration effect where excitons are no longer able to bind to single isolated donors. Instead they are forced to interact more loosely with pairs (or small clusters) of dopants which results in an overall reduction in luminescence energy. One such formalism for this was presented previously in relation to a similar study of bulk doped phosphorus donors [128, 129] where the observed shift down in energy was attributed to the energy cost of an exciton transferring between donor sites. It was found the accompanying theoretical model for this interaction does a reasonable job of accounting for the shift down in luminescence energy observed in the highest doped sample this study. However the observed asymmetry of the slightly lower density sample is not very well represented using this model. Additionally it was found that, for every sample fabricated, the ratio between the Si:Bi no-phonon and TO replica $D^0X$ peak matched well the known literature values for equivalent bulk doped systems. This therefore gives confidence that an annealing regime of 900 °C for
300 s was successful in incorporating implanted bismuth donors in an environment largely free of implantation damage. This is particularly striking in the highest doped sample as, even though the overall transition strength was greatly reduced, the continuity between the two transitions still remained. In the case of this high density sample the donors unaffected by concentration effects must exist in a more dilute region of the donor profile and therefore were related to the diffusion tail where the donor density is greatly reduced.

This chapter has demonstrated that there is a close relationship between the Bi\(^+\) ion beam fluence and the post implantation properties of active donor profiles. In order to be effective in the fabrication of ion implanted bismuth donor devices it is of great importance to understand how to both maximise the donor EAY, and minimise the effects of ion diffusion. It appears that this will be particularly challenging in devices which require a high density population of bismuth donors. One potential route to overcome this could be to implement the annealing technique known as solid phase epitaxial regrowth. Using SPER samples are annealed at lower temperatures (600 °C) over longer timescales (tens of minutes) in order to achieve a full crystal recovery and an ion incorporation that has been reported to be as high as 90 % in high density samples [58]. However crucially, in order for SPER to be effective, it is required that the implanted crystal region is completely amorphised during the ion bombardment. Therefore, in order to fully utilise SPER for non-amorphising implants, it would likely be necessary to precede the Bi\(^+\) implant step with an amorphising Si\(^+\) bombardment. This has been demonstrated to be a viable fabrication technique in the case of indium implants into preamorphised silicon [132].
Chapter 6

THz spectroscopy of implanted Si:Bi devices

The previous chapters in this thesis have explored bismuth ion implantation into silicon with respect to large scale bulk substrate characterisation. As such it was demonstrated that it is possible to fabricate ion implanted Si:Bi substrates that are of very high quality and, in the context of $D^0X$ spectroscopy, are indistinguishable from bulk bismuth doped samples. However one of the significant benefits of ion implantation is that it is well suited to the fabrication of a wide range of donor based devices. Therefore, in this chapter implanted Si:Bi samples have been fabricated into simple two terminal device structures with the aim of probing the electrical response of bismuth donors to THz radiation. THz illumination of donors in silicon has vast potential for integration into quantum technologies. For example the Stoneham Fisher Greenland scheme for quantum computation (section 1.3) identifies that, through the coherent interaction with THz light, it is possible to alter the properties of electron wavefunctions and therefore control the exchange interaction between neighbouring donor qubits. This would be achieved through resonantly pumping the relevant donor electron transitions with THz radiation. Therefore the observation and characterisation of these electron transitions in a system of implanted bismuth donors would hold significance in being a step towards realising a system of this nature.

In the first instance, electrically detected FTIR has been used to determine that the electron orbital transitions of the implanted bismuth donors are accessible spectroscopically. Both the quality of extracted spectra and the measurement response to changing the substrate temperature has been characterised using this technique. Having established that
the implanted devices yield high quality FTIR spectra, the source of THz radiation is then switched to resonant illumination using a free electron laser. Donor electron transitions are pumped directly and the characteristic properties of extracted spectra are analysed. It is crucial to have a good understanding of the behaviour of silicon donor based devices during the high power THz illumination of a FEL in order to realise a quantum computation architecture such as the SFG scheme.

6.1 Sample preparation

6.1.1 Implantation

The implanted substrates used in the fabrication of devices in this chapter were kept to be consistent with implant energies used in chapter 4 with a dose corresponding to the lowest density sample in chapter 5. As such the energy and fluence used in each Bi⁺ implantation step are displayed in table 6.1. Furthermore a SRIM Monte Carlo simulation has been used to predict the implanted ion volumed density profile of samples in this chapter.

Table 6.1: Implantation energies and fluences used in the fabrication of substrates in this study.

<table>
<thead>
<tr>
<th>Implant #</th>
<th>Energy (keV)</th>
<th>Fluence (10¹¹cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2000</td>
<td>6.12</td>
</tr>
<tr>
<td>2</td>
<td>1400</td>
<td>2.40</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>2.40</td>
</tr>
<tr>
<td>4</td>
<td>700</td>
<td>1.38</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>1.08</td>
</tr>
</tbody>
</table>

After implantation substrates were annealed at 1000 °C for 5 minutes to incorporate bismuth ions and repair crystal damage. This annealing temperature was selected having established, in chapter 4, that the minimum temperature required to incorporate bismuth donors in an environment free of implantation strain is 900 °C. Moreover, the samples that have been used to fabricate devices in this chapter are the same as those used in section 4.6 to
Figure 6.1: SRIM Monte Carlo simulation of Bi$^+$ ion implantation into silicon using beam energies and fluences as specified in table 6.1. Filled distributions indicate individual implantation steps whereas the solid black line is the cumulative bismuth ion density profile.

measure the temperature dependence of the $D^0X$ photo-conductivity spectra. In that result, it was demonstrated that the quality of bismuth incorporation was identical to that of an equivalent bulk substrate. Additionally, for the sake of comparison, devices were fabricated using a sample annealed at 800 °C. Using chapters 4 and 5 as a guide, it is expected that the samples in this study will have a EAY and peak bismuth volume density of $\sim 75\%$ and $\sim 2 \times 10^{16}\text{cm}^{-3}$ respectively. Implanted substrates were float-zone grown ⟨100⟩ silicon with a bulk resistivity $> 5000 \text{ohm.cm}$. This corresponds to a phosphorus concentration of $< 8.6 \times 10^{11}\text{cm}^{-3}$.

### 6.1.2 Device fabrication

Implanted substrates in this study were fashioned into simple two terminal devices using a series of fabrication techniques that are outlined in this section. A combination of photolithography and reactive ion etching, RIE, was used to convert the bulk silicon substrate into the device structure geometry. $O_2$, $SF_6$ and $CHF_3$ were used as process gasses in the RIE procedure with a RF power of 100W, under these conditions a silicon etch rate of approximately 100 nm·min$^{-1}$ was achieved. The first etching step was used to create an island structure to isolate the implanted bismuth donors within the channel of the device. Using the specified RIE conditions, this region was fabricated to extend approximately 800 nm

100
below the surface of the substrate in order to contain the vast majority of the implant profile as outlined in figure 6.1, not accounting for large scale thermal diffusion. A second etching step of approximately 300 nm was then used to define the contact regions of the device, this allows for the electrodes to sit within the implant region and therefore would restrict any potential effects from surface damage. Figure 6.2 provides an illustration of both etching steps, a & b, and a profilometer measurement displaying the etching cross section, c.

The final step in the device fabrication process was to deposit aluminium electrodes on top of the defined contact regions. Aluminium was chosen for the contact material as it has a favorable work function in terms of n-type transport in silicon. Further discussion of the device contacts is included in the coming sections. A 15 second wet etch using 8% dilute hydrofluoric acid was used immediately prior to Al deposition to remove any native SiO$_2$ from the surface of the contact region. A ~250 nm thick film of Al was deposited using an electron beam evaporation system. The samples were then annealed on a hot plate at a temperature of 180 °C for 45 minutes to allow the aluminium contacts to sufficiently penetrate into the silicon implant region. Annealing was done in a nitrogen glove box environment to avoid any oxidation of the contacts during the heat treatment.
Figure 6.3: a & b) Illustrations of finished devices with channel dimensions of 500 × 700 µm and 100 × 100 µm respectively. Optical microscope image of device substrate, larger and smaller channel devices are labeled as A and B respectively.

Using this procedure devices with 2 different spacial geometries were fabricated. Figure 6.3(a) displays an illustration of the structure with a larger channel region of 500 × 700 µm whereas figure 6.3(b) presents the smaller channel device of 100 × 100 µm. Henceforth the nomenclature used to describe each geometry will be ‘device A’ for the larger device and ‘device B’ for the smaller. For clarity this is also presented in figure 6.3(c).

6.1.3 Electrical characterisation

The electrical contacts to devices in this study were ∼250 nm thick aluminium electrodes which were deposited directly onto the silicon substrate. Therefore it is expected that the mismatch in energies between the chemical potential of the silicon and the meal work function will result in the formation of a Schottky barrier. There are three process by which charge carriers can traverse a Schottky barrier, which are known as thermal emission, TE, thermionic field emission, TFE, and field emission, FE [133]. Figure 6.4 presents an illustration of the three different mechanisms for a reference. At room temperature thermal emission is the dominant process whereby electrons have enough energy to ‘jump’ over the potential barrier and enter the substrate. However as the temperature is lowered thermal emission becomes suppressed and the remaining two processes become more significant. Both field emission and thermionic field emission correspond to electrons tunneling through the potential barrier. In the former, the electrons tunnel directly through the barrier with the lowest possible energy,
Figure 6.4: Illustration of the potential landscape of a metal–semiconductor junction under reverse bias conditions. Indicated are three primary charge injection mechanisms.

whereas in TFE electrons at the junction have a raised thermal energy and therefore can pass through a thinner potential barrier. The various importance of each of the three processes can be evaluated by considering a parameter known as $E_{00}$ [134],

$$E_{00} = \frac{h}{4\pi} \left( \frac{N}{m^* \varepsilon_0 \varepsilon} \right)^{1/2}$$  \hspace{1cm} (6.1)

where $N$ is the impurity concentration, $m^*$ is the effective mass of the majority charge carrier and the remaining symbols have their usual meaning. When $E_{00} \gg kT/q$, FE dominates whereas if $E_{00} \ll kT/q$ then TE becomes important and TFE if $E_{00} \approx kT/q$. Thus, the leading charge injection mechanism depends strongly on both the temperature of the substrate and the impurity concentration. Using equation 6.1, and the implantation profile of the devices in this study $E_{00}$ can be estimated to be 0.78 meV. In the implemented experimental temperature range it is expected that a combination of TFE of TE are the dominant charge injection mechanisms, however it is unlikely that FE is significant.

The I–V characteristics of the devices in this study are presented in figure 6.5 under various experimental conditions. Firstly figure 6.5(a) displays the device response in the absence of black body radiation where it is observed that there is no measurable current until a temperature of approximately 40 K. This onset of current is due to the ionisation of bulk doped phosphorus donors in the handle of the substrate. Figure 6.5 displays the
I–V characteristics at 20 K with no attempt to restrict black body radiation and with (or without) illumination from the FTIR infrared source. Now it is observed that, in both cases, current is measurable at this temperature set point due to the direct ionisation of neutral donors through both sources of radiation.

For each of the measurements the current response is measured to be non-linear which is indicative of Schottky contact. It has been asserted that if TFE is the dominant transport mechanism through a metal-semiconductor junction, then the measured I–V curve should have a exponential relation \[134\]. However figure 6.5 displays that, for the devices in this study, this is not the case and rather the I–V curves are more indicative of thermal emission of charge carriers through a Schottky diode under reverse bias conditions [133]. Moving forward in the future, it is clear that it would be beneficial for the primary mechanism by which electrons enter the substrate through the contact to be FE. This could be achieved by including a degenerate doped region in between the metal contact and the substrate area that is of interest to the measurement in future fabrication schemes. This would result in a thinner potential barrier through which electrons can directly tunnel through without the
requirement of additional thermal energy. Thus I–V characteristics would become more linear in nature. Additionally, it would also be beneficial to move to four contact Van der Pauw contact geometries in future devices. In this operation two of the contacts are used to drive a current through the device and the remaining two are implemented to measure the resulting voltage drop. This setup therefore largely eliminates the effect of contact resistance and furthermore has been demonstrated as a suitable detection system for coherent experiments of donors in silicon [135].

However for the purposes outlined in this work, it is believed that the contacting of the present devices is sufficient, providing the biasing conditions are appropriate. Therefore, in order to operate in the linear region of the I–V relationship, a voltage bias of 3.6 V is applied across the device. As such, a device current ranging between \(\sim 1 \mu A\) and \(\sim 3 \mu A\) is expected depending on the temperature set-point.

6.2 FTIR spectroscopy

The first spectroscopic measurement used in the characterisation of the devices in this study is electrically detected FTIR. A full breakdown of the experimental technique can be found in section 3.4.1. In the first instance the THz optical absorption spectra of samples annealed at either 800 °C or 1000 °C are compared to identify any effects of implantation defects. Secondly the sample temperature is varied and a comparison between measured spectra is drawn. This temperature dependence allows for both a estimation of the implanted bismuth excited states binding energy and will serve as a useful comparison when considering the alternative spectroscopic techniques discussed in the later sections of this chapter.

6.2.1 Annealing dependence

The first comparison drawn is between the measurements of implanted devices which have been annealed at temperatures of either 800 °C or 1000 °C. Figure 6.6 displays extracted spectra from annealed substrates fabricated into devices with geometry A. For both sets of devices clear structure is observed corresponding the Rydberg transitions of the bulk doped phosphorus [136] in the substrate and the implanted bismuth donors [137] in the device channel region, figure 6.6 (a) and (b) respectively.

By observation of figure 6.6(a) it is apparent that, in both devices measured, orbital transitions from ion implanted bismuth donor centres up to the \(1s(A_1) \rightarrow 4p_{\pm}\) are accessible.
Figure 6.6: FTIR spectra of implanted Si:Bi devices with channel dimensions of 700x500 µm. 
a) Implanted Si:Bi orbital transitions (as indicated). b) Bulk doped Si:P orbital transitions 
(as indicated). Measured at 22 K
Higher lying transitions are not observable as they are subject to concentration broadening where excited state orbitals are overlapping to such an extent that they form a continuum and isolated states are no longer resolvable [138]. This is consistent with the implant dose and annealing conditions used in the fabrication of this device. Comparatively, in figure 6.6(b) Si:P electron orbital transitions up to the $1s(A_1)$ to $6p_{\pm}$ state are clearly resolvable in the same sample. This observation is compatible with the very dilute bulk doped phosphorus donor concentration known to be present in the substrate. The silicon wafers used in the fabrication were ‘ultra high resistivity’ and as such were specified to have a bulk phosphorus volume density between approximately $10^8$ cm$^{-3}$ and $10^{11}$ cm$^{-3}$. This therefore serves as an example of the extreme sensitivity of this technique and the benefits of electrical detection as a measurement of such a dilute donor concentration would be challenging using solely optical means.

Moreover, at first glance, it is observed that the quality of the measured Si:P spectra are similar between the two devices. This therefore indicates that the majority of phosphorus donors measured are situated far away from the implant region and are hence identical for both devices. In comparison there is a clear difference in the quality of spectra of the measured Si:Bi devices. Transitions in the sample annealed at 800 °C are both broader and lower in intensity than equivalent lines in the 1000 °C device. This can be accounted for by considering that substrates annealed at 800 °C will have a correspondingly higher population of implantation defects which will contribute to the inhomogeneous broadening of transition lines this is consistent with the observations made in chapter 4 regarding lower annealing temperatures.

In an effort to fully evaluate the effect that changing the annealing temperature has on the nature of measured spectral lines, the peaks displayed in figure 6.6(a) have been fit using Gaussian distributions. The same background subtraction was used for both the 1000 °C and 800 °C spectra. The baseline used for this is displayed in figure 6.7. It is apparent that the current density of each data set overlays well for regions of the spectrum that are far away from transitions ($\sim 15.4$, 16.0 & 17.0 THz). This therefore provides confidence that regions of inconsistency between the two measured devices are caused by the nature of the bismuth donors in each device. Inherently this must be linked to the post-implantation annealing treatment of each substrate as the devices are identical in every other regard.

After the removal of the background signal, each peak displayed in figure 6.7 was fit using Gaussian distributions which are displayed in figure 6.8. In addition to each of the
transitions already indicated in figure 6.7 (the $1s(A_1)$ to $2p_\pm$, $3p_\pm$ and $4p_\pm$) spectral features corresponding to the excitation of bound electrons to the $4p_0$ orbital state also became identifiable. This appears as an asymmetric low energy shoulder to the $3p_\pm$ transition at $\sim$16.35 THz. This is consistent in both devices. Corresponding fitting parameters are also displayed in tables 6.2 and 6.3 for the 800 °C and 1000 °C annealing temperatures respectively. Firstly, evaluating figure 6.8 and tables 6.2 and 6.3, it is observed that the energy centroids of the $2p_\pm$, $3p_\pm$ and $4p_\pm$ transitions are consistent between the two devices. There is however a discrepancy in the positions of the $4p_0$ transition. This can be accounted for by considering the relative ambiguity associated with identifying the position of this peak caused by its low size and close proximity to the $3p_\pm$ transition. This is particularly significant in the 800 °C structure (figure 6.8(b)). Furthermore, it is apparent that the energy centroid of the $4p_0$ transition in the device annealed at 1000 °C is a much better match to
Figure 6.8: Gaussian fits to Si:Bi orbital transition peaks (as indicated). Data are presented as points and fits are solid grey lines, where appropriate dashed lines are used to represent overlapping fits. a-c) Fits to the 800 °C device. d-f) Fits to the 1000 °C device.

Next, the linewidths of orbital transitions are compared between the two devices. It is found that the broadening of transition lines in the 800 °C device is remarkably consistent. Each Gaussian fit for the 1000 °C structure has a width corresponding to between 48% and 54% of the equivalent 800 °C annealed sample. This therefore is a strong indication that the transition lines of the 800 °C device have undergone a significant amount of inhomogeneous broadening. This is consistent with the observations made in chapter 4 where the effects of strain were observed as an unexpected splitting in the $D^0X$ photoconductivity measurements of the sample annealed at 800 °C. It was speculated that the splitting was a manifestation of implantation strain lifting the valley degeneracy of the valence band which is reflected in the formation energy of $D^0X$ complexes. However, in the context of FTIR measurements, it
seems appropriate that an inhomogeneous broadening of transition lines is instead observed as the valence band does not have a bearing on the process. This is consistent with literature where it has been reported that lattice impurities can contribute to a splitting in the spectroscopic measurements of acceptors and a broadening of donors \[139\].

An additional point of interest is that the integrated area of each transition peak is approximately equal between the two devices. This therefore indicates that even though the ‘quality’ of spectra is dramatically improved in the device annealed at 1000 °C, the absolute number of active bismuth impurities is comparable between substrates. This is consistent with the previous study in chapter 4 that indicated above annealing temperatures of 800 °C the electrical activation yield of bismuth ions does not significantly increase. Thus supporting the argument that annealing at 800 °C is adequate in terms of donor yield, but for applications within quantum technologies higher temperature heat treatment is necessary.

To confirm that it is only the bismuth donors that are subjected to this broadening effect, an identical line of analysis is performed on the measured phosphorus transitions.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$E_T$ (THz)</th>
<th>FWHM (THz)</th>
<th>Area (pA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p_\pm$</td>
<td>15.61 ± 0.02</td>
<td>0.093 ± 0.005</td>
<td>12.7 ± 0.4</td>
</tr>
<tr>
<td>$4p_0$</td>
<td>16.32 ± 0.07</td>
<td>0.056 ± 0.008</td>
<td>3.3 ± 0.5</td>
</tr>
<tr>
<td>$3p_\pm$</td>
<td>16.40 ± 0.03</td>
<td>0.083 ± 0.005</td>
<td>21.1 ± 0.5</td>
</tr>
<tr>
<td>$4p_\pm$</td>
<td>16.63 ± 0.02</td>
<td>0.063 ± 0.005</td>
<td>9.8 ± 0.4</td>
</tr>
</tbody>
</table>

Table 6.3: Parameters corresponding to fits displayed in figure 6.8 d-f) for 1000 °C device.
Figure 6.9: Gaussian fits to Si:P orbital transition peaks (as indicated). Data are presented as points and fits are solid lines, where appropriate dashed lines are used to represent overlapping fits. a-d) Fits to the 800 °C device.  e-h) Fits to the 1000 °C device.
Table 6.4: Parameters corresponding to fits displayed in figure 9 a-d) for 800 °C device.

<table>
<thead>
<tr>
<th>Transition from 1s(A1)</th>
<th>$E_T$ (THz)</th>
<th>FWHM (THz)</th>
<th>$A$ (pA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2p±</td>
<td>9.476 ± 0.001</td>
<td>0.0222 ± 0.0007</td>
<td>44.9 ± 0.8</td>
</tr>
<tr>
<td>4p0</td>
<td>10.228 ± 0.008</td>
<td>0.023 ± 0.001</td>
<td>3.6 ± 0.4</td>
</tr>
<tr>
<td>3p±</td>
<td>10.268 ± 0.001</td>
<td>0.0247 ± 0.0006</td>
<td>29.3 ± 0.3</td>
</tr>
<tr>
<td>4p±</td>
<td>10.492 ± 0.003</td>
<td>0.0241 ± 0.0007</td>
<td>14.9 ± 0.3</td>
</tr>
<tr>
<td>4f±</td>
<td>10.566 ± 0.006</td>
<td>0.0235 ± 0.0009</td>
<td>4.0 ± 0.2</td>
</tr>
<tr>
<td>5p±</td>
<td>10.669 ± 0.003</td>
<td>0.0216 ± 0.0007</td>
<td>9.8 ± 0.3</td>
</tr>
<tr>
<td>6p±</td>
<td>10.759 ± 0.006</td>
<td>0.0177 ± 0.0009</td>
<td>3.0 ± 0.2</td>
</tr>
</tbody>
</table>

It is noteworthy that the background for the phosphorus spectra is much flatter than the equivalent bismuth transitions. This is due to the fact that phosphorus has a much lower binding energy (45.59 meV) than bismuth donors (70.98 meV). Therefore any photon with sufficient energy to support a bismuth orbital transition will also serve as a source of ionisation for phosphorus donors. This non-resonant excitation will increase the photoresponse of the device in this frequency region which will appear as an enhanced background signal. Once again the same background subtraction was used for both spectra. Figure 6.9 displays the Gaussian fits of spectral peaks corresponding to phosphorus donor orbital transitions from the 1s(A1) ground state to the 2p±, 4p0, 3p±, 4p±, 4f±, 5p± and 6p± orbital levels in both devices. As previously, fitting parameters are displayed in tables 6.4 and 6.5 for the device annealed at 800 °C and 1000 °C respectively. A high degree of consistency is found between the spectra of both devices. Extracted values for the energy centroid, width and integrated areas of equivalent transition peaks are reasonably consistent between samples. Therefore it can be confirmed that the source of spectral broadening in the 800 °C bismuth spectra is local only to the implant region and does not effect the transitions of phosphorus donors in the bulk.
Table 6.5: Parameters corresponding to fits displayed in figure 9 e-h) for 1000 °C device.

<table>
<thead>
<tr>
<th>Transition from 1s(A1)</th>
<th>$E_T$ (THz)</th>
<th>FWHM (THz)</th>
<th>$A$ (pA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p_\pm$</td>
<td>9.477 ± 0.001</td>
<td>0.0231 ± 0.0007</td>
<td>45.8 ± 0.3</td>
</tr>
<tr>
<td>$4p_0$</td>
<td>10.221 ± 0.008</td>
<td>0.023 ± 0.001</td>
<td>3.4 ± 0.5</td>
</tr>
<tr>
<td>$3p_\pm$</td>
<td>10.268 ± 0.003</td>
<td>0.0266 ± 0.0006</td>
<td>30.1 ± 0.3</td>
</tr>
<tr>
<td>$4p_\pm$</td>
<td>10.491 ± 0.004</td>
<td>0.0267 ± 0.0008</td>
<td>16.4 ± 0.4</td>
</tr>
<tr>
<td>$4f_\pm$</td>
<td>10.563 ± 0.008</td>
<td>0.020 ± 0.001</td>
<td>3.9 ± 0.4</td>
</tr>
<tr>
<td>$5p_\pm$</td>
<td>10.667 ± 0.005</td>
<td>0.0231 ± 0.0008</td>
<td>9.6 ± 0.4</td>
</tr>
<tr>
<td>$6p_\pm$</td>
<td>10.758 ± 0.008</td>
<td>0.019 ± 0.001</td>
<td>3.0 ± 0.3</td>
</tr>
</tbody>
</table>

6.2.2 Temperature dependence

To explore the significance of environmental temperature on the implanted bismuth devices, spectra were measured in both devices at a range of temperature set-points. The mechanism whereby electrons are promoted into the conduction band under THz illumination is known as photothermal ionisation, PTI, which is inherently temperature dependant. A full discussion of this process can be found in section 3.5.1. Lower spectral resolution of 1 cm$^{-1}$ (0.03 THz) was used in these measurements therefore it is expected that the widths of transition peaks in this dataset will be resolution limited, as compared to the data analysed in the previous section. However the integrated spectral area of transitions will prove useful in identifying the temperature dependence of the photoresponse. In the lower resolution spectra the effect that Fabry-Pérot oscillations are observed to be much more significant and can be identified as a constant background oscillatory feature. Figure 6.10 presents the measured bismuth donor spectra of both the 800 °C and 1000 °C devices measured at various temperatures. The features observable in this spectra are directly comparable to the equivalent dataset displayed in figure 6.6(a) which was measured using a higher resolution of 0.4 cm$^{-1}$.

It is observed that as the temperature rises, the strength of transition peaks also increases. This is consistent with the PTIS model whereby the electrons are graduated from their bound state into the conduction band through the absorption of a thermal phonon. Furthermore, it is notable that as the excited state energy increases, the dependence on temperature becomes less significant. This can be explained by considering that as the excited state
Figure 6.10: Implanted Si:Bi electrically detected FTIR spectra measured at different temperature set points (as indicated). a) Displays data from the 800 °C annealed device whereas b) presents equivalent 1000 °C spectra.
orbital energy increases, its corresponding ionisation energy, $E_n$, decreases. Therefore, small changes in temperature will not have a great effect on the signal strength. Moreover, the temperature of the system is observed to be of virtually no significance to electron transitions into the continuum at $>16.8$ THz. This is because excitations of this nature are a 1 photon process and therefore will not depend on temperature. In an effort to more fully analyse the temperature dependence of the measured bismuth donor spectral features, each peak in figure 6.10 has been fit and their integrated areas are compared as a function of temperature. The background subtraction and fitting procedure is identical to the previous section. Figure 6.11 displays the integrated spectral area of the $2p_{\pm}$, $3p_{\pm}$ and $4p_{\pm}$ transitions as a function of temperature for both devices.

It is found that the temperature dependence of both devices appears to be generally consistent. This is such that as the $2p_{\pm}$ transition has the strongest temperature dependence whereas the $4p_{\pm}$ peak area doesn’t change as much. More numerical analysis will follow although this observation supports the previous discussion. However it is worth noting that, because the spectral features are much broader and lower intensity, Fabry-Pérot oscillations

Figure 6.11: a & b) Integrated spectral density of Si:Bi transition peaks (as indicated) as a function of temperature set point for the 800 °C and 1000 °C annealed devices respectively. c) The natural log of integrated Si:Bi transition spectral density (as indicated) as a function of inverse temperature. Solid lines represent linear fits to data. Temperature values have been shifted by +2.4 K from their initial set point, as explained in the text.
are of comparable size in the 800 °C device and therefore appropriately fitting the transition peaks becomes challenging. This is particularly significant in the spectra measured at 16 K. Whereas the 1000 °C device features are much more strongly resolved. Whilst figure 6.11(a) remains useful as a qualitative comparison between the two devices, extracting meaningful quantitative results would prove challenging. Therefore the following analysis will focus on the data measured in the 1000 °C device.

The expected PTIS signal has been discussed previously in section 3.5.1 using equations 3.10 and 3.11 however for convenience the expression for the rate has been stated again here. The rate of a reaction as a function of temperature can be described using the Arrhenius equation,

$$\sigma_I(\omega) = \sigma(\omega) I^{(n)} = A \exp \left( -\frac{E_n}{k_B T} \right)$$

(6.2)

where $E_n$ is the excited state binding energy, $I$ is the integrated spectral density and $A$ is a constant that pertains to the optical absorption cross section. Therefore if $T$ and $\sigma_I(\omega)$ are both known quantities, equation 6.2 can be used to evaluate the activation energies of each orbital state. Figure 6.11(c) plots the natural log of $\sigma_I(\omega)$ as a function of $1/T$ for the spectral lines evaluated in figure 6.11(b). By evaluating equation 6.2 it is clear that the relationship between these two parameters should be linear in nature with gradient that is equal to $-E_n/k_B$. Using the temperature values as provided by the cold finger cryostat, the extracted values of $E_n$ for each of the measured orbital states do not match up well with those established in literature. However by introducing a correction of +2.4 K to each temperature set point yields much more reasonable energies. With this offset in place $E_n$ values are calculated to be 6.4 ± 0.2 meV, 3.0 ± 0.3 meV and 2.2 ± 0.6 meV for the 2p±, 3p± and 4p± states respectively. This therefore suggests that the temperature of the substrate during the measurement was higher from that of the cold finger by approximately +2.4 K.

For the sake of completeness the temperature dependence of observed phosphorus transitions is also discussed. Figures 6.12(a & b) display the measured phosphorus spectra as a function of temperature. Figures 6.12(c & d) illustrate the integrated spectral density of each peak indicated in figures 12(a & b) with the exception of the 4f±. Here, compared to the equivalent bismuth lines discussed previously, a slightly different behaviour is observed as the temperature of the system is raised. As the temperature set point rises between 16 K and 20 K the strength of each peak increases which is a result of an increase in photothermal ionisation. However above 20 K the peak intensity drops significantly which can
be justified by considering the fact that phosphorus donors will begin to thermally ionise. This will also have the additional effect of causing a decrease in electron mobility due to an increase in scattering events [118]. Therefore it is expected that, in this temperature range, equation 6.2 will not yield accurate values for the activation energy of the various excited orbital states in this system. Comparatively, bismuth donors have a much higher binding energy and therefore would expect to undergo this drop off in signal at higher temperatures.

Finally, a device with the smaller channel dimensions (labeled as B in figure 6.3(c)) was measured and corresponding spectra are displayed in figure 6.13(a) over a range of temperatures. Here it is found that measurements of the smaller device yielded spectra that were overall consistent with the larger devices, including the spectral response to increasing temperatures. Furthermore, by applying the same +2.4 K temperature correction that has been inferred by the measurement of the larger device and implementing equation 6.2, the binding energies of the $2p_{\pm}$, $3p_{\pm}$ and $4p_{\pm}$ orbital states have been extracted as $6.3 \pm 0.2$ meV, $3.1 \pm 0.2$ meV and $2.5 \pm 0.3$ meV respectively.
Figure 6.13: a) Electrically detected FTIR spectra of ion implanted Si:Bi devices with a 100 µm electrode spacing and annealed at 1000 °C. Spectra were measured at different temperatures (as indicated). b) Integrated spectral density of Si:Bi transition peaks as a function of temperature set point. The natural log of integrated Si:Bi transition spectral density as a function of inverse temperature. Solid lines represent linear fits to data. Temperature values have been shifted by +2.4 K from their initial set point, as explained in the text.
6.3 FEL spectroscopy

The previous sections if this chapter have demonstrated the electrically detected Rydberg spectra of the implanted bismuth devices under the low illumination power regime. This section will explore the much higher intensity, coherent excitation through the use of a free electron laser, FEL. Section 3.4.2 contains a general overview of the operation of a FEL and also a more detailed discussion of the experimental setup implemented in this study. Unlike the infrared FTIR source, FELs provide pulses of high power coherent light that resonantly pump donor electron transitions. Using this technique the orbital excitation spectra of ion implanted bismuth donors can be measured and hence a comparison with FTIR can be drawn. Figure 6.14 displays a typical measured FEL spectra of a device in this study as well as an equivalent FTIR measurement (taken from figure 6.6(a)).

Upon first observation the spectra measured using the two different techniques appear to be generally consistent, this is such that orbital transitions from the 1s(A1) to the 2p±, 3p± and 4p± states are visible. However, it is also apparent that in the FEL spectrum a transition to the 3p0 level is also present, but is absent in the FTIR measurement. Furthermore, it is clear that there is a discrepancy in the relative spectral peak intensities between the two measurement techniques. This is such that in the FTIR measurement the 3p± transition strength was observed to be much greater than the corresponding 2p± signal whereas in the FEL spectrum the two peak strengths are much more comparable. This is discussed in more detail later in this section. In addition it is clear that in the FEL measured spectrum transition linewidths are significantly greater than when using FTIR. While the resolving power of FTIR can be optimised by altering various experimental properties such as the interferometer path length, mirror speed etc, during a FEL sweep the resolution is limited by the bandwidth of the laser itself. This broadening is a result of the variation in energies of electrons passing through the undulator. Additionally, transitions can present larger linewidths as a result of power broadening from the higher intensity illumination [140].

In the previous section it was determined that, during electrically detected FTIR, the primary mechanism by which electrons are promoted into the conduction band is photo-thermal ionisation. This was shown by evaluating the temperature dependence of the measured electron orbital excitation spectra. Therefore it is useful to explore the temperature dependence of measured FEL THz excitation spectra. Figure 6.15 contains bismuth donor electron orbital spectra measured at temperature set-points ranging from 8 to 20 K. Two
different device bias voltages are presented for reasons that will become clear in the following discussion. Firstly, by evaluating the spectra measured with a 3 V device bias it is found that there is no discernible temperature dependence between the various measurements. In fact it is found that the spectra measured at each set-point are remarkably consistent, this is in direct contradiction with the observations made during the previous FTIR measurements. Two possible explanations for this observation could be as follows. Firstly it may be possible the temperature of the sample is not varying by the amount defined by the cryostat set-point and is instead remaining constant. Or an alternative justification is that the mechanism by which free charges are being generated is not exclusively photothermal ionisation and thus not solely temperature dependent.

The cryostat used in this measurement was a liquid helium cooled cold finger and therefore care was taken to ensure a good thermal contact with the PCB (on which the device was mounted). However, even with poor thermal contact it is unlikely that the cooling power of the cryostat can account for this lack of a temperature dependence. For context, an identical cryostat was used in the previous FTIR measurement where, as discussed, the temperature discontinuity between the cold finger and substrate was approximated to be only +2.4 K.
Figure 6.15: Electrically detected Si:Bi FEL photoconductivity spectra of Bi$^+$ ion implanted devices, measured at a range of temperature set points (as indicated). a) Uses a device bias of 2 V whereas b) uses 3 V.

Clearly this not enough to explain figure 6.15. It is also possible that the sample is being heated to a constant temperature by a mechanism present during the experimental procedure. A possible candidate for this could be direct heating from the FEL macropulse itself. By considering the amount of energy absorbed by the sample from the incident beam, it is possible to estimate the extent of any effects due to sample heating. FEL radiation used for this measurement was attenuated such that it had a total energy of 15.6 $\mu$J per macropulse. The formalism that is used to estimate the change in sample temperature will utilise the Debye theory of heat capacity in the low temperature limit where it is assumed that the silicon heat capacity, $C(T)$, rises with the third power of the temperature. In other words,
Figure 6.16: Calculated temperature change of the device sample under illumination of a FEL macropulse at various initial temperatures, $T_1$. The red line assumes all energy is contained within the path traversed by the beam whereas the blue line illustrates the heating if the macropulse energy is evenly distributed throughout the whole sample. The focal spot was estimated to be 2 mm $\times$ 2 mm with a macropulse energy of 15.6 $\mu$J. The model assumes 100 % absorption.

$C(T) = \alpha T^3$, where $\alpha$ is a material constant [141]. It is possible to define the change in temperature, $\Delta T$, for a given substrate having undergone a change in energy, $\Delta E$, as,

$$\Delta T = \frac{\Delta E}{C(T) \cdot m}$$  \hspace{1cm} (6.3)

where $m$ is the mass of the material. Therefore, by evaluating the integral expressed in equation 6.4, and knowing the macropulse energy, it is possible to estimate the change in lattice temperature through absorption THz radiation. Here $V$ and $\rho$ are the volume and mass density of the sample.

$$\int_{T_1}^{T_2} C(T) dT = \frac{dE}{V \rho}$$  \hspace{1cm} (6.4)

For the samples in this study the final temperature, $T_2$, has been approximated for a range
of initial temperatures, $T_1$, under the assumption that 100% of the 15.6 $\mu$J macropulse has been absorbed by the sample. This temperature relation has been plotted in figure 6.16 where two different scenarios have been considered. The red line illustrates the change in sample temperature if the heat dissipation were contained solely within the volume defined by the incident FEL beam spot. Here it is observed that significant heating would occur for $T_1$ values of approximately 15 K or less. By comparison the blue line is if the heat dissipates evenly over the entirety of the substrate. Under this condition it is estimated that the effect of heating would be greatly reduced and only significant for $T_1$ values of less than $\sim$8 K. It is worth stating that in both cases this calculation is certainly an over estimate of the heating power of the macropulse as it is extremely unlikely that 100% of the pulse would be absorbed and in reality the absorbance would be much lower. Additionally this simple expression for $T_2$ does not take into the account of the cooling power of the cryostat. Therefore figure 6.16 should be regarded as only the most extreme case of heating. This is particularly true of the red line as it assumes that the energy is concentrated within the beam path. In reality, energy will dissipate throughout the substrate however the effect of heating will be greatest at the focal point. In the experiment the beam was focused such that radiation was incident onto the device structure. Figure 6.16 indicates that, in the most extreme case of heating, the minimum temperature achievable is approximately 17 K. Although, as the energy dispersion over the whole sample is considered, this value is observed to drop significantly. This observation, coupled with the overestimation in absorption, would suggests that a single FEL macropulse is not able to heat the sample enough to justify the lack of a temperature dependence observed in figure 6.15. However it is also true that this model only takes into account the heating power of a single macropulse. Therefore the assumption is that the cooling power of the cryostat is sufficient enough that, between macropulses, the sample cools back down to $T_1$. If this assumption is not true, then a sequence of macropulses may have a more significant cumulative heating effect. This assertion would require a more sophisticated treatment which is not within the scope of this simple formalism. However, one thing that this model does illustrate is that in the very low temperature regime ($< 4$ K) FEL heating effects will almost certainly play a significant role.

The other possible justification for figure 6.15 is that PTIS is no longer the dominating ionisation mechanism through which device conduction is generated. Section 3.5.1 includes a discussion of the various possible mechanisms by which electrons can be promoted into the conduction band from a given bound state. In addition to PTIS, possible alternatives could
be multi-photoexcitation or ionisation via electron scattering events, neither of which would be expected be significantly effected by a change in substrate temperature (in the region of 8 to 20 K). To explore this further, figure 6.15(a) presents measured Si:Bi orbital excitation spectra using a lower device bias of 2 V. Here it is apparent that, in this regime, a temperature dependence emerges in the $1s(A1) \rightarrow 2p_{\pm}$ transition (at $\sim$15.6 THz). This is such that at 8 K the transition intensity is less than at higher temperature set-points, however it is also noticeable that the strength of the $1s(A1) \rightarrow 3p_{\pm}$ transition (at $\sim$16.35 THz) remains temperature independent. It is therefore possible that this observation lends itself to the model that ionisation through electron collisions is a mechanism present in this measurement. This is because at lower voltage biases the average kinetic energy of free electrons within the active device region will be reduced. As such electron collisions will be less likely to transfer enough energy to liberate a bound electron into the conduction band. Naturally this effect will be more significant for bound states with higher binding energies and therefore it is plausible that a reduction in bias voltage will effect transitions to the $2p_{\pm}$ before the $3p_{\pm}$. Therefore temperature effects will become comparatively more effective in the lower energy excitation and hence potentially explain the observation made in figure 6.15(a). This discussion is reflected in the impact ionisation model presented in section 3.5.2 (taken from Dierickx et al [113]). Furthermore, it is intuitively clear that the rate of impact ionisation events will scale with the population of electrons in the conduction band. Figure 6.15(b) displays that, under a 3 V device bias, the current flowing through the device is of the order of $\sim$100 $\mu$A. By comparison figure 6.5 shows that under illumination from the FTIR source the device current is only $\sim$2 $\mu$A. This therefore indicates that the speculated onset of impact ionisation in FEL spectroscopy could be a result of the increased current density caused by a significantly higher power THz illumination. Crucially it is worth noting that the temperature dependence uncovered in this transition is still far away from matching the model described by PTIS (as displayed in figures 6.10 and 6.11). It is difficult to draw any conclusions from the (lack of a) temperature dependence presented in figure 6.15 as it is likely that various mechanisms contribute to the measured electrical signal simultaneously. Therefore, a greater understanding of each one is required in order to fully decompose and understand this measurement. Unfortunately, that is beyond the scope of this body of work.

To explore the idea that the FEL macropulse is heating the device, it is useful to consider the effect that increasing the illumination energy has on the measured electron excitation spectra. Figure 6.17 presents measured data taken using energies ranging from 0.49 $\mu$J to
Figure 6.17: Electrically detected Si:Bi FEL photoconductivity spectra of Bi$^+$ ion implanted devices, measured at a range of macropulse energies (as indicated). Spectra have been normalised using either a) their FEL macropulse energy or b) the peak intensity of the 1s($A_1$) $\rightarrow$ 2$p_{\pm}$ transition.

Table 6.6: Relative photoconductivity peak intensities between the 2$p_{\pm}$ and 3$p_{\pm}$ transitions under a range of FEL illumination energies (taken from figure 6.17). Corresponding substrate temperatures have been calculated using the model for PTIS. Also included for the sake of comparison are values from equivalent FTIR measurements (taken from figure 6.10(b)).

<table>
<thead>
<tr>
<th>Macropulse Energy ($\mu$J)</th>
<th>Measured 2$p_{\pm}$ : 3$p_{\pm}$ Ratio</th>
<th>Calculated Temperature (K)</th>
<th>Temperature Setpoint (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.49</td>
<td>1 : 1.49</td>
<td>31.0 $\pm$ 0.9</td>
<td>20</td>
</tr>
<tr>
<td>4.93</td>
<td>1 : 1.39</td>
<td>32.9 $\pm$ 0.9</td>
<td>20</td>
</tr>
<tr>
<td>15.6</td>
<td>1 : 1.21</td>
<td>38 $\pm$ 1</td>
<td>20</td>
</tr>
<tr>
<td>49.3</td>
<td>1 : 1.05</td>
<td>43 $\pm$ 1</td>
<td>20</td>
</tr>
<tr>
<td>156</td>
<td>1 : 1.01</td>
<td>45 $\pm$ 1</td>
<td>20</td>
</tr>
<tr>
<td>FTIR</td>
<td>1 : 2.70</td>
<td>20.6 $\pm$ 0.3</td>
<td>18</td>
</tr>
<tr>
<td>FTIR</td>
<td>1 : 2.34</td>
<td>22.4 $\pm$ 0.3</td>
<td>20</td>
</tr>
</tbody>
</table>
J. For each of the presented data plots a temperature set-point of 20 K was used with a fixed voltage bias of 3 V. For the sake of comparison each of the spectra have been normalised and are plotted in two different ways. In figure 6.17(a) each of the spectra have been normalised by the energy of the FEL macropulse whereas in (b) the peak intensity of the $1s(A_1) \rightarrow 2p_{\pm}$ transition has been used. Firstly, in (a) it is displayed that, as the energy of the macropulse is increased, the relative intensity of the measured electron transitions decreases. Additionally, figure 6.17(b) indicates that there is a trend between the relative $2p_{\pm} : 3p_{\pm}$ peak intensities and the energy of FEL illumination. For low energies the $3p_{\pm}$ signal is much greater than the $2p_{\pm}$, however, as the intensity of the FEL increases the two peaks become much more comparable. In other words, as the illumination power rises the measured signal from the $2p_{\pm}$ transition increases at rate greater than that of the $3p_{\pm}$. This indicates that accompanying the global reduction of spectral intensity, the $1s(A_1) \rightarrow 3p_{\pm}$ peak is saturating at lower powers than transitions to the $2p_{\pm}$ level.

To speculate on this observation, it is beneficial to once again consider the mechanisms by which electrical signal is generated in a measurement of this nature. It is well established that the oscillator strength of each transition in the Rydberg series of donors in silicon is larger for transitions with a smaller principle quantum number [142]. Therefore it would be expected that, in a purely optical measurement, the $1s(A_1) \rightarrow 2p_{\pm}$ transition rate will be greater than the $1s(A_1) \rightarrow 3p_{\pm}$. This is plainly observable in the bulk doped absorption FTIR spectrum which was presented previously in figure 3.6 (section 3.4). However, in an electrical measurement it also necessary to consider the mechanism by which excited electrons are promoted into the conduction band. In relation to PTIS, it is well understood that the thermal ionisation rate is higher for states with a lower binding energy. Therefore, by measuring the ratios between the spectral intensities of the $2p_{\pm} : 3p_{\pm}$ transitions, and knowing the corresponding transition strengths, it is possible to use the PTIS model to estimate the temperature of the substrate. This is effectively just rearranging equation 6.2 to extract $T$. In this instance $A$ is the known strength ratio between the two transitions. Table 6.6 displays the measured spectral intensity ratios between the $2p_{\pm} : 3p_{\pm}$ transitions for each of the FEL energies presented in figure 6.17 and the calculated sample temperatures. For the sake of comparison, corresponding FTIR spectra (taken from figure 6.10(b)) have also been included in this line of analysis. Through observation of table 6.6, is clear that for each of the measured FEL spectra, the extracted substrate temperature is significantly higher than the experimental temperature setpoint. This is particularly striking as it suggests that
Figure 6.18: Electrically detected Si:P FEL photoconductivity spectra of bulk doped P donors. The blue plot is measured using FTIR (taken from figure 6.6) whereas the grey line is an equivalent measurement using illumination from a FEL. In the FEL spectra a series of transition lines are observed due to transitions from the split-off valley levels known as the $1s(T_2)$ and $1s(E)$ states.

Even the lowest macropulse energy used in this measurement (0.49 µJ) corresponded to a sample heating in excess of +10 K. By comparison, the measured FTIR spectra match much more closely with the experimental temperature setpoints. Here a temperature discrepancy between the sample and cryostat of approximately +2.5 K is calculated which is consistent with the conclusions drawn from section 6.2.2. It is difficult to justify such a substantial heating effect in the FEL spectra, particularly given the worst case heating scenario outlined in figure 6.16 is still far away from the change in sample temperature suggested in table 6.6. This therefore suggests that there are additional, significant sources of heating that are not considered in that model. An alternative explanation could also be that the observed saturation is a result of power broadening. It has been reported that pumping a transition in a two-level atom with increasing energies can both significantly reduce the transition intensity and broaden its spectral linewidth [140]. This is also consistent with the spectral broadening observable in figure 6.17(b).

Finally, the spectrum of the bulk doped phosphorus donors is examined using FEL spec-
Figure 6.18 displays a measured spectrum at a temperature set-point of 20 K and a 3 V device bias. The energy of the FEL macropulse illumination was approximately 15 \( \mu \)J. Also included for the sake of comparison is the equivalent FTIR spectra. It is immediately clear that the spectrum measured using the FEL dramatically differs from FTIR. This is such that a series of lower energy transitions become observable which were not present in the previous measurement. For the most part these spectral features match up well to transitions from the Si:P \( 1s(T_2) \) and \( 1s(E) \) split ground states to higher lying orbital levels. It has been demonstrated in literature that the minimum temperature at which the \( 1s(E) \) state in phosphorus become thermally populated is at approximately 30 K [143]. Therefore, the observation of these transitions in this spectrum further add to the suggestion that the sample in this measurement is being heated. As with the previously discussed bismuth spectra it is possible to estimate the substrate temperature using the measured spectral intensities of the various transition lines. Using the appropriate theoretical oscillator strengths for each transition [142], and the measured strength ratios of the \( 2p_0 : 2p_\pm \) and \( 2p_\pm : 3p_\pm \) spectral lines, the temperature of the sample is calculated to be \( (35.5 \pm 0.5) \) K. As with the previous discussion, this temperature value is estimated under the assumption that PTIS is the only significant ionisation mechanism. This would therefore account for the thermal population of the \( 1s(T_2) \) and \( 1s(E) \) states. However, as discussed previously, it is not expected that the typical FEL macropulse energies used in a measurement of this nature to significantly alter the temperature of the substrate. It is evident that, by some mechanism, transitions from these valley states are becoming active. This therefore leads to the interpretation that, either the sample is in fact being heated an additional +15 K by a mechanism inherent to the FEL measurement, or the \( 1s(T_2) \) and \( 1s(E) \) split states are being populated by some means other than temperature.

The ultimate desire of a system of this nature would be the ability to coherently control the donor state wavefunction through interactions with the applied THz radiation. Therefore it is useful to consider the necessary macropulse energies that would be required to achieve interactions of this nature. This can be evaluated by defining the donor as a simple two level system with a wavefunction, \( |\psi\rangle = c_1 |1\rangle + c_2 |2\rangle \), where \( c_1 \) and \( c_2 \) are the amplitude coefficients for the ground and excited states, \( |1\rangle \) and \( |2\rangle \) respectively. In the high illumination regime, the probability of manipulating the donor such that it ends up in the excited state,
Table 6.7: FEL macropulse energies that correspond to a $\pi$-pulse for transitions from the $1s(A_1)$ to $2p_\pm$ and $3p_\pm$ levels in phosphorus and bismuth donors in silicon.

<table>
<thead>
<tr>
<th>Donor Species</th>
<th>Transition from $1s(A_1)$</th>
<th>$\pi$-pulse Energy ($\mu J$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus</td>
<td>$2p_\pm$</td>
<td>7.9</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>$3p_\pm$</td>
<td>37</td>
</tr>
<tr>
<td>Bismuth</td>
<td>$2p_\pm$</td>
<td>132</td>
</tr>
<tr>
<td>Bismuth</td>
<td>$3p_\pm$</td>
<td>571</td>
</tr>
</tbody>
</table>

$|c_2|^2$ is given by equation 6.5.

$$|c_2|^2 = \sin^2 \left( \frac{A}{2} \right)$$  \hspace{1cm} (6.5)

This is known as the Rabi theory of a two level system [144] where $A$ is a quantity referred to as the pulse area. By observation of equation 6.5 it is clear that when $A = \pi$, $|c_2|^2 = 1$ which means there is a 100% probability that the donor will end up in its excited state. This is known as a $\pi$-pulse. In practice $A$ is determined by the energy of FEL macropulse which is approximated to have a beam spot with a Gaussian distribution. Therefore $A$ must be defined as a function of radial distance, $r$, from the centre of the beam spot:

$$A(r) = A_0 \exp \left( -\frac{r^2}{2r_0^2} \right)$$  \hspace{1cm} (6.6)

where $r_0$ is the spatial e-folding radius of FEL power distribution across the sample. The maximum pulse area, $A_0$, can be described analytically as,

$$A_0 = \frac{8 \ln(2) \frac{\pi}{2} d_{\text{eff}}}{r_{\text{FWHM}}} \sqrt{\frac{\alpha t_0 E_M}{\hbar N}}$$  \hspace{1cm} (6.7)

where $E_M$ is the macropulse energy, $r_{\text{FWHM}}$ is the full half width maximum of the FEL beam spot, $\alpha$ is the fine structure constant, $t_0$ is the e-folding radius of the FEL power in respect to time and $N$ is the number of micropulses per macropulse. $d_{\text{eff}} = |d| F$ is the effective dipole moment where $|d|$ is the dipole matrix element of transition in question and $F$ is a factor that accounts for transmission effects. The relationship described in equation 6.7 was first proposed by P.T. Greenland in an unpublished communication.
Using this formalism it is possible to estimate the FEL macropulse energy that would be required to achieve a $\pi$-pulse in the experimental conditions that have been implemented in this section. Table 6.7 displays that, for both phosphors and bismuth donors in silicon, the energy required per macropulse to achieve a $\pi$-pulse for transitions from the $1s(A_1)$ to the $2p_{\pm}$ and $3p_{\pm}$ excited levels range between 7.9 to 571 $\mu$J. This is significant as these energy values are directly comparable to the energies which appear to be causing a significant amount of heating in the devices measured during this study. This therefore identifies that, in order to successfully manufacture a system whereby the state of a two level donor is coherently manipulated through interaction with THz radiation, it is essential that a great deal of care is taken to inhibit any effects of substrate heating.

6.4 Summary

This chapter has demonstrated that the measurement of high quality THz electron excitation spectra is achievable using ion implanted Si:Bi devices. In the first instance, electrically detected FTIR was used to probe the electron transitions of both ion implanted bismuth donors and bulk doped phosphors impurities. It was found that there was a significant improvement in the quality of the measured Si:Bi spectrum using the sample annealed at the highest temperature. Thus reaffirming the importance of utilising the appropriate post implantation annealing conditions on the quality of bismuth donor incorporation. Additionally, it was demonstrated that there is a strong correlation between the temperature of the substrate and the measured resonant electrical response of the device. This was identified to match well with the model outlined by photothermal ionisation spectroscopy. A small offset in temperature (+2.4 K) between the cryostat setpoint and extracted lattice temperature was identified and was attributed to the limitations in thermal contact between the sample and cold finger.

The second half of this chapter switched focus towards the high intensity, resonant THz excitation of ion implanted bismuth donors using a free electron laser. Much like the FTIR measurements, FEL photoconductivity spectra clearly contained features corresponding to electron transitions from both species of donor. However, while it was found the FTIR measurement matched well with the model for PTIS, the FEL spectroscopy yielded less conclusive results. Broadly speaking the measured FEL Si:Bi excitation spectra matched well what was obtained using FTIR in terms of spectral features however there were significant
departures in terms of the device response to experimental conditions such as temperature. For example, altering the experimental temperature appeared to have virtually no effect on the spectral properties of the measurement. Furthermore, as the power of the FEL illumination increased a saturation in the measured spectral features was observed that strongly indicated heating of the device substrate. Using the model for PTIS this was evaluated to correspond to an increase in lattice temperature of +25 K under the highest illumination power. This is far more significant than any heating effect that is predicted by even the worst case scenario of the low temperature Debye theory of heat capacity. Additionally, it is also possible that in the high current regime caused by the intense illumination of the FEL alternative channels of excited donor ionisation such as impact ionisation become significant. This is supported by the observation a slight temperature dependence in the FEL spectra that becomes apparent when the device bias voltage is reduced.

Plainly, more work is required to fully uncover the effects of sample heating and impact ionisation during a measurement of this nature. Identifying the effects of impact ionisation can be achieved by measuring the IV characteristics of the device with and without FEL illumination. The onset of impact ionisation is commonly associated with a sharp increase in device conduction as the bias voltage crosses a given threshold value. A similar line of investigation to this has been displayed previously in the context of $D^0X$ spectroscopy using epitaxially grown Si:P devices [145]. However, it is first essential to comprehensively understand the extent of substrate heating caused by the FEL macropulse. The natural next step would be to simply repeat the measurements in this chapter using a cryostat with a higher cooling power in an attempt to uncover a reasonable temperature dependence. Alternatively it could prove fruitful to integrate a donor bound exciton spectroscopy measurement as a readout mechanism during the FEL scan. It has already been established in this thesis (section 4.6) that the energy of the $D^0X$ transition is a very effective measurement for the silicon lattice temperature and therefore measuring $D^0X$ lines under FEL illumination would definitively uncover the extent of sample heating. However, given the limitations in FEL beam time availability, it would also be greatly beneficial to develop a finite element model that can more accurately predict the dynamical change in substrate temperature under pulsed illumination.

This chapter has clearly demonstrated that in an experiment where it is required to illuminate a low temperature device with coherent THz radiation, the effects of sample heating simply cannot be ignored. A great deal of care must be taken into ensuring the lattice
temperature is closely controlled in order to eliminate any ambiguity in measured spectra. Although further work needs to be done in order fully understand the heating effects and donor ionisation mechanisms during FEL spectroscopy, the results of this chapter are of note as they include some of the first measurements of this nature that have been performed on a substrate other than bulk doped silicon. As such it opens up for the possibility of a wide range of device architectures that revolve around the optical interaction with bismuth donors (and other impurities) in silicon. For example, the Stoneham Fisher Greenland scheme for quantum computation (discussed in section 1.3) relies on the ability to manufacture a system whereby two different species of donor coexist in the same environment and can be selectively excited to induce an exchange interaction between neighbouring qubits. While it is clear that in order to fully realise the SFG scheme more development needs to be done to position donors into appropriate spatial geometries, this work has successfully demonstrated that it is possible to introduce a second species of donor through ion implantation and achieve a selective excitation by tuning the FEL pumping wavelength. Moreover, this chapter acts as a pragmatic demonstration that it is possible to fabricate ion implanted bismuth doped samples that yield high quality THz electron excitation spectra and therefore should be considered as an alternative to bulk doped substrates.
Chapter 7

Self assembled single Si nanowire transistors

Until this point the work presented in this thesis has focused on evaluating ion implanted bismuth donors in silicon for applications within silicon donor based quantum technologies. However in this final results chapter an alternative to bulk silicon is explored as a vehicle to support donor based quantum technologies.

One of the primary difficulties in the fabrication of quantum devices in silicon is the requirement of extremely small scale structures to achieve electron confinement. Typically the leading technique to achieve devices on this scale is electron beam lithography, EBL, where an electron beam is used to pattern structures onto the surface of bulk silicon using a resist. A subsequent etching step is then used to define the device. This technique can achieve very high resolutions of up to \( \sim 10 \text{ nm} \) however it is quite time and cost expensive and is not particularly well suited to scaling up to large scale production. In addition, etched devices can result in structural roughness or potential dopant fluctuations. An alternative to defining structures using EBL could be by utilising the natural 2D confinement of single-crystal silicon nanowires. Silicon nanowire quantum dots have been demonstrated as early as 2005 where the coherent transport of charge carriers through quantum confined levels was achieved in simple back–gated single electron transistor, SET, devices \cite{146}. The wires in this study had a core diameter of 3 to 6 nm and were observed to display SET behaviour in devices with source/drain electrode separations of up to 400 nm. Achieving a channel diameter as small as \( \sim 6 \text{ nm} \) would be extremely challenging using standard EBL and etching techniques. Subsequently, numerous examples of single nanowire SETs have been reported in recent years.
using various material compositions and electrode geometries [147, 148, 149, 150]. However, there are challenges associated with the fabrication of single nanowire devices in a controllable and scalable manner. In fact the most common procedure for electrically contacting a single nanowire is using EBL to deposit electrodes onto nanowires that have been arbitrarily drop casted onto a substrate. While this procedure is sufficient for demonstrating that single nanowire devices have potential for integration into quantum technologies it is very much limited in terms of scalability. Therefore, in this chapter scalable scheme for the alignment of single silicon nanowire transistors is presented. This fabrication method is designed to be extremely versatile in an effort to be compatible with as many different device geometries as possible.

7.1 Dielectrophoresis

Single crystal nanowire transistors have vast potential for integration within quantum technologies, however for many applications a high degree of control over wire positioning is required. One promising technique to achieve this is known as dielectrophoresis, DEP, whereby nanoparticles can be manipulated by applying a localised AC electric field [151]. DEP works on the basis that an applied non-uniform field exerts a force, \( F_{\text{DEP}} \), onto an electrically neutral, anisotropic nanoparticle which is suspended in a dielectric solution. This force arises as the field causes a redistribution of charges within the particle that results in the formation of an electric dipole moment. This induced dipole causes a movement which can be utilised to align particles between two contact electrodes. The exact nature of \( F_{\text{DEP}} \) depends on various conditions of the system including the particle shape and composition material, the dielectric properties of the diluting medium and of course the nature of the applied electric field. In the context of nanowires it has been demonstrated on various occasions that DEP can be utilised to align nanowires of different materials to electrical contacts in numerous electrode geometries. A thorough review of the underlying principals and application of dielectrophoresis, with a specific emphasis on single nanowire DEP can be found in reference [152], however a brief overview will be provided in this section.

Figure 7.1 displays both a schematic depiction of a typical nanowire DEP experiment and an illustration of the attractive \( F_{\text{DEP}} \) acting on a nanowire within an non-uniform electric field gradient caused by two thin electrodes. In a typical DEP fabrication scheme nanowires are dispersed in a liquid medium and drop casted onto a pair of alignment electrodes. An
alternating voltage, $V(t) = V_{pp} \sin (\omega t)$, is passed between the electrode tips to create a non-uniform electric field which will induce a DEP force on the wire. Here $V_{pp}$ and $\omega$ correspond to the voltage signal amplitude and frequency respectively. Under the appropriate experimental conditions, this induced force can cause the nanowire to become trapped in between the two electrodes and hence become aligned. $F_{\text{DEP}}$ can be expressed analytically using equation 7.1 where $L$ and $d$ are the nanowire length and diameter respectively, $\varepsilon_{\text{sol}}$ is the permittivity of the solution, $E$ is the magnitude of the electric field and $K(\omega)$ is the Clausius-Mossotti factor.

$$F_{\text{DEP}} = \frac{1}{8} \pi L d^2 \varepsilon_{\text{sol}} \text{Re} [K(\omega)] \nabla E^2$$  \hspace{1cm} (7.1)$$

$K(\omega)$ relates to the nature and magnitude of the dipole strength that is induced within a given nanoparticle in the presence of an external electric field [153]. This parameter is defined by the conductivity and permittivity of both the nanowire and the solution and has a formalism that relates to the particle geometry. Moreover $K(\omega)$ is strongly dependent on the frequency of the applied AC electric field.

DEP has repeatedly been displayed to be a powerful technique for the alignment of a large quantity of nanowires simultaneously [154, 155]. However, when it comes to aligning only one single nanowire controllably between a pair of electrodes, the optimal DEP conditions become discernibly more complex. The efficiency of a single DEP nanowire alignment depends on various factors including the nature of the applied voltage and the electrode geometry. There have been a handful of studies pertaining to the alignment of a single nanowire
where it has been identified that the optimal electrode structure is long and thin such that there is a large field potential emanating from the tip of the contact [151, 156]. Additionally, it was realised that, while the relationship between $F_{\text{DEP}}$ and $V_{pp}$ was to be expected, the effect of $K(\omega)$ on the probability of a single wire alignment event is more subtle and required careful consideration. As such the single silicon nanowire fabrication process described in this chapter largely takes inspiration from the work of Raychaudhuri et al [156] where the alignment of several parallel single InAs nanowires was achieved through tailoring the electrode geometries and DEP conditions. However, while this study was highly successful in aligning a large number of InAs nanowires, it lacks practicality in the fact that the final product is not a single nanowire transistor, rather a large number of single wires connected in parallel. Therefore the work presented in this chapter looks to design a versatile fabrication plan which succeeds in aligning a large number of silicon nanowires simultaneously but results a register of truly single nanowire transistors. Understanding how to efficiently fabricate a large quantity of single nanowire transistors would be vital for any infrastructure within quantum technologies which is based on this material.

7.2 Fabrication techniques

The silicon nanowires in this study were fabricated using the chemical vapour deposition, CVD, technique [157] at the National Institute of Standards and Technology, NIST, in Maryland, US. During this procedure nanowires are grown using a randomly deposited distribution of Au nanoparticles that act as catalysts when exposed to the silicon precursor gas known as silane, SiH$_4$, and heated at a temperature of 900 °C. This process induces an anisotropic, epitaxial silicon growth underneath each of the nanoparticles which results in a ‘forest’ of single crystal silicon nanowires. Nanowire properties can be controlled by tailoring the Au particle diameter and growth duration. The nanowires in this study had an average diameter of 60 nm and were approximately $\sim 20 \mu$m in length. Figure 7.2 displays an scanning electron microscope, SEM, image of a typical region of CVD grown silicon nanowires rooted to the silicon handle wafer. In order to process the nanowires, the handle substrate was sonicated for around 2–3 minutes in isopropanol, IPA, in an effort to dislodge the nanowires into the solvent. The density of nanowires was carefully monitored by controlling the volume of IPA and sonication duration.

Aluminium DEP alignment electrodes were patterned using photolithography and metal-
ised using an e–beam evaporator. Electrode tip dimensions were fabricated to have widths of 5 \( \mu m \), lengths of 100 \( \mu m \) and a separation of 16 \( \mu m \). This tip separation was selected as it is 80% of the average nanowire length, this ratio has been demonstrated to maximise the DEP force [158]. Each pair of alignment electrodes are separated by a distance of 600 \( \mu m \) in an effort to isolate each DEP site. This geometry was selected to achieve a strong field enhancement at the tip of each electrode and to replicate contacts which have previously demonstrated to be successful in achieving a high yield of aligned single nanowires [151]. Aluminium was specifically selected as an electrode material as it can easily be removed using an alkaline etch. This will prove useful later on in the procedure. The handle substrate comprised of a thin 160 nm layer of SiO\(_2\) on top of a heavily doped n++ silicon wafer which will act as a back gate for the final nanowire transistor devices. Additionally, in [156] it was demonstrated that by covering the entire substrate in a thin layer of SiO\(_2\) after depositing the DEP electrodes, and opening up small windows over alignment regions, it is possible to screen the nanowires from stray field gradients caused by the larger regions of the electrodes. While it is possible to remove this oxide layer from the substrate, it would involve implementing a chemical etch that would also attack the SiO\(_2\) underneath the nanowire and thus degrade the back gate capacitance. Therefore in this fabrication scheme the oxide screening layer is replaced with a bi–layer photoresist structure which can easily be removed post align-
ment. Specifically a ~300 nm bottom layer of SF6 PMGI resist is deposited with a top layer of ~300 nm of S1805 Microposit resist. This resist structure is commonly implemented in fabrication to achieve an undercut which is favourable for lift off purposes. However it serves a different purpose in this process. Here, the S1805 acts as the imaging resist to define the windows using photolithography however when exposed to common solvents such as acetone or IPA the layer is easily removable. This would be problematic as the Si nanowires are dispersed in IPA, however fortunately SF6 is much more resilient and can only be removed using a more aggressive resist stripper such as 1-methyl-2-pyrrolidon, NMP, based solutions. Therefore the top layer of S1805 is removed by rinsing the substrate in acetone, followed by IPA, leaving a single layer of SF6, with alignment windows, that can be utilised for DEP. Figure 7.3 provides both an optical microscope image and schematic illustration of
Having removed the surface layer of S1805, it is now possible to attempt dielectrophoresis. Nanowires are deposited onto the DEP chip using a micropipette to drop approximately 2 μL of the wires dispersed in IPA directly onto the alignment electrodes. The substrate was tilted at an angle of approximately 10° to induce a solution flow that will encourage the alignment of nanowires. A function generator was used to apply an alternating voltage signal, \( V(t) \), to the alignment contacts and hence induce a non-uniform electric field focused at the electrode tips. Drops were deposited onto the alignment region continually for a duration of 60 seconds at which point the function generator was switched off. The substrate was then rinsed in IPA and gently blown with dry nitrogen to remove any excess solvent.

It was found that, under the appropriate DEP conditions, the implemented electrode geometry and resist screening layer was successful in achieving a small number of wires aligned between the aluminium contact electrodes. Figure 7.4 displays typical examples of alignment regions of DEP electrodes using three different sets of AC voltage parameters. Firstly 7.4(a) depicts that by applying a 12 V bias with a frequency of 10 kHz multiple nanowires are attracted to the electrode regions, including several wires protruding from only a single contact. As the frequency is increased to 50 kHz it is plainly observed that, while there are still numerous wire bridging the electrode gap, there are far fewer wires attached to only one. Finally, as the voltage across the electrode gap is reduced, the number of aligned nanowires decreases until only one remains. These observations are consistent with a previous study in similar systems where it was established that a reduction in \( \omega \) resulted...
in a higher fraction of singly aligned nanowires [156]. This was justified by considering the nature of the induced dipole moment within the wire, for a given modulation frequency, as defined by the Clausius-Mossotti factor, $K(\omega)$ in equation 7.1. Here $K(\omega)$ was separated into two different functions, one describing the induced dipole in the long axis of the nanowire and another for the short axis. It was determined that at low frequencies the induced dipole in the long axis direction of the wire is several orders of magnitudes greater than the corresponding short axis polarisation. However as $\omega$ is reduced, the long axis dipole strength drops significantly and the short axis becomes more important. In the former case, the induced DEP force is completely in the direction of the electric field and as such wire can tend become attached to only a single contact. However as $\omega$ reduces, the nanowires are more inclined to move in the direction of the electric field gradient and consequently become aligned between the two electrodes. However this also results in an overall reduction in $F_{\text{DEP}}$ and so fewer wires become aligned overall. This is consistent with the observations in this study. Having identified the optimal modulation frequency it was found that varying the applied voltage allowed for a degree of control over the number of aligned wires. As such it was found that a 10 V bias at 50 kHz was optimal for the alignment of single silicon nanowires in this study. Using these DEP parameters a successful wire alignment yield of approximately 65 % was achieved.

Once the DEP step has been completed, and a number of single nanowires have been aligned, it is now necessary to remove the screening layer of SF6. In this study a NMP based Microchem resist stripper was used for this purpose. This will also have the added effect of lifting off any stray nanowires which remain on the surface of the substrate. At this stage the substrate now contains a number of single silicon nanowires which are connected in parallel by the alignment DEP contacts. However, for the purpose of fabricating a single nanowire transistor it is required that only one wire is electrically active per device. Therefore this fabrication process specifies that the DEP alignment contacts are separate from the final device electrode architecture. Therefore it is necessary to deposit, on top of the alignment electrodes, the contacts for desired device geometry. In the example presented in this work, the top contacts were a simple two terminal geometry with a source–drain separation of 5 $\mu$m. These were fabricated by depositing 200 nm of gold on top of a thin, $\sim$8 nm layer of titanium which was used as a wetting layer to aid adhesion. Additionally a 15 s wet etch of 8 % diluted hydrofluoric acid was used to remove the native layer of silicon dioxide immediately before metal deposition. Figure 7.5 provides an illustration and an image of
a typical substrate with both sets of contacts. At this point it is possible to selectively remove the aluminium alignment electrodes whilst leaving the deposited gold electrodes in place. This can be achieved by using an alkaline etching process to dissolve the aluminium contacts. In the case of the devices in this study, substrates were submerged in MF–319 Microposit developer, which has an active ingredient of Tetramethylammonium hydroxide, TMAOH, for approximately 30 seconds. The final step is then to anneal the deposited Ti/Au contacts at a temperature of 200 °C for 20 minutes. This was done in a nitrogen environment to avoid any effects of oxidation.

Therefore, this process has successfully fabricated a series of individual single nanowire transistors using dielectrophoresis. An example of the operation of typical transistor fabricated using this procedure can be found in figure 7.6. (a) displays a series of transfer curves using a range of source–drain bias voltages from 7 to 10 V and (b) contains output curves at fixed back gate voltages ranging from -5 to -25 V. It is observed that the fabricated devices act in the p-type transport regime such that a negative back gate voltage is required to switch on the current. This is to be expected because the work function of gold is in close proximity to the silicon valence band and as such the transport of holes is favourable [159]. Electrode materials which would be more suited to n-type transport are titanium, tungsten or even aluminium. In the case of aluminium, an additional fabrication step would be required differentiate between the device contacts and the DEP alignment electrodes. This
could simply be achieved through depositing a photoresist layer over the desired contact region. From figure 7.6(a) it is possible to extract various device parameters, for example the on/off ratio is measured to be $\sim 10^3$ with a threshold voltage of $-6.4$ V, an and a sub-threshold slope of $1.03$ V/decade. This therefore demonstrates that fully functional single Si nanowire transistors have successfully been fabricated with a high degree of control using dielectrophoresis.

### 7.3 Summary & future work

This chapter has demonstrated that it is possible to utilise dielectrophoresis to fabricate a series of single nanowire transistors. The versatility of this fabrication scheme lies in the fact that the DEP alignment electrodes are completely separate from the final device contacts. The specific requirements of alignment electrodes which are necessary for single nanowire dielectrophoresis are very unlikely to be useful for any novel application and likewise any novel device contact geometry is unlikely to be appropriate for DEP. Therefore by fabricating alignment electrodes out of materials that are straightforward to selectively remove this problem has been overcome. Furthermore, while this study finishes with a simple $5 \mu$m transistor device, it is relatively straightforward to include additional fabrication steps to fully
integrate this process into quantum technologies. For example it would be possible to use EBL to restrict the source/drain separation down to the nanometre scale which would allow for quantum confinement and SET operation. Or alternatively side gates could be deposited in close proximity to control the electrostatic potential landscape of the nanowire and hence form a series of quantum dots. Similar device to this were realised in InAs nanowires using a series of local gate electrodes and randomly deposited wires [148]. Additionally, it has been demonstrated that, by careful selection of the device contact material, it is possible to fabricate ultra short SET devices using intruded silicide contacts [147, 160]. Specifically, by depositing nickel electrodes, and annealing high temperatures, it is possible to fabricate nickel silicide contacts which diffuse into the wire itself and can significantly reduce the source/drain separation. In fact dots with channel dimensions of less than 12 nm were reported in this study. This, in conjunction with the fabrication scheme outlined in this thesis, would open the possibility of fabricating a self assembled silicon nanowire quantum dots without the need for sophisticated lithographic techniques such as EBL. However plainly a great deal of control would need to be achieved over the annealing conditions to ensure the desired contact diffusion.

It is clear that in order to realise any quantum platform that utilises silicon nanowires a great deal of control is required over the position of the wires themselves. This chapter has demonstrated that single nanowire dielectrophoresis is a potential candidate for achieving this without the need to sacrifice any functionality of the final device.
Chapter 8

Conclusion & future work

Bismuth donors in silicon display vast potential as a platform for quantum technologies. This is particularly due to their large nuclear spin which manifests as a 20 dimensional Hilbert space and a hyperfine interaction which results in a ground state spin splitting that is resolvable even in the absence of a magnetic field. However, unlike lighter group V species, there are very few fabrication techniques through which bismuth donors can be controllably incorporated within a silicon crystal. In fact, the only feasible process to achieve this is through ion implantation however there had been fears that the violent mechanism by which ions are introduced into the silicon crystal will result in lattice defects that could severely inhibit qubit operation. Therefore, one of the primary goals of this work was to ally some of these concerns and demonstrate that ion implanted bismuth donors in silicon are suitable for applications within quantum technologies.

In chapter 4, various experimental characterisation techniques were used in an effort determine the optimal annealing temperatures to both repair lattice damage and incorporate implanted bismuth atoms. Samples were fabricated using a chain of sequential Bi$^{+}$ implantation steps, with various energies and beam fluences, to introduce a ~500 nm layer of implanted bismuth ions with a peak volume density of $3 \times 10^{17} \text{cm}^{-3}$. Post implantation annealing at temperatures ranging from 700 °C to 900 °C were then implemented to explore both the donor incorporation and residual lattice strain. While it was found that there was only a small difference in electrical activation yield between the samples annealed at 800 °C and 900 °C, there were significant differences in the apparent quality of donor incorporation. This was demonstrated using a variety of electrical and spectroscopic measurements. It was found that the sample annealed at 800 °C displayed both a suppression in the TO
phonon assisted $D^0X$ transition line in above bandgap PL measurements and an additional splitting in the hyperfine structure during resonant $D^0X$ photoconductivity. Conversely, the sample annealed at 900 °C matched well with the known characteristics from bulk samples. This therefore served to indicate that annealing ion implanted samples at 900 °C for 300 s is sufficient to incorporate a significant fraction of bismuth donors in an environment free of the effects of lattice strain. To further demonstrate this, the temperature dependence of the resonant $D^0X$ photoconductivity spectra of an equivalent sample annealed at 1000 °C was measured to be in excellent agreement with a corresponding bulk sample. This is of great importance because it identifies that the most significant source of strain in this implanted sample was actually the temperature dependence of the silicon bandgap. This is an extremely strong indication that the post implantation annealing treatment has been successful in repairing the native silicon lattice to a high degree of quality. Therefore this line of work has demonstrated that ion implanted bismuth donors in silicon are a viable candidate for applications within quantum technologies and are very much comparable with bulk doped substrates.

Additionally, the effect of increasing the Bi$^+$ ion dose on the characteristic properties of the samples in this study was explored. In the first instance it was determined that there is a correlation between implant fluence and donor EAY. This is such that approximately 75 % of implanted ions became substitutional donors in the lowest doped sample, whereas that number reduces to ~60 % in the highest density substrates. Furthermore it was found that, while bismuth ion diffusion had occurred in every sample, this effect was much more significant in the highest doped substrate. This is consistent with the model of transient enhanced diffusion whereby the movement of implanted ions is encouraged by the migration of silicon lattice vacancies and interstitials. A further effect of TED is an overall ‘flattening’ of the dopant profile which in turn contributes to a reduction in the peak donor concentration from the targeted value. One question that naturally follows on from this study is whether it is possible to increase the bismuth donor activation yield closer to a value of 100 %. A potential method through which this could be achieved is the utilisation of a preamorphising silicon self-implantation step. It has been demonstrated on numerous occasions that solid phase epitaxial regrowth is a reliable method to achieve EAY values in excess of 90 % [58, 62], however this is only the case when the Bi$^+$ ion dose is high enough that the substrate becomes amorphous post implantation. This is because the primary concept behind SPER is that the amorphous region is epitaxially regrown from the crystalline seed of the bulk substrate.
handle. Therefore, in lieu of an amorphising implantation dose, it would be possible to preamorphise the substrate with a Si\(^+\) implant which would then allow for the utilisation of the SPER annealing mechanism in a low dose bismuth implanted sample. This would also have the added benefit of inhibiting the formation of extended defects such as dislocation loops because they are an artifact of lattice vacancies and interstitials which would not be present in this system.

Moreover, the natural progression of this study in terms of applications within quantum technologies, would be to transition to implanting bismuth donors into silicon on insulator, SOI. SOI substrates differ from bulk silicon as they comprise of a thin crystalline silicon layer which is positioned on top of an electrically insulating SiO\(_2\) layer. This wafer design has significant benefits over conventional wafers, for example using SOI it is possible to fabricate small channel devices which are completely isolated from the bulk of the substrate. An example in this thesis where that feature would have been hugely beneficial is the study of the THz response to implanted devices, presented in chapter 6. Here, in both FTIR and FEL measurements, a significant signal was measured from the extremely low concentration of phosphorus donors in the bulk of the sample. This is of consequence because bismuth is the deepest group V donor and as such any corresponding electron orbital transition energy would also result in the direct ionisation of a shallower phosphorus dopant. This would lead to undesirable background electrical signals that could significantly inhibit sensitive electrical measurements. Additionally, fabricating devices using SOI allows for the utilisation of a built in back gate whereby the handle substrate can be biased and effect the potential landscape of the device layer. However, while it is clear that there are vast benefits to fabricating devices using SOI, there are also certain pragmatic considerations that must be made regarding the optimal fabrication techniques. Specifically in reference to the work in this thesis would be the question of low energy ion implantation into a very thin SOI device layer. For applications within quantum technologies typical SOI wafers would have thin device BOX layers which would each be less than 200 nm in thickness. Therefore it is expected that the effect of the surface will play a much more important role in Bi\(^+\) implantation into SOI, both as a source of ion diffusion and any surface based implantation defects. In chapters 4 and 5 evidence of a surface layer of p-type implantation defects was observed in various samples, however they were not found to significantly degrade the quality of donor incorporation as the vast majority of bismuth donors were situated much deeper into the bulk of the substrate. However, for shallow implants into SOI this will not be the
case and the surface will almost certainly play a more important role. It is a possibility that SPER could be a useful mechanism to implement for low dose implantation into SOI as the damage profile would be much more uniform and therefore the surface could be repaired to the same quality as the bulk of the substrate. However, for SPER to be effective, it would be essential that care is taken to ensure there remains a suitable region of crystalline silicon in the device layer for the regrowth to take place. It is also possible that enhanced ion diffusion will occur during SPER as the recrystallisation travels towards the surface of the substrate. Observations similar to this have been made during the implantation of indium ions into preamorphised silicon [132]. An additional exciting development in this field is the emergence of single ion implantation FIB technologies through which it is possible to deposit individual bismuth ions into a silicon lattice with a spatial resolution of <20 nm [39]. These systems are typically limited to beam energies of less than 30 keV and as such correspond to a very shallow implantation of approximately 20 nm below the surface. Therefore a great deal of care must be taken to anneal these implanted samples such that the quality of the lattice is recovered and a high percentage of dopant activation is achieved.

Chapter 6 demonstrated the response of a simple implanted Si:Bi device to two different types of THz spectroscopy. In the first instance electrically detected FTIR was used to measure the electron orbital excitation spectra of the implanted bismuth donors. Here, a significant improvement was found in the measured peak linewidths using the sample annealed at the highest temperature. Additionally, the dependence of the measurement temperature on the various spectral transition intensities was studied and observed to mach well with the model described by photothermal ionisation. Using this formalism the binding energies of each of the observed excited states was extracted and found to agree with known literature values. However this well defined temperature relation was not observed in equivalent spectral measurements using a free electron laser. Rather, virtually no temperature dependence was observed at all, other than a small change in the $1s(A_1) \rightarrow 2p_{\pm}$ transition when the device voltage bias was dropped. This therefore led to two possible explanations, either the temperature of the substrate is not changing, or the mechanism through which excited donors are ionised is not solely thermal. An alternative ionisation channel was speculated to be impact ionisation whereby bound electrons are liberated via collisions with moving charges in the conduction band. The possibility that the sample was being heated considerably by the FEL macropulse was also explored. By observing the change in spectral features as the power of the FEL macropulse is varied, an estimation for the lattice temperature during illumination
was obtained. Here it was found that an increase in sample temperature of approximately +25 K was calculated for the device measurement under 156 \( \mu \text{J} \) FEL illumination. In an attempt to account for such a significant heating, the Debye theory of heat capacity in the low temperature limit was used to estimate the change in silicon lattice temperature under illumination. However ultimately it was determined that, while the change in sample temperature was not insignificant, it is very unlikely that a single macropulse is high enough to account for the observations made previously. Although, it is possible that between each macropulse the sample does not cool sufficiently and a cumulative heating effect could occur over a series of pulses. Additional sources of sample heating could also come from the devices themselves through mechanisms such as the Peltier effect or Joule heating [161].

One thing that is clear is that such a significant heating will severely inhibit any desirable qubit operation and therefore a great deal of consideration must be made in order to counter these effects. In the first instance there is plenty of room for the future optimisation of device geometries and contact materials with a specific view towards minimising the transfer of heat into the active region of the device. This could be achieved by ensuring that the metal/semiconductor junction is far away from the device region or alternatively by implementing a four terminal contact geometry. There are also a series of future experiments that could be implemented to better understand these systems. For example, an initial test could simply be to repeat the measurement with a cryostat that has a greater cooling power and determine if a recognisable temperature dependence manifests. It would also be beneficial to take a more complete bias voltage dependence on the measured photocurrent signal. This would potentially allow for an observation of the onset of impact ionisation as the electric field strength increases. However, due to the significant experimental limitations regarding the availability of a free electron laser, it would be crucial to also obtain a more sophisticated finite element model for the various heating and ionisation mechanisms involved in a measurement of this nature.

Finally, chapter 7 contains a short fabrication study into an alternative to bulk silicon as a platform for quantum technologies. Specifically it was demonstrated that, using dielectrophoresis, it is possible to position individual silicon nanowires between a pair of alignment electrodes. This is of significance because in order to fully utilise the potential of single crystal silicon nanowires within quantum technologies, it is first a requirement that the wires themselves are controllably manipulated into the desired orientation. Moreover, the fabrication scheme presented in this work demonstrates the alignment of multiple isolated
nanowires consecutively with the result being an array of single nanowire transistors. This methodology was designed to be as versatile as possible in an effort to be pairable to numerous device architectures. Therefore there are multiple applications for this fabrication plan within the field of quantum technologies. One that may be of specific interest in relation to the previous chapters of this thesis would be the pairing of controllably aligned single silicon nanowires with the deterministic implantation of single Bi\(^+\) ions. It has previously been demonstrated that it is possible to alter the electrical properties of silicon nanowires through the implantation of either phosphorus and boron ions [162] and additionally, provided the implantation dose is not too high, a full recovery of the single crystal nanowire structure can be achieved [163]. In each of these cases a large number of ions were stochastically implanted into a random assortment of nanowires that had been deposited onto the substrate. Therefore, by utilising both single nanowire DEP and deterministic FIB implantation technologies the controllable single ion doping of an isolated, aligned silicon nanowire could be achieved. This fabrication channel would have vast potential for the realisation of a number of different silicon donor qubit architectures.
Bibliography


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