Structural and Electrical Properties of In and C + In implanted Ge, Si, and Si$_{1-x}$Ge$_x$

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Declaration

This thesis is an account of research undertaken between August 2012 and January 2016 at the Department of Electronic Materials Engineering, Research School of Physics and Engineering, College of Physical and Mathematical Sciences, The Australian National University, Canberra, Australia.

Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

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Abstract

It is widely accepted that when transistors are scaled beyond the 10-nm technology generation in the near future, Ge, or alternatively Si$_{1-x}$Ge$_x$ will potentially replace Si as the channel material to maintain CMOS device performance improvement. In is one of the most promising p-type dopant in Ge and Si$_{1-x}$Ge$_x$. Hence, this thesis has contributed to the field of semiconductors by performing systematic studies on the structural and electrical properties of In doped and C + In co-doped Ge, Si, and Si$_{1-x}$Ge$_x$.

In (and C) atoms were incorporated into Si, Si$_{0.35}$Ge$_{0.65}$, Si$_{0.1}$Ge$_{0.9}$, and Ge thin films by ion implantation. Electrical properties of the implanted samples were determined by Hall effect measurement, while the identification of the sample structural properties was performed using TEM, Raman spectroscopy, DFT calculation, and X-ray absorption spectroscopy.

The dopant concentration effects on the structural and electrical properties of In-implanted Ge were investigated. For In concentrations lower than 0.2 at. %, all In atoms occupy a substitutional lattice site. The formation of metallic In precipitates and In-vacancy complexes are apparent for In concentrations greater than 0.6 at. %. Electrical measurement results were correlated with the determined structural properties.

Aiming to enhance the electrical activation of In in Ge, C was introduced as a co-dopant with In. With C + In co-doping, the electrically active fraction was significantly enhanced. This dramatic improvement was found to be the result of C-In pair formation such that In-induced strain in the Ge lattice was reduced while the precipitation of In and the formation of In-vacancy clusters were both suppressed.

Si$_{1-x}$Ge$_x$ alloys have the potential to combine the positive aspects of Si and Ge as the substrate for In doping. Thus, we performed a systematic study on the dopant concentration and substrate stoichiometry effects on the electrical and structural properties of In-implanted Si$_{1-x}$Ge$_x$ (including Si and Ge). Correlating the fraction of electrically-active In atoms and the In atomic environment, we observed the transition from electrically-active, substitutional In at low In concentration to electrically-inactive metallic In at high In concentration. The In solid-solubility limit has been quantified, which was found increased as the Ge fraction of the Si$_{1-x}$Ge$_x$ alloy increased.

Since we found that the Si fraction in Si$_{1-x}$Ge$_x$ affected its In solid solubility significantly, an above-equilibrium solid solubility threshold is needed to maintain a high In
electrical activation. To that end, the co-doping strategy with C was again employed. With C + In co-doping, the solid solubility of In in Si$_{0.35}Ge_{0.65}$ is at least tripled from that of In doped Si$_{0.35}Ge_{0.65}$, as a result of C-In pair formation in suppression of In metal precipitation. Dramatic improvement of the sample electrical properties was attained.

This thesis demonstrated a promising future for In doped Ge and Si$_{1-x}Ge_x$, towards the application to $p$-type field-effect transistors in future CMOS devices. C co-doping was verified as an effective method for enhancing the In solid solubility and electrical activation in both Ge and Si$_{1-x}Ge_x$. These results inspire potential future work like In implantation in Si$_{1-x-y}Ge_xC_y$. 
Publications


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1

Introduction

1.1 Background

In the past decades, the advent of electronic devices like computers and mobile phones has transformed our modern lives. It is not hard for one to notice that almost every year, there are new generation(s) of electronic products with significantly improved performance released on the IT market (for example, new Apple iPhones, Intel CPUs, Nvidia GPUs and so on). Such a high upgrade speed has been achieved by scaling down the feature size of the transistor by a factor of $\sim 0.7$ in approximately every 18-24 months, as demonstrated in Figure 1.1 [1], keeping pace with the famous Moore’s Law [2]. A shrinkage of transistor dimension by a factor of 0.7 means double the amount of transistors that can be incorporated in the same area ($0.7^2 \approx 0.5$) as shown in Figure 1.1 so that the integrated circuit of the microchip can have roughly double the complexity as well as functionality, with the same cost. Hence, the feature size of the transistor commonly represents the advancement of the microchip and is the technology cutting edge of semiconductor manufacturing processes [3]. For example, the first commercially available processor, Intel 4004 [4] produced in 1971, with a CPU clock rate of 740 kHz had a feature size of 10 $\mu$m and transistor density of about $200 / \text{mm}^2$, while the Core i7-6700K processor [5] launched in 2015 packed over 10 millions / $\text{mm}^2$ of 14 nm transistors on a single chip, and its CPU speed is 4 GHz.

Gorden Moore’s scaling prediction made in 1965 has been maintained for half a century [6]. In the past 50 years, huge efforts have been made by semiconductor specialists to maintain the exponential transistor size-scaling, with technological evolutions in almost every aspect of the semiconductor manufacturing processes [7]. In the earlier decades, re-
searchers mainly focused on improving fabrication methods such as wafer doping, lithography, etching and annealing techniques etc. [7]. In 2002, Intel introduced a new kind of channel material, called uniaxial strained silicon (Si), to its 90 nm transistors [8]. This is a milestone event on the pathway of advancing Moore’s Law, which heralds a shift of the transistor scaling strategy. The field started to realize that further scaling down of the device dimension is reaching the physical limits of the fabrication techniques, it is essential to apply new materials [7]. The replacement of the transistor insulating material is an example. In 2007 Intel announced that high dielectric (i.e. high-\(k\)) material has replaced the traditional \(\text{SiO}_2\) as the insulator in the 45 nm technology node transistor [9]. Using new material is becoming the mainstream of semiconductor technology innovation [6].

Figure 1.1: Transistor density and feature size as a function of years (Reference: [1]).

Although the first transistor was built on germanium (Ge), Si has been the dominating base material of semiconductor devices for the past decades. Even in our most up-to-date generation 14 nm technology CMOS (complementary metal-oxide-semiconductor) devices, the fin shaped (vertical) metal-oxide-semiconductor field-effect transistors (FinFET) [10] (Figure 1.2) that comprise the integrated circuits are still Si-based [11]. However, since several years ago, semiconductor physicists have started to discuss a critical question: will Si continue to survive Moore’s Law? [12] Forecasting from our current position, the answer is very likely to be no, or not for long. At Semicon West 2015, Jo De Boeck, senior vice president of IMEC (Interuniversity MicroElectronics Center), argued that future Si-based device scaling to 10 and 7 nm is beginning to reach practical and fundamental limits [13]. Intel also said at the 2015 international solid-state circuits conference (ISSCC): “new materials will be required to hit 7 nm, looks like 10 nm (next generation following 14 nm) will finally be the end of the road for Si.” [14]

To maintain the march of the industrial golden rule towards 7 nm and beyond, III-V semiconductors, nanowires and even graphene have been considered as substitutes for Si [6,12,14]. For the near future (next numbers of nodes), one of the most promising candidates is Ge, or alternatively \(\text{Si}_{1-x}\text{Ge}_x\), in \(p\)-type field-effect transistors (FETs) and III-V
1.1. Background

materials (e.g. InGaAs) in n-type FETs, according to the transistor pathway proposed by the Silicon Systems Group of Applied Materials Inc. (see Figure 1.2). The main reason for such a replacement is that both Ge and III-V semiconductors provide higher carrier mobility than Si (which benefits device performance). Furthermore, the industrial transition from Si to Ge / III-V semiconductors is not as difficult as that to other new materials, such as nanowires and graphene. The application of Ge and III-V semiconductors was limited in the past because of the poor quality of their semiconductor-to-insulator interfaces compared to the Si - SiO$_2$ interface. The recently developed high-$k$ materials have the potential to address such an issue.

Replacing dopant elements is one approach to achieve further transistor shrinkage. For instance, in Si-based semiconductors, boron (B) is the primary p-type dopant as it has a low activation energy and high solid solubility in Si. However, its high diffusion coefficient in Si becomes an obstacle in realizing shallow junctions. Heavy elements, like indium (In), are usually slow diffusers in Si and Ge substrates, and their sharply defined dopant profiles can be key contributors to CMOS device scaling.

As discussed above, a transformation of the semiconductor industry from using light element-doped Si to heavy element-doped Ge (or Si$_{1-x}$Ge$_x$) / III-V materials is essential to realize further device performance improvement in the future. However, it also necessitates comprehensive research on the processing procedures as well as the properties of the new dopant-substrate combinations. These include: the doping, annealing and etching.
protocols; the substrate defect, strain and bandgap engineering; the diffusion configuration, lattice location, solid solubility limit and electrical activation of the dopant in the substrate, etc. Among all these, a systematic study on the structural properties of the doped material is fundamental, since many crucial electrical properties are decided or influenced by that. This thesis has contributed to the field by performing such a study on In doped and C + In co-doped Si, Ge or Si$_{1-x}$Ge$_x$.

In Si, Ge or Si$_{1-x}$Ge$_x$ substrates, the group III or group V atoms are usually electrically-active when they are four-fold coordinated in substitutional sites of the lattice (Figure 1.3 (a)), where they contribute free charge carriers (holes or electrons that make the semiconductor p or n-type, respectively). The carrier density of the material represents the quantity of charge carriers per unit volume. A fraction of dopant atoms can be electrically inactive, as they form dopant clusters, pair with vacancy(s) or occupy interstitial sites, as shown in Figure 1.3 (b), (c) and (d), respectively. The most common deactivation mechanism is the formation of dopant precipitation at high concentration. Thus, the dopant solid solubility limit in the substrate commonly determines the maximum carrier density that one can achieve. The disorder and strain conditions of the substrate lattice significantly affect the mobility of the carriers. Both carrier density and carrier mobility determine the resistivity of the semiconductor, which is a key factor in device performance.

![Figure 1.3: Schematics of (a) an In atom in the substitutional site of Ge lattice, (b) an In cluster, (c) an In atom coordinating with a vacancy in the substitutional sites of Ge lattice, and (d) an In atom in the interstitial site of Ge lattice.](image)

Consequently, in this thesis, we used ion implantation to incorporate the dopants within the substrate lattice and then determined the properties of the samples with multiple characterization methods. X-ray absorption spectroscopy was employed as well as a few other supplementary techniques to determine the environment of the dopant incorporation in the substrate lattice. Correlating that with electrical properties of the samples measured by Hall effect measurement, we investigated the dopant electrical activation and deactivation mechanism of In doped and C (carbon) + In co-doped Si, Ge and Si$_{1-x}$Ge$_x$.
1.2 Aim

The objective of this thesis is to perform systematic investigations of the structural and electrical properties of In doped as well as C + In co-doped Ge, Si and Si$_{1-x}$Ge$_x$. We aim to identify the dopant lattice environment and its effect on the sample electrical properties, to examine the potential of these materials on CMOS device application. Four individual studies were carried out on different dopant - substrate combinations, the aim of each is described as below:

- Since In doped Ge is a promising candidate material for $p$-type FETs, the first goal of the thesis (Chapter 4) is to characterize the atomic-scale environment of In atoms doped in Ge, the In induced damage to the Ge lattice, and their effects on the electrical properties, over a broad In concentration range.

- The following part (Chapter 5) is dedicated to enhance the In electrical activation in Ge by co-doping with C. We also aim to identify the mechanisms by which a significant In electrical activation improvement is attained.

- The work then extends to examine not only the dopant concentration but also the substrate chemical composition effect on the structural and electrical properties of In doped Si$_{1-x}$Ge$_x$ (including Si and Ge) (Chapter 6), to constitute a feasibility study of combining the positive aspects of In doped Si and In doped Ge.

- The last aim (Chapter 7) is to attain an above-equilibrium solid solubility threshold of In in Si$_{1-x}$Ge$_x$ by C co-doping. That is necessary to maintain a high In electrical active fraction since in the previous chapter the In solid solubility in Si$_{1-x}$Ge$_x$ was found to decrease rapidly as a function of the substrate Si composition.

These four topics have been reported in a limited number of previously published works, yet a significant amount of complementary and important information is still unknown, especially that from using the technique of X-ray absorption spectroscopy. Systematic studies of lattice structural identification in correlated with electrical measurements are still lacking. Specific introductions and detailed literature reviews relating to the individual projects are provided in the corresponding result chapters.

1.3 Thesis structure

A brief overview of the structure of this thesis is given in the the following outline.

- Chapter 2 describes the experimental details of the sample preparation and characterization processes of this thesis, including ion implantation, Rutherford Backscattering Spectrometry, Hall effect measurement, electron microscopy, Raman spectroscopy and density functional theory. Background introductions to each technique as well as comprehensive specifications of all the samples are also given.
• Chapter 3 discusses X-ray absorption spectroscopy, the main technique in this thesis to quantitatively identify the local environment of the implanted dopant atoms, from its basic concepts and theories to experimental and data analysis methods.

• Chapter 4 reports on the effects of dopant concentration on the structural and electrical properties of In-implanted Ge.

• Chapter 5 demonstrates a significant increase in the electrically-active dopant fraction of In-implanted Ge by co-doping with the isovalent element C, and analysis of the mechanisms that lead to the improvement.

• Chapter 6 investigates the electrical and structural property dependencies of In doped Si$_{1-x}$Ge$_x$ on both In concentration and substrate stoichiometry, and provides a theoretical explanation to such a dependence relation.

• Chapter 7 presents an In solid solubility enhancement in Si$_{1-x}$Ge$_x$ with C co-doping, which results in a dramatic increase in carrier density.

• Chapter 8 summarizes the previous result chapters and gives the direction for potential future work following the steps of this thesis.
1.3. Thesis structure
This chapter describes the experimental details of the sample preparation and characterization processes performed in this thesis. Background introductions to each technique are included with comprehensive specifications of all the samples. X-ray absorption spectroscopy (XAS), the main technique for the dopant local environment analysis, is explained thoroughly in Chapter 3.

2.1 Ion implantation

In semiconductor fabrication, doping plays a crucial role in adjusting a material’s electrical properties. By introducing specific impurities into the semiconductor, important properties such as conductivity, carrier density and band structure can be modified by selecting the doping element and concentration, in order to reach the requirement of individual devices. Doping can be achieved initially during the growth of most semiconductor wafers. However, further doping by means of ion implantation is usually applied, taking advantage of the technique which allows control over doped area, depth and concentration. In ion implantation, an ion accelerator (implanter) is used to accelerate the (positively or negatively) charged dopant ions to the desired energy towards the target material, as in Figure 2.1. Simulations are usually carried out before the implantation process to predict the ion distributions and select the implantation energies and fluences. In semiconductor processing, an annealing process is commonly applied after the implantation to recover the
induced damage and to activate dopant atoms. Dopant activation is essential for obtaining the desired electronic contribution from the impurity species in the semiconductor host.

Figure 2.1: Schematic of ion implantation, implantation damage, sputtering, and atomic mixing process [21].

2.1.1 Ion implanter

The design and specifications of each ion implanter vary depending on their individual purpose, but in general, an ion implanter has the following components: an ion source to generate ions from the source material, an acceleration section to propel the ions, a set(s) of beam optics to shape and guide the ion beams, a bending magnet(s) to select the desired ions for transmission, diagnostic elements and a target chamber. The fundamental aspects of a specific ion implanter are given below, interested readers can refer to [22] and [23] for more details.
2.1. Ion implantation

In this thesis, the ion implantation process was performed on the “High Energy Implanter” at the department of Electronic Materials Engineering at the Australian National University, a schematic of which is shown in Figure 2.2. The implanter uses a SNICS source (Source of Negative Ions by Cesium Sputtering) to produce negatively charged ions from the source material for acceleration. Cs (Cesium) is evaporated from a molten Cs reservoir and ionized by a heated ionizer at $\sim 1100 \, ^\circ C$. The positively charged Cs ions are then accelerated towards the $\sim -5 \, kV$ negatively biased Cu cathode which contains the packed source material for the individual element to be implanted. The source material on the surface is sputtered by the Cs ions (as in Figure 2.1), the negatively charged sputtered ions (monatomic or molecular depending on the source material) are focused and then extracted at up to 15 kV with a source voltage up to 80 kV and accelerated towards the analysing magnet.

In the mass analysing magnet, a magnetic field with strength $B$ is set to bend the path of the accelerated ions with energy $V_1$ through a $90^\circ$ angle with given radius (R), according to:

$$B = \frac{1}{R} \sqrt{\frac{2m_T V_1}{eq}} \quad (2.1)$$

where $m_T$ is the mass of ions desired for transmission, $e$ is the electronic charge and q is the charge state. An Einzel lens and X and Y electrostatic steerers further focus the ion beam into the accelerating tube of the tandem accelerator.

The main ion acceleration process is performed on a National Electrostatics 5SDH-4 1.7 MV tandem accelerator [24] from the National Electrostatics Corporation (NEC). In the accelerator tank, a uniform potential gradient along the accelerating tube is generated by numerous equi-potential rings connected in series. A high voltage terminal with a maximum of 1.7 MV is in the center of the accelerating tube, positively charged by a pelletron charging system with four chains. The terminal potential is stabilized by a generating voltmeter (GVM) and a set of movable corona points forming a feedback circuit to control the charge added to the chains. The tube is also electrically insulated in a tank filled by high pressure sulphur hexafluoride gas ($SF_6$, which has a much higher dielectric strength than air or dry nitrogen), while the beamline is maintained under high vacuum ($\leq 10^{-7} \, mbar$) using cryogenic pumps. The positively charged terminal (at voltage $V_T$) attracts the negative ions from the injection port, and a $N_2$ gas cell at the terminal is used to strip electrons from the negative ions. The stripping effect converts negatively charged ions into neutral or positively charged ions with multiple charge states, depending on the stripper gas pressure. In the case of accelerated polyatomic ions, monatomic ions in different charge states are obtained from the molecule after stripping and selected for implantation. After passing through the terminal, the positively charged ions are repelled by a positively charged terminal at a voltage of $V_T$ and re-accelerated through the tank, with energy given by:
Chapter 2. Sample preparation and characterization techniques

\[ E_f = e\left[\frac{m_i}{m_T}V_1 + \frac{m_i}{m_T} + q\right]V_T \]  

(2.2)

where \( m_i \) is the mass of the monatomic ion chosen for implantation and \( m_T \) is the molecular mass before \( N_2 \) gas stripping. \( m_i = m_T \) in the case where only electrons from monatomic ions are stripped. The tandem accelerator thus is capable of accelerating ions up to an energy of \( \sim 10 \) MeV depending on the charge state. For ion energies less than 100 keV, the stripper gas is not introduced in the acceleration process. Ions accelerate and decelerate before and after the terminal respectively with the same potential energy in the tank. The total energy of an ion equals the energy it obtained from the source and negative ions are implanted instead of the positive ions.

After acceleration, the ion beam is focused utilizing the X and Y quadrupole lenses and travels towards the energy analysing magnet. The magnet bends the ion beam by \( 15^\circ \) with a magnetic field required to select the accelerated ions with desired charge state, mass and energy, similar to the situation in the mass analysing magnet. The selected ions then pass through a rastering system to perform a homogeneous scan over an aperture placed before the sample, which defines the implantation area.

The samples are attached to a sample holder with metal clips and carbon thermal conductive paste, perpendicular to the incident ion beam. In the case of implanting into crystalline samples, the sample holder is usually tilted at a certain angle to minimize channeling. Furthermore, the sample holder can be heated up to 500 °C or cooled down with liquid nitrogen to -196 °C depending on the required implantation temperature. To enable accurate implantation fluence measurement, a Cu radiation shield surrounding the sample holder was maintained at \( \sim -300 \) V to suppress secondary electrons (which are produced by the ions impacting the atoms in the sample).

2.1.2 TRIM

Transport and Range of Ions in Matter (TRIM) is a Monte Carlo computer program that calculates the interaction of energetic ions with target matter [26][27]. In this thesis, the “Ion Distribution and Quick Calculation of Damage” function of the program was applied to estimate the depth distribution of implanted ions into the target substrate. For each ion and target combination, the simulated implantation results using multiple energies and relative fluences, were summed to create a uniform ion distribution as in Figure 2.3. The implantation fluence for each energy was determined proportionally to the dopant concentration of each sample. The actual ion distributions and concentrations were further confirmed with Rutherford Backscattering Spectrometry (Section 2.3) after implantation.
Figure 2.2: Schematic of the NEC 1.7 MV tandem accelerator. [25]
Chapter 2. Sample preparation and characterization techniques

Figure 2.3: A uniform Indium ion distribution (0.2 - 1.2 µm) in a germanium substrate using multiple energies simulated in TRIM.

2.1.3 Implantation damage recovery and dopant activation with annealing

One of the major drawbacks of ion implantation as a doping process is that energetic ions can cause undesired structural damage to implanted substrates, especially in crystalline materials. The energetic ions undergo both electronic and nuclear collisions with the target atoms (which also cause successive collisions) and lose energy to slow down until they come to rest as in Figure 2.1. Depending on the amount of energy transfer and the material properties, implanted crystalline materials can experience disorder including point defects (vacancies and interstitials), extended defects (dislocations, divacancies, trivacancies, etc) and amorphization. Although some semiconductor fabrication processes utilize the implantation induced disorder to modify the material properties, most processes involve damage prevention and recovery. For more theory and application details of ion beam effects on solids, the reader is referred to [28] and [29].

Another problem of ion implantation in semiconductor fabrication is dopant inactivation, as discussed in the previous chapter. Instead of occupying the substitutional sites of the lattice, the dopant atoms can be in defective configurations including interstitial, clustering with a vacancy (or vacancies), or clustering with each other. This inactivation of dopant atoms becomes more severe as the implantation concentration increases or approaches the solid solubility of the doping element to the substrate where the dopant atoms start to precipitate.

The implantation-induced damage can be controlled to a certain extent by the implantation temperature. In this thesis, implantations were performed at 250 - 350 °C to reduce defects and minimize amorphization (Table 2.2). Thermal annealing is a widely
used method to recover the lattice disorder from implantation and activate the dopant atoms. A three stage annealing process was applied in this thesis. Samples were annealed at three different temperatures (considering the melting temperature of the material) from high, medium to low subsequently for 0.5, 1 and 2 hours, respectively. This annealing process was chosen to initially activate dopants atoms and reduce lattice disorder, and also enhance the dopant-defect concentration by lowering the solid solubility limit during the final low temperature anneal. As a consequence, a lower implantation concentration was needed to create dopant related defects and study their clustering mechanisms.

### 2.2 Sample preparation and specification

In this thesis, multiple types of ions and substrates were implanted with varying energies and fluences. As listed in Table 2.1, negative ions containing the desired implantation element (In and C) were generated with individual cathode materials. After the negative ions passed through the terminal of the ion accelerator, monatomic ions with certain charge state were selected for implantation with the switching magnet.

![Table 2.1: Specifications of different ion beams used in the thesis.](image)

<table>
<thead>
<tr>
<th>Implanting element</th>
<th>Cathode material</th>
<th>Ion species from the source</th>
<th>Ions species implanted</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>crushed InP wafer</td>
<td>In(^{\text{+}})</td>
<td>In(^{2+}) (energy (\geq 1.9) MeV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>In(^{\text{+}})</td>
<td>In(^{\text{+}}) (energy (&lt; 1.9) MeV)</td>
</tr>
<tr>
<td>C</td>
<td>crushed 99.99% pure graphite</td>
<td>C(^{-})</td>
<td>C(^{\text{+}}) (energy (&gt; 100) keV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C(^{-}) (energy (&lt; 100) keV)</td>
</tr>
</tbody>
</table>

Si, Ge, Si\(_{0.35}\)Ge\(_{0.65}\), and Si\(_{0.1}\)Ge\(_{0.9}\) were the four substrates used in the thesis. The substrates were produced in a commercial laboratory, and the fabrication method has been optimized to minimize contamination and ensure epitaxial quality, as described below. The crystallographic quality of the substrates was examined by means of transmission electron microscopy and Rutherford Backscattering Spectrometry before ion implantation. Except for Si, they comprise of (100) crystallographically oriented Ge or Si\(_{1-x}\)Ge\(_{x}\) thin films (~ 2\(\mu\)m thick) on bulk substrates (GOS and SGOS, respectively). For Si samples, Si on insulator (SOI) wafer was used, which has a 2.5 \(\mu\)m thick (100) crystallographically oriented Si on bulk Si substrate with a 1 \(\mu\)m SiO\(_2\) layer between the two. The main reason for employing thin films on substrate wafers instead of bulk crystal wafers is better Hall effect measurement and XAS samples can be prepared, as will be explained later in Sections 2.4.2 and 3.3.1, respectively. To ensure the high quality (single crystal with low strain and defect levels) of the thin films, special growth methods were used. To prepare a SOI wafer, a SiO\(_2\) layer was deposited onto a back Si wafer and thermally bonded to another Si wafer on top, with the back Si wafer polished down to a thin film. The Ge thin film was deposited on Si substrate by UHVCVD (ultra high vacuum chemical vapor deposition) while a MBE
(molecular beam epitaxy) method was used to create the Si$_{1-x}$Ge$_x$ thin layers. During the implantation processes, the samples were mounted on a sample holder with a 7° tilt to the incident ion beam direction to minimize channeling, and they were maintained at high temperature to reduce the implantation-induced damage. After the implantations, the three stage annealing process in a N$_2$ atmosphere was applied, with the annealing temperatures proportional to the melting points of the individual substrates (the highest annealing temperature $\sim$ 70% to the melting temperature). Lower annealing temperatures were set for the implanted Ge samples, because a dis-attachment of the Ge layer from the Si substrate can occur if the annealing temperature is above 600 °C. Table 2.2 lists the specifications of the four substrates.

Table 2.2: Specifications of different substrates used in the implantation and their melting and annealing temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness</th>
<th>Wafer</th>
<th>Growth method</th>
<th>Implantation temperature</th>
<th>Melting point</th>
<th>Annealing temperature : time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2.5 µm</td>
<td>SOI</td>
<td>bond and etch back</td>
<td>300 °C</td>
<td>1412 °C</td>
<td>1000 °C : 0.5 h 800 °C : 1 h 600 °C : 2 h</td>
</tr>
<tr>
<td>Ge</td>
<td>1.8 µm</td>
<td>GOS</td>
<td>UHVCD</td>
<td>200 °C</td>
<td>938 °C</td>
<td>550 °C : 0.5 h 450 °C : 1 h 350 °C : 2 h</td>
</tr>
<tr>
<td>Si$<em>{0.35}$Ge$</em>{0.65}$</td>
<td>2.5 µm</td>
<td>SGOS</td>
<td>MBE</td>
<td>250 °C</td>
<td>$\sim$1043 °C</td>
<td>700 °C : 0.5 h 550 °C : 1 h 400 °C : 2 h</td>
</tr>
<tr>
<td>Si$<em>{0.1}$Ge$</em>{0.9}$</td>
<td>2.7 µm</td>
<td>SGOS</td>
<td>MBE</td>
<td>250 °C</td>
<td>$\sim$960 °C</td>
<td>650 °C : 0.5 h 500 °C : 1 h 350 °C : 2 h</td>
</tr>
</tbody>
</table>

Combining the individual ion beams and substrates, 13 types of ion implanted samples were obtained, and the samples of each type have different dopant concentrations by varying the implantation fluence. We used multiple energies and fluences to create a uniform ion distribution over the depth of the substrate, the implantation order is from the highest to lowest implantation energy. Table 2.3 shows the ion energies and the corresponding fluences used to produce a dopant concentration of 1 at. % (atomic percent, percentage of dopant atomic density to substrate atomic density). The samples with implantation concentration other than 1 at. % in Table 2.3 were made by adjusting the fluences accordingly. The implantation concentrations for the samples with Si$_{0.35}$Ge$_{0.65}$ and Si$_{0.1}$Ge$_{0.9}$ as substrates were calculated based on the atomic density of Si$_x$Ge$_{1-x}$ provided by Reference [31]. In the case of co-implantations (where two or more ion species were implanted into one substrate), the dopant and co-dopant ions were implanted to the same concentrations, with ion energies and fluences appropriate to yield overlapping depth distributions. The actual dopant concentration of each sample was measured by Rutherford Backscattering Spectrometry as shown in Table 2.3.
2.3. Rutherford Backscattering Spectrometry

Table 2.3: Implantation fluences and energies for each sample type at dopant concentration of 1 at.%, and implantation concentration and actual concentration corrected by RBS of individual samples.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Energy (MeV) : Fluence (atoms / cm$^2$) (implantation concentration at 1 at. %)</th>
<th>Implantation concentrations (at. %)</th>
<th>RBS corrected concentrations (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In implanted Si</td>
<td>2.7 : 2.69e16 : 1.9 : 1.75e16 : 1.1 : 1.32e16</td>
<td>0.002, 0.0037</td>
<td>0.0012, 0.0022</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.006, 0.01</td>
<td>0.0036, 0.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0332, 0.1</td>
<td>0.02, 0.06</td>
</tr>
<tr>
<td>In implanted Ge</td>
<td>3.4 : 2.72e16 : 2.3 : 1.16e16 : 0.7 : 5.90e15</td>
<td>0.03, 0.1, 0.3, 1, 2</td>
<td>0.02, 0.06, 0.2, 0.6, 1.2</td>
</tr>
<tr>
<td>C implanted Ge</td>
<td>0.75 : 1.87e16 : 0.45 : 1.21e16 : 0.25 : 1.10e16</td>
<td>0.1, 0.3, 1, 2</td>
<td>Not applied</td>
</tr>
<tr>
<td>In + C implanted Ge</td>
<td>Identical to In implanted Ge but with C implantation before with same concentration in the same region</td>
<td>0.1, 0.3, 1, 2</td>
<td>0.07, 0.2, 0.65, 1.3</td>
</tr>
<tr>
<td>Si$<em>{0.35}$Ge$</em>{0.65}$</td>
<td>4.0 : 3.61e16 : 2.7 : 1.30e16 : 2.0 : 8.67e15</td>
<td>0.03, 0.1, 0.3, 1</td>
<td>0.02, 0.06, 0.2, 0.6</td>
</tr>
<tr>
<td>In implanted Si$<em>{0.35}$Ge$</em>{0.65}$</td>
<td>3.8 : 3.49e16 : 2.5 : 1.26e16 : 1.8 : 8.40e15</td>
<td>0.03, 0.1, 0.3, 1</td>
<td>0.02, 0.06, 0.2, 0.6</td>
</tr>
<tr>
<td>C implanted Si$<em>{0.35}$Ge$</em>{0.65}$</td>
<td>1.1 : 2.15e16 : 0.7 : 1.83e16 : 0.4 : 1.67e16</td>
<td>0.03, 0.1, 0.3, 1</td>
<td>Not applied</td>
</tr>
<tr>
<td>In + C implanted Si$<em>{0.35}$Ge$</em>{0.65}$</td>
<td>Identical to In implanted Si$<em>{0.35}$Ge$</em>{0.65}$ but with C implantation before with the same concentration in the same region</td>
<td>0.03, 0.1, 0.3, 1</td>
<td>0.02, 0.06, 0.2, 0.6</td>
</tr>
</tbody>
</table>

2.3 Rutherford Backscattering Spectrometry

Although simulations in TRIM were performed to determine the implantation fluences for the required doping concentration, and secondary ions were suppressed during the implantation, the predicted dopant concentrations were not obtained in most cases. The difference between the predicted and actual dopant concentration can be up to ∼ 40% resulting from several factors including: the stability of the ion beam, the accuracy of the ion beam current measurement, the secondary ion suppressor performance, the ion channeling effect in the crystalline target, and the dopant diffusion loss during the thermal annealing. In this thesis, Rutherford Backscattering Spectrometry (RBS) was employed to confirm the concentration and depth profile of the implanted atoms. Some basics of the technique are discussed below. More theory and application details of RBS can be found in [32] and [33].

2.3.1 Basics

RBS is a technique similar to ion implantation, while the latter uses different kinds of ion beams to achieve material modification, RBS uses energetic He$^+$ or H$^+$ ion beams to perform material analysis. The He$^+$ or H$^+$ ions are accelerated to a desired energy by
an ion accelerator, and directed on to a target material to undergo elastic collisions with the nuclei of atoms on the surface and in the bulk of the target material. As shown in Figure 2.4, a fraction of these incident ions were backscattered (scattering angle $> 90^\circ$) ions, and the backscattering yield (counts of backscattering events) as a function of the backscattered ion energy is measured by a nuclear particle detector. The maximum yield can be obtained when the RBS is performed on an amorphous material or a crystalline material in a random orientation (without ion beam alignment to major crystallographic axes or planes). While the backscattered energy is representative of the atomic species and the depth it is scattered from, the backscattering yield of the random spectra can be converted to the atomic density of each element with further analysis and simulations.

In the case of doped materials, the RBS spectrum of the doped atoms can be distinguished from the spectrum of the substrate atoms (as in Figure 2.4) when the doped atom has a larger mass than that of the substrate atom, since the backscattered energy of the incident ions is larger for the former. To achieve this, an ion beam with an energy higher than a certain value is needed. That value depends on the mass of the incident ion, the mass of the substrate atom and the mass and depth distribution of the doped atoms. A RBS spectrum of this kind provides the depth distribution and concentration of the dopant. This thesis used a 4.5 MeV He$^{2+}$ beam to perform the sample analysis.

![Figure 2.4: A RBS spectrum of In implanted SOI on a random condition.](image)
2.3.2 RBS apparatus

This thesis employed the RBS analysis system at the department of Electronic Materials Engineering at the Australian National University. This system is also basically an ion accelerator, similar to the ion implanter introduced in the previous section. The main difference between the RBS system and the High Energy Implanter is that a radio frequency (RF) source is used to generate H and He ions and additional detectors are employed in the target chamber. The ion source for the RBS system is a NEC “Alphatross” RF source [24], which contains two pressured vessels filled with H and He gas. As one of the gases is selected and delivered through a fine metering valve into a glass source bottle, an RF field is applied to ionize the gas using the two electrodes on the outside of the source bottle. The ionized gas is forced by a probe voltage towards the exit channel (a small tantalum tube) where an electromagnet surrounding the exit end of the source bottle is used to intensify the ionized plasma. When the positively charged ions leave the source bottle, they pass through a charge exchange chamber filled with Rubidium (Rb) vapour, which gives up electrons to negatively charge the ions. Immediately after leaving the source with a source bias voltage (normally 18 kV), the ions pass through a velocity selector that is used to select the correct species for acceleration. The velocity selector is a 4° kink in the beam line and an electrostatic steerer is used to direct the selected beam. With the help of an electrostatic Einzel focusing lens, the ion beam enters a 1.7 MV tandem NEC Pelletron accelerator and goes through the same process as in the High Energy Implanter: accelerates towards the positively charged terminal, being stripped by nitrogen gas to become positive and re-accelerated by the terminal. After acceleration, a set of magnetic quadrupoles is used to focus the ion beam and then a switching magnet is employed to select the correct ion beam. A long beam line ensures that a well collimated ion beam is obtained with the size defined by the adjustable X and Y slits before entering the target chamber. When the ion beam impacts the sample in the target chamber, two sets of surface barrier detectors measure the energies of the scattered ions. One is for the backscattered ions and the other is for the scattered ions at a glancing angle to the sample surface, the output of each is multiplexed into a computer for collection and analysis. The implanted samples in this thesis were attached to a goniometer sample holder with conductive paste. A randomized mode was used, in which the sample holder was tilted by up to +/- 10° about the horizontal axis and vertical axis simultaneously and continuously to minimize channeling.

2.3.3 RUMP

The analysis and simulations of the RBS spectra in this thesis were performed using RUMP (RBS Universal Master Package) [36]. It was used for the spectra reading, calibration and for other basic manipulations. It included SIM and PERT programs for supplementary RBS spectra simulations and fittings. The detailed algorithm of the code is in [37] and [38].
2.4 Electrical measurements

In a semiconductor material study, it is necessary to carry out accurate electrical measurements to determine the electrical properties of the samples. This helps to determine the potential applications for the material. After the sample preparation process (ion implantation and annealing) in this thesis, Hall effect measurements were employed to investigate the electrical resistivity, carrier density and mobility of the semiconductors. Besides the fundamental electrical resistivity, the carrier density and mobility are two of the most crucial parameters for semiconductors, as they represent the density of the holes or electrons in the sample and how fast they can move through the material. A separate four point probe technique was used for the electrical resistivity measurements to support and confirm the results from the Hall effect measurements.

2.4.1 Hall effect

The underlying theory of the Hall effect is the Lorentz force. With a model set up as in Figure 2.5, the force acts perpendicular to both the directions of the current and magnetic field directions and deflects the electrons towards the negative Y-axis. The accumulated electrons on the sample surface generate an electric field with a potential of $V_H$ (i.e. the Hall voltage). The Hall voltage is negative for an $n$-type semiconductor and positive for a $p$-type semiconductor, since the Lorentz forces applied to the charge carriers of both are in the same direction, but opposite electric fields are created for the two. A second component of the Lorentz force from the generated electric field is applied to the charge carriers in an opposite direction to the one of the magnetic field. By setting the net Lorentz force to zero, the carrier density of the material can be obtained from:

$$n = \frac{I \cdot B}{q \cdot V_H \cdot d}$$  \hspace{1cm} (2.3)

where $n$ denotes the carrier density, $V_H$ represents the Hall voltage, $I$ is the current, $B$ is the magnetic field, $d$ is the sample thickness and $q$ is the elementary charge. The Hall mobility can also be determined as:

$$\mu = \frac{V_H \cdot d}{\rho \cdot I \cdot B}$$  \hspace{1cm} (2.4)

where $\mu$ is the hall mobility and $\rho$ is the resistivity derived from Ohm’s Law.

The experimental determination of these properties requires significant departures from the ideal model (e.g. one cannot directly measure the electrical field inside the sample) [39]. Hall measurement samples are commonly made into thin layer geometries with several electrical contacts on the surface. As the contacts usually have higher conductivity than the sample material, the electric current tends to flow through the contacts via the sample [44]. That makes an electric field measurement inside the sample possible by al-
ternatively measuring the voltage difference between the contacts. In order to obtain the resistivity, carrier density and Hall mobility of a sample, a Hall effect experiment consists of a series of current-voltage measurements on the contacts under a magnetic field. The measurement processes and the calculation methods for the properties vary according to individual sample geometries and the positions of the contacts (Equations 2.3 and 2.4 are the fundamentals). Readers interested in its experimental aspects are referred to [40–43].

Figure 2.5: A schematic of the Hall effect in a long, thin bar of n-type semiconductor with a thickness d and a width w applied to a magnet field of B and a current I, generating a Hall voltage $V_H$, from Reference [39].

2.4.2 Sample preparation

Many practical aspects must be considered when a Hall effect measurement is carried out, like the current, voltage and magnetic field intensity measurement accuracies, the measurement environment (e.g. light and temperature) and the sample uniformity etc. However, the research in the past has shown that the sample geometry and the contact material, quality, size and positions are some of the factors that can influence the measurement most significantly [44,45]. The sample preparation protocol for the specified sample geometries and contacts is dependent on the individual sample material and measurement, and it is commonly considered as the most difficult but important part of the measurement process [44,45].

Hall effect measurements commonly use two kinds of sample geometries: (1) the long, narrow Hall bar geometries and (2) the nearly circular or square van der Pauw geometries as shown in Figure 2.6 [44]. Hall bars of similar geometries are usually used when measuring magnetoresistance, or the Hall mobility on samples with low resistances, though extended arms on the sides are required for a high accuracy measurement [44]. Van der Pauw
Figure 2.6: The common van der Pauw (top) and Hall bar (bottom right) sample geometries, the contacts are black, from [44]. Bottom left of the figure is a photo of the mask used for photolithography to produce the samples in clover leaf and Hall bar (with 6 extended arms) geometries, with the corresponding contacts.

geometries are simpler yet the errors are more sensitive to the contact size and placement [44]. De Mey analyzed the geometrical errors on Hall measurement and found that the measurement on clover leaf design had the lowest error due to its small effective contact size [45,46]. Although the complex geometries (clover leaf and Hall bar with extended arms) are generally more desirable, they require extra patterning techniques and are harder to obtain.

A number of ohmic contacts are needed between the sample and the measuring instrument. To produce contacts on semiconductors with an adequate ohmic behavior, one needs to carefully select the depositing materials and methods. Potential contact materials are mainly metals (Al, Ag, Cu, Ti...) or metal alloys, taking the benefit of their low electrical resistance. Deposition methods include evaporation, sputtering, ion-implantation, molecular beam epitaxy and others, depending on the sample and the contact materials. An annealing process is commonly used after the deposition to improve the quality of the contacts. Much effort has been made in this area. Processes for different sample materials were reviewed in [47–49] and well summarized in [44].

Last but not least, the contacts need to be sufficiently small and deposited precisely on the circumference of the sample as the design shown in Figure 2.6. The contact size and position deviation effects on Hall measurements were discussed by Chwang [50].

To conclude, an accurate Hall effect measurement requires well designed sample prepa-
2.4. Electrical measurements

The samples used in the project are thin films (Si, Ge or Si$_{1-x}$Ge$_x$) on substrates as described in the previous section, so only the thin films on the top surface were patterned into a clover leaf (CL) geometry with four Al contacts on top, as shown in Figure 2.7. In the Hall measurement sample preparation process for ion implanted SOI, a 150 nm Si$_3$N$_4$ film was firstly deposited on the surface with PECVD (plasma-enhanced chemical vapor deposition), followed by a spin coating of 2 µm AZ5214 positive photo resist (PR). A mask with chromium patterns on quartz (Figure 2.6) was designed for the photolithography process used afterward. By aligning the desired CL pattern of the mask to the top of the sample, the PR was developed into the same pattern after a UV (ultraviolet) light exposure. The area of the Si$_3$N$_4$ film uncovered by the PR was then etched by a BHF (Buffered HF) solution, 10 : 1 mixture of ammonium fluoride (NH$_4$F) and hydrofluoric acid (HF). BHF was used instead of HF because it was able to etch the Si$_3$N$_4$ without damaging the PR layer. KOH (potassium hydroxide) further etched the exposed Si as in Figure 2.7, the Si$_3$N$_4$ layer was initially created for this step to mask the Si surface since the PR dissolves in KOH. Herein, a Si thin film in a CL pattern was obtained after the Si$_3$N$_4$ removal by HF. Sample fragility was the main reason that this photolithography plus multiple selective etching method was chosen instead of a direct cut.

Before depositing the metal contacts, an RCA clean was required for the removal of organic and ionic contamination and the native oxide. In order to precisely control the contact sizes and positions, the designed mask has corresponding chromium patterns of the contacts for each sample geometry, as shown in Figure 2.6. By repeating the photolithography process above with the contact pattern of the mask aligned to the sample, the PR covered the whole sample surface, leaving a few holes exposed (for the contacts). The PR acted as a mask when a 200 nm thick Al layer was thermally deposited onto the sample surface. The metal contacts following the contact patterns were created on the sample surface, after the PR was lifted off by acetone. The final step was thermal annealing of the samples at 450 °C for one hour, which leads to improved contact quality. The Ohmic nature of the contacts was confirmed with IV (current - voltage) measurements.

Ge (i.e. Ge thin film on Si substrate) samples were prepared for Hall measurement utilizing a similar method, as in Figure 2.7 (b). H$_2$O$_2$ was used instead of KOH for the Ge etching. H$_2$O$_2$ does not react with the PR thus the Si$_3$N$_4$ layer was not needed in this case. The same procedures were used on the Si$_{1-x}$Ge$_x$ thin films as on the Ge samples. The samples prepared in this thesis are all with the CL pattern with 1 cm diameter, and the contact sizes are 0.75 mm in diameter. Therefore, high accuracy Hall effect measurements were performed on these samples, taking advantage of the geometry and the contact quality.
Chapter 2. Sample preparation and characterization techniques

Figure 2.7: Flow charts showing the basic procedures of Hall effect measurement sample preparations for (a) Si on insulator (SOI) and (b) Ge on Si (GOS). A photo of a sample after the process is shown in (a).
2.4.3 Hall effect measurement system

Each Hall effect measurement system varies according to the specified functions and measuring conditions, but the main components include an electromagnet power supply, an electromagnet, a sample holder module, and a measurement and control unit. The electrical measurements in this thesis were performed on a model 7707A Hall measurement system from Lake Shore Cryotronics, Inc., in the department of Electrical Materials Engineering of the Australian National University. Figure 2.8 shows the set up of the system. On the left is the electromagnet power supply, the long rod shaped sample holder module in the middle goes through a platform vertically, and its bottom end is sandwiched by the pole face sets of the electromagnet. The measurement and control unit is on the right. The sample is mounted on a sample card with conductive metal clips pressing on the contacts, and is electrically connected to the measurement and control unit through the sample holder rod and the junction box on top. A sample enclosure can be used to shield the sample from the external light, to minimize the photoconductive and photovoltaic effects. A magnetic field is generated by the electromagnet perpendicular to the sample surface as the pole faces are parallel to the sample surface on two sides. Moreover, the room temperature sample holder module can be replaced by a low temperature module with a compressor or a high temperature module with a furnace, which enables the measurement to be carried out with sample temperatures from 2 K to 800 K. During a Hall effect measurement, the computer controls the measurement parameters, including to which contacts the currents are applied, the current intensity, the magnetic flux density and the sample temperature. Measurement of the voltages on the contacts is performed to calculate the electrical conductivity, carrier density and mobility under different measurement conditions. The Hall measurements in this project were carried out at room temperature, using a variable current and a variable magnetic field from -1 to 1 mA and -10 to 10 kG, respectively. Regarding the ratio between the real carrier concentration and the Hall carrier concentration (i.e. the Hall factor, $r_H$),
we approximate $rH = 1$ for all experiments. More information about this factor can be found in L. Romano et al [51].

2.5 Electron microscopy

Electron microscopy is considered to be one of the most efficient and versatile tools in material science for determining the crystallography, microstructure and composition of a specimen. The resolution limitation of the visible light microscope initially led to the development of the electron microscope [52]. The best resolution of a visible light microscope is about 300 nm according to the Rayleigh criterion:

$$\delta = \frac{0.61\lambda}{\mu \sin \beta} \quad (2.5)$$

where $\delta$ is the smallest distance that can be resolved (resolution), $\lambda$ denotes the wavelength of the radiation, $\mu$ represents the refractive index of the viewing medium and $\beta$ is the semi-angle of collection of the magnifying lens [52]. A resolution of 300 nm corresponds to about 1000 atom diameters, while in some cases a material study requires imaging detail down to an atomic level. An electron microscope provides a higher resolution by taking the advantage of the smaller wavelength of electrons compared to that of visible light. Broglie’s equation $\lambda = 1.22 / E^{1/2}$ (where $\lambda$ and $E$ are respectively the wavelength and the energy of an electron) shows that a theoretical resolution of the order of $10^{-3}$ nm can be achieved given that the electron has a potential of $\sim 100$ keV, which is sufficient for atomic level imaging [52].

The electron microscope focuses an energetic electron beam into a nm sized spot and directs it onto a sample. The interactions between the incident electrons and the atoms in the sample generate a range of secondary signals: backscattered electrons, secondary electrons, Auger electrons, Bremsstrahlung and fluorescence x-rays, cathodoluminescence etc. A scanning electron microscope (SEM) scans over the desired area of a sample, and collects these signals in real time, which is then analyzed and converted to information about the surface topography and the chemical composition of the sample. If the sample is thin enough ($< \sim 100$ nm), the energetic electrons are able to pass through the material. A transmission electron microscope (TEM) detects the transmitted and the forward-scattered electrons to probe the lattice structure of the specimen. Combining SEM and TEM, a scanning transmission electron microscopy (STEM) technique was established and is becoming increasingly popular [53]. High resolution TEM (HRTEM) was employed in this thesis for substrate lattice structure characterization and identification of the dopant-atom lattice locations.
2.5.1 Transmission electron microscopy

A TEM has a similar illumination system to an optical microscope but uses an electron beam instead of a light beam as shown in the schematic of Figure 2.9. The electron beam is generated by an electron gun and is accelerated to a potential of hundreds of keV. While the 1st condenser lens controls the spot size of the beam on the specimen, the 2nd condenser lens and the condenser aperture determine the beam current (brightness of the image). As the electron beam falls on the specimen, the incident electrons can be divided into two components, one undergoes Bragg scattering and the other is transmitted through the sample. Hence, a TEM has two basic operation modes: diffraction and imaging. In the diffraction mode, a selective area diffraction (SAD) aperture is inserted in the image plane to choose the area of interest of the sample, and the objective lens creates the diffraction pattern in the back focal plane from the scattered electrons. An objective aperture is used in the imaging mode to choose the beam(s) in the diffraction pattern (or the central beam) on the back focal plane, and the objective lens generates the intermediate image in the image plane from the selected beam(s). With the intermediate lens focusing on either the back focal plane or the image plane, a diffraction pattern or a TEM image, respectively, is projected on the fluorescent screen or a CCD (charge-coupled device) camera by the projector lens.

The electron diffraction pattern of a sample carries information about its crystal structure such as the crystallinity and the lattice plane spacing. A discrete scattering pattern means the investigated sample is crystalline and the distances between the diffraction spots represent the atomic plane spacing in reciprocal space. On the other hand, the diffraction pattern of an amorphous or polycrystalline material is a series of concentric rings. The TEM imaging mode is able to switch between bright field and dark field by means of choosing the central beam, or a diffracted beam from the diffraction pattern, respectively, with the objective aperture. HRTEM imaging is achieved by collecting both the central beam and a few diffracted beams, and utilizes their phase contrast \[53\]. In bright field imaging, the contrast of a TEM image depends on the thickness, composition and lattice damage conditions of the target sample. A higher value of both the sample thickness and the atomic number \(Z\) of the atoms in the specimen lead to stronger electron beam absorption, which results in the corresponding region appearing darker. Brightness contrast can be created between the low and high \(Z\) regions in the case where a sample is composed of more than one element and their \(Z\) difference is large enough to be distinguished in a TEM image. Thus, the TEM technique is commonly employed to identify the dopant atom location. When the dopant atoms precipitate from the substrate, a contrasted region can be observed because of their \(Z\) difference. If both the substrate material and the precipitated dopant are crystalline, a Moiré pattern can be created by the overlap of the substrate and the impurity lattice in the image. TEM can also be used to characterize the lattice disorder of a crystalline sample, while the void defects appear brighter, the regions with high strain are darker in a bright field TEM image.
In this thesis, the TEM images and the electron diffraction patterns were taken with the Phillips CM300 TEM system, at the Center of Advanced Microscopy at the Australian National University. Equipped with a LaB$_6$ filament as the electron source, the system accelerates the electrons with a voltage of 300 kV, reaching a maximum magnification of $750 \times 10^3$ with a resolution of 2 Å.

2.5.2 TEM sample preparation

The primary concern for a TEM sample is its thickness; it is essential that the sample is thin enough ($< \sim 100$ nm) to ensure a sufficiently intense electron beam is transmitted. In the area of material science, there are normally two types of TEM samples: the plan view and the cross section view. While a plan view sample is observed in a direction perpendicular to the original sample surface in a TEM, a cross section sample has the original sample surface parallel to the electron beam direction. There are a range of different sample preparation methods for different materials. In this thesis, cross section TEM samples were prepared and the conventional method was employed, via mechanical milling and ion beam polishing. The cross section TEM sample was selected because it allows an investigation of the dopant depth distribution. At first, the ion implanted sample was...
stacked and glued to another five Si dummy samples face to face, with the sample surface in the middle. After being cut into 300 $\mu$m thick pieces by a low speed wafer cutter, and into 3 mm diameter discs with an ultrasonic cutter, the sample was mechanically milled to 80 $\mu$m thick and then further thinned by dimple grinding on both sides to 10 - 20 $\mu$m thick. The final polishing step was carried out in a precision ion polisher system (PIPS). Two 4 keV Argon beams at angles of $\pm 4^\circ$ were used in the polishing process with the sample maintained at a temperature of -169 °C. Figure 2.10 is a picture of a TEM sample taken with an optical microscope. The dimple grinding creates a circular thickness gradient from the center of the sample, so after ion milling, the thin film of the sample has a depth gradient along the radius as shown in the inset TEM image of Figure 2.10. Therein, HRTEM imaging can be performed at different depths of the thin film.

Figure 2.10: A picture of a cross section TEM sample under an optical microscope, with the inset showing the TEM image of the region of interest.

2.6 Raman

Raman spectroscopy (named after its discoverer C. V. Raman) is a light scattering technique that has been considered as an important analytical and research tool in a wide range of fields such as pharmaceuticals, geology, mineralogy, and life sciences [54]. In semiconductor material research, it has the capability to determine sample composition, crystallinity, crystal lattice strain, disorder, and orientation, etc.

The fundamental theory of the technique can be briefly explained as following. When a sample is irradiated by a monochromatic light, the light interacts with the sample and is either scattered, absorbed, or reflected in some manner. If one analyzes the frequency of the scattered radiation, it can be found that most of the light maintains the same frequency
as that of the incident beam due to elastic scattering, also called Rayleigh scattering. However, a dramatically small amount (∼ 1 in 10 million) of photons of the incoming light undergo an inelastic scattering with the target material and have their wavelengths changed afterward, which is known as Raman scattering \[54\]. Raman scattering can be classified into two types, Stokes and anti-Stokes, depending on the incident photon having either a decrease or an increase of energy, respectively. The energy difference between the incoming photon having a frequency of \(v_0\) and a Raman scattered photon having a frequency of \(v_1\) is \(\Delta E = h v_0 - h v_1\), where \(h\) is the Planck constant. Hence, the Raman shift is defined accordingly and expressed in wavenumber:

\[
\tilde{\nu} = \frac{1}{\lambda_0} - \frac{1}{\lambda_1}
\]  

(2.6)

where \(\tilde{\nu}\) is the Raman shift, \(\lambda_0\) and \(\lambda_1\) denote the wavelengths of the incident and the Raman scattered light respectively. The value of the Raman shift depends on the vibration frequency of the molecule, if it is high the energy change is significant (light atoms held together with strong bonds), if it is low the energy change is small (heavy atoms held together with weak bonds) \[55\]. Therefore, the sample chemical composition and structural properties determine the intensity of the Raman scattered light in each wavenumber. A Raman measurement records the Raman spectrum (counts of photons) as a function of the Raman shift, which is normally in a unit of cm\(^{-1}\) as shown in Figure 2.11.

![Figure 2.11: Raman spectra of crystalline Si, Ge, Si\(_{0.35}\)Ge\(_{0.65}\), and Si\(_{0.1}\)Ge\(_{0.9}\)](image)

A typical Raman spectrum features several peaks and is a distinct chemical fingerprint for a particular material. An identification of the sample composition can be achieved with a Raman spectral library \[54\]. Figure 2.11 serves as an example, the single sharp
peak at the wavenumber of 521 cm$^{-1}$ defines the corresponding sample as a crystalline Si, the peaks at 400 cm$^{-1}$ are from the signals of the Si-Ge bonds of the samples and the Ge-Ge bonds contribute to the peaks at 300 cm$^{-1}$. The lattice strain in a sample causes its Raman peak(s) to shift to a higher or lower wavenumber. This effect is commonly utilized for intrinsic stress/strain studies of a material. The crystallinity of a sample can also be characterized, since the crystal lattice disorder or amorphization leads to broader and less intense Raman peaks (i.e. higher full width half maximum magnitude of the peak(s)). SiGe alloys normally have higher lattice strains and disorders than those of the pure Si or Ge, so significantly shifted and broader peaks are observed as shown in Figure 2.11. These are the main applications of Raman spectroscopy in semiconductor material research, and were used this thesis.

A Raman spectrometer has five basic elements: a light source(s), collecting optics, a straylight rejection filter, a wavelength selector and a detector. Green ($\lambda = 532$ nm), red ($\lambda = 633$ nm) and near infrared ($\lambda = 785$ nm) lasers are three of the most common light sources. The main purpose of switching lasers is to avoid interfering fluorescence signals in the Raman spectrum, enhance resonance, and optimize the laser penetration depth into the sample. Most Raman spectrometers thereby are equipped with multiple types of lasers. As the selected laser beam enters the sample surface, the objective lens is used to collect the scattered light from the desired sample spot(s) (size of $\sim 1\mu m$). Since the Rayleigh scattered photons dominate the scattered light, a straylight rejection filter is introduced to block the light with unchanged wavelength and pass the Raman signal through. The beam through the filter consists of Raman scattered light in a variety of wavelengths, its separation, selection and record processes are accomplished by a spectrograph. Diffraction gratings are employed to disperse the Raman scattered light after it enters the confocal system from a confocal hole. A CCD detector measures the intensity of the dispersed light as a function of the individual wavelengths. A higher groove density grating or a longer focal length of the confocal system provides a larger level of light dispersion, hence a higher spectral resolution can be obtained. However, the measurable wavelength range is consequently reduced due to the fixed size and number of pixels of the CCD detector [56].

The Raman spectroscopy experiments in this thesis were carried out with the Renishaw Raman System in the department of Electronic Material Engineering at the Australian National University. The red laser of the system was employed. The scattered light was collected by a $100\times$ objective lens of a confocal optical microscope with a spot size of 0.91 $\mu m$. A high performance edge filter was used for the Rayleigh scattered light rejection, and allowed the measurements to have the lowest Raman shift down to 100 cm$^{-1}$. The Raman scattered light dispersion was achieved by a grating whose groove density is 1200 lines/mm, and a Peltier cooled ($-70$ °C) CCD detector was used for the Raman data recording. The Raman spectra were normalized after the acquisition, and fitted with a Lorentz function to calculate the positions and full width half magnitudes of the Raman peaks, which were used to characterize the strain and disorder conditions of the ion implanted samples.
2.7 Ab-initio modeling

Ab-initio modeling is an important tool in material science which can be applied to a variety of materials to simulate a wide range of material properties such as structural, electrical, optical and magnetic. In this thesis, ion dynamics and relaxation were performed with density functional theory (DFT) to determine the local configuration of the implanted atoms in the substrate lattice. The simulation results were used as input and compared with that from the EXAFS and XANES simulations and fittings (Section 3.5). The dopant-defect clustering properties were also investigated by calculating the binding energies using DFT. A basic background of the technique is given below explaining its fundamental theories, followed by the details of the modeling process in this thesis.

2.7.1 Background

Materials modeling methods can be basically divided into three categories: tight-binding modeling, force-field simulations and the ab-initio techniques (in fact, they are closely related and sometimes used in a combined manner) [57]. A tight binding model simulates the material electronic band structure mainly with LCAO (linear combination of atomic orbitals) related methods [58], while force-field simulations include the well known MC (Monte Carlo) and MD (molecular dynamics) techniques, and the modeling approaches that are carried out entirely from first principles (only established physics laws are used without assumptions, empirical factors and fittings) are ab-initio ("from the beginning" in Latin) techniques.

The Schrödinger equations are the original theory used to perform atomic scale ab-initio modeling. In 1926, Erwin Schrödinger published the first accounts of his now famous wave equation [59]. His wavefunctions are extremely promising as described by Paul Dirac (who shared the Nobel prize with Schrödinger in 1933): “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble.” [60] The computational intensity of the theory has an exponential trend as a function of the number of electrons in a system. Thus the calculation is limited to a small number of relevant electrons (<~10 [61]), which is obviously not sufficient for material modeling.

Much effort has been made to improve the algorithm since the equation was published, the Hartree-Fock (HF) method [62, 65] developed soon after in 1928 is one of the most successful attempts. It made multiple approximations of the wavefunctions using atomic and molecular orbitals to reduce the computational demand. Although its functions are still too complicated to be solved for most many-electron systems [66], the HF method is still utilized today, mainly in quantum chemistry studies, along with the density functional theory, as two of the most popular ab-initio modeling techniques.

In the 1960s Kohn-Sham (KS) equations were introduced so that the many-body
Schrödinger equation solution can be approximated in a simple enough manner and applied to general materials modeling. Based on the HF method, the basic idea of the KS equations is to reduce the problem of many interacting electrons in an external potential in the Schrödinger equation by mapping it exactly to a set of noninteracting electrons in an effective external potential [67]. Its formulation foundation is the Hohenberg and Kohn theorems, in which the calculation of the ground state total energy of a system of interacting electrons is done by a unique functional of the electron density of the system [68], and this is the origin of the “Density Functional Theory” (DFT).

The ground state total energy of a single particle derived from the KS equations is given by:

$$E = \sum_j \epsilon_j + E_{xc}[n(r)] - \int v_{xc}(r)n(r)dr - \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|}dr'dr$$

(2.7)

where $E_{xc}[n(r)]$ is the exchange-correlation energy functional, $\epsilon_j$ denotes the $j^{th}$ KS orbital energy, $n(r)$ is the ground state density and $v_{xc}(r)$ represents the exchange-correlation potential. This equation is theoretically exact, the form of $E_{xc}[n(r)]$ is the only unknown, whose approximation is thus a crucial parameter in the KS approach. The two main types of exchange-correlation functionals used within DFT are the local density approximation (LDA) and the generalized gradient approximation (GGA) [57]. In LDA, the exchange-correlation energy density at each point of the system is treated to be the same as in a homogeneous electron gas with a constant density, $n$ [67]. It is accurate for a material with a uniform or slowly varying electron gas, but less valid for molecules and solids, whose electron density tends to vary substantially in space [69]. GGA is often implemented as a corrective function of LDA, which includes corrections on the electron density gradients [57]. Different GGA parametrization schemes can be chosen depending on the individual DFT model one is trying to build, PW91 [70], PBE [71] and BLYP [72,73] are the mainstreams. Some hybrid functionals (mixture of DFT and HF calculations, eg. B3LYP [74]) and the recently developed meta-GGA [75] are sometimes employed in the simulations, besides LDA and GGA.

Another central issue of DFT modeling is the approach to solve the KS equation, in other words, the description method of the electronic structures of the particles in the calculation. Typically, there are three basic methods that can be utilized: the localized atomic(-like) orbitals (e.g. LCAO), the atomic sphere (e.g. augmented plane wave (APW) method with muffin-tin orbital approximation), and the plane wave and grids method [76]. There are no fundamental disagreements between them and all three methods can lead to converged solutions, but each has its own advantages. The plane wave methods are especially appropriate for periodic crystals where they are able to provide intuitive understanding as well as simple algorithms for practical calculations [76].

When modeling a periodic solid with the plane wave method, the wave function of an electron can be expressed as the product of a plane wave and a function of the periodicity
of the material using Bloch’s theorem [77]. For a periodic system with defect(s), periodicity does not exist in a single unit cell. Thus a supercell subjected to periodic boundary conditions needs be generated before the defect(s) are introduced, and its size must be large enough to avoid the interactions between the defects in the neighboring supercells [57]. In addition, to get a perfect electron wave function, one needs to expand the KS orbitals into an infinite number of plane wave basis sets (a set of basis functions). Fortunately, the magnitude of a plane wave tends to zero in high energy, so it is justified that the basis sets can be truncated above a certain energy in a practical calculation, and this selected energy is known as the plane wave cutoff energy. Convergence tests are normally essential for the supercell size and the cutoff energy determinations.

The core electrons of an atom usually require large quantities of plane waves to expand their wave functions since they are highly localized, although their contributions to bonding are negligible compared to that of the valence electrons. Consequently, a pseudopotential was proposed to replace the atomic potential due to the core electrons to reduce the computational expense [57]. Orthogonality between the valence electrons and the core states are still ensured, so the accuracy of the simulation is not affected to a major extent [78]. There are essentially two kinds of pseudopotentials, the norm-conserving soft pseudopotentials [78] and the Vanderbilt ultrasoft pseudopotentials [79]. Fewer plane waves are needed in the latter one (“softer”).

The computational efficiency can be further enhanced by using the projector augmented wave (PAW) technique within the plane wave method. The general concept of the technique is to smooth the rapid oscillating wave functions of the valence electrons by using auxiliary projector functions, so less Fourier components are necessary for the wave functions [80, 81]. Pseudopotentials can be implemented within the PAW method to describe the potentials from the core electrons in an atom, taking advantage of both techniques.

Moreover, many properties of the models (e.g. matrix elements, charge density, density of states...) are integrals of the wave functions over the Brillouin-zone, and evaluation of these properties is achieved by a weighted sum over special k-points with fast Fourier transform (FFT) [82]. Thus, the mesh scheme and the meshing density in the k-point sampling process play crucial roles in the modeling accuracy. The Monkhorst - Pack scheme, generating a uniform grid of k-points, is one of the common methods [83]. A greater number of k-points generally leads to higher calculation accuracy, whereas it makes the simulation more computationally expensive. Convergence tests on the results are usually implemented here as well.

Last but not least, after solving the KS equation, not only the total energy of the system is obtained, the other properties (structural, electrical, optical, and magnetic) of the model can be further calculated (or more exactly, approximated within minor errors) from its electronic structure. An ion relaxation process is often carried out to optimize the model geometry before determination of the properties to ensure the system is stable (i.e. has a
mineral total energy). The ion relaxation can be performed with conjugate gradient (CG), Quasi-Newton or other algorithms \[84\]. Ab-initio MD is also available, which runs MD from first principles and is capable of simulating the experimental annealing process. Readers interested in the ab-initio modeling technique would have a better understanding of its quantum mechanics background, theories and applications by referring to \[58\], \[59\], \[63\], \[76\], \[85\].

### 2.7.2 Modeling process

DFT modeling in this thesis was carried out using the Vienna ab initio simulation package (VASP) \[86\], as this computer program is capable of performing both HF and DFT methods with a variety of calculation techniques (e.g. GGA, PAW, CG... as mentioned above) to determine different material properties \[87\]. A variety of models were built, including substitutional and interstitial In, C atoms and vacancy(s) in Si, Ge and Si\(_{1-x}\)Ge\(_x\) lattices. The simulated lattice structures were obtained after multiple steps of ion relaxation, and in each ion relaxation step, a DFT calculation was performed (solving the KS equation) on the system with several electronic steps. The total energies of their optimized geometries were then used to compare the stability of the models.

To calculate the electronic structures of the models (for total energy calculation) within DFT, the PBE parameterization scheme of the GGA method was employed to approximate the exchange - correlation functionals, and \(2 \times 2 \times 2\) Si, Ge and Si\(_{1-x}\)Ge\(_x\) supercells were generated with \(10 \times 10 \times 10\) k - point meshes using the Monkhorst - Pack sampling scheme. The projector augmented wave (PAW) pseudopotentials method implemented in VASP was used with the planewave cut off energies up to 400 eV depending on the specific material. The convergence criterion of the KS equation solution was set to \(1 \times 10^{-5}\) eV for the total energy difference between two electronic steps, with a minimum of four electronic steps for a solution. The total energy convergence of all proposed models on supercell size, \(k\) - point mesh density and cut off energy were tested, by increasing them to \(3 \times 3 \times 3\), \(15 \times 15 \times 15\) and by an additional 100 eV, respectively. The difference of the results was negligible from the ones with the selected parameters.

In order to obtain the electronic structures of the models, the ionic relaxation processes were performed utilizing the CG geometry optimization algorithm. The geometry was considered as “optimized” when the total energy of the system had a less than \(1 \times 10^{-4}\) eV change between two ionic steps. The process also followed a progressive relaxation procedure: ion relaxations were firstly performed between the dopant(s) or defects and the surrounding atoms over an increasing region size, and then a cell parameter relaxation and the final relaxation of all atoms, cell volume and cell shape \[88\]. A zero ionic step calculation (no atomic displacements, electronic structure calculations only) was carried out to define a more accurate total energy of the model. An ab initio molecular dynamics (MD) run was performed for each model within the VASP code, from the highest annealing temperature of the corresponding sample (Section 2.2) to 300 K with up to 1500 ionic steps under the RMM-DIIS scheme \[89\] before the DFT geometry optimization, to simulate the
annealing process and ensure that a global minimum total energy was obtained in the later DFT calculations.

Figure 2.12: The average bond lengths of Ge to Ge ($r_{\text{Ge-Ge}}$), Ge to Si ($r_{\text{Ge-Si}}$) and Si to Si ($r_{\text{Si-Si}}$) atoms and their mean ($r_{\text{mean}}$) as functions of Ge fraction in Si$_x$Ge$_{1-x}$ random alloy simulation models, dash lines are their linear fits.

Si$_{1-x}$Ge$_x$ models with five different stoichiometries ($x = 18.75\%$, 34.38\%, 50\%, 65.63\% and 81.25\%) were established. Given Si$_{1-x}$Ge$_x$ is a random binary alloy, 15 models were generated for each stoichiometry with the appropriate number of Ge atoms randomly substituting Si atoms in a Si lattice. Calculations were performed individually for all 15 models and the results were averaged. Such an approach for modeling random Si$_{1-x}$Ge$_x$ alloys has been previously justified [90–92]. The validity of the models was further confirmed as the Si-Ge bond lengths and the topological rigidity parameter [93, 94] (without In atoms present) agreed well with those in the published literature [95]. The atomic bond lengths of the relaxed Si$_{1-x}$Ge$_x$ models were plotted as functions of $x$ in Figure 2.12. The topological rigidity parameter of the models is $a^{**} = 0.715$, in excellent agreement with the previous EXAFS study on the alloy, which has $a^{**} = 0.72$ (+0.13/-0.05) [95].

The local structural environments of the dopant atoms were investigated using DFT by adding impurities to the substrates’ model and going through a geometry optimization process. The calculated bond lengths of the dopant atom(s) to the substrate atoms were used to compare with the EXAFS fitting results and some of the predicted dopant-atoms-clustering configurations served as inputs to the EXAFS and XANES fitting and simulations (see Section 3.5).

The stability of the dopant related clusters in the models was quantitatively studied
and compared by means of calculating their binding energies (also known as the “cluster formation energy”). For instance, the binding energy, $E_b(In_nV_mGe_{N-n-m})$, of an $In_nV_m$ cluster formed by $n$ substitutional In dopant atoms and $m$ vacancies (V) in a Ge supercell with $N$ sites is given by:

$$E_b(In_nV_mGe_{N-n-m}) = E(In_nV_mGe_{N-n-m}) - nE(InGe_{N-1}) - mE(VGe_{N-1}) + (n + m - 1)E(Ge_N)$$

where $E(In_nV_mGe_{N-n-m})$ denotes the total energy of a Ge supercell containing $n$ substitutional In atoms, $m$ vacancies and $N-n-m$ Ge atoms; $E(InGe_{N-1})$ is the total energy of a Ge supercell with one substitutional In atom and $N-1$ Ge atoms; $E(VGe_{N-1})$ is the total energy of a Ge supercell with one vacancy and $N-1$ Ge atoms; and $E(Ge_N)$ is the total energy of a N atom Ge supercell [96]. The physical meaning of a negative binding energy is that the $In_nV_m$ cluster is more stable than $n$ isolated substitutional In atoms and $m$ isolated vacancies [96]. Therefore, the preferred dopant-defect configurations were found by comparing the binding energies of the different cluster formations in the model lattices.

Despite multiple approximations being made when solving the many body Schrödinger equation as discussed above, an accurate \textit{ab-initio} model still required a significantly large computational power and time to develop (e.g. it took 128 CPUs and 128 Gb memory up to 24 hrs to perform the geometry optimization of a model in this thesis). The computing resources of this thesis were provided by the Australian National Computational Infrastructure (NCI), with the DFT calculations carried out on its Raijin supercomputer system at the Australian National University.
This chapter discusses X-ray absorption spectroscopy, which is the main tool used in this thesis to quantitatively characterize the local environment of the implanted dopant atoms. First, its basic concepts and theories are introduced, which are fundamental to the understanding of the experimental methods and data analysis methods that follow.

### 3.1 Introduction

X-ray absorption spectroscopy is a unique tool for studying, at the atomic scale, the local structure around a selected element contained within a material [97]. The basic physics behind the technique is that a core electron of a selected element in the sample is excited by an incident X-ray, and it is scattered by the atoms nearby as a photoelectron wave. This scattering effect is reflected in the sample X-ray absorption as a function of the X-ray energy. By analyzing the measured X-ray absorption spectrum, the local environment around the selected atom can be investigated.

#### 3.1.1 X-ray absorption

Since the discovery of X-rays by Roentgen in 1895, they have been applied to the determination of the material structural properties by studying their interaction with matter. When an X-ray is incident onto a sample, several things may happen: the X-ray can pass through and be unchanged, it can be scattered by an atom, and it can be absorbed by an atom. X-ray diffraction, for example, is a well developed lattice structure identification
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tool that is based on the elastic scattering of the incoming X-ray with the sample.

The X-ray absorption of a material is characterized by an absorption coefficient $\mu$. When an X-ray beam with an intensity of $I_0$ is incident on a material with a thickness, $t$, as in Figure 3.1 (a), according to the Beer-Lambert law, the intensity of the transmitted X-ray beam, $I_t$ is given by:

$$I_t = I_0 e^{-\mu t} \quad (3.1)$$

where $\mu$ is dependent on the incident photon energy $E$, approximated as:

$$\mu \approx dZ^4/mE^3 \quad (3.2)$$

where $d$ denotes the target density while $Z$ and $m$ are the target atomic number and mass, respectively [98]. Common X-ray imaging techniques (e.g. the X-ray computed tomography for medical applications), for example, are based on the transmitted X-ray beam intensity contrast caused by both the $Z$ and $E$ dependent absorption.

![Figure 3.1: (a) Schematic of an incident and transmitted X-ray beam through a sample, (b) the photoelectric effect, and (c) $\mu(E)$ as a function of $E$ around an absorption edge (source: References 99 and 100).](image)

In most cases, $\mu(E)$ decreases smoothly with an increasing X-ray energy according to Equation 3.2. However, when the incident X-ray has an energy equal to or slightly higher than the binding energy of a core level electron in the absorbing atom, a photoelectric effect occurs in which the core electron is excited to an unoccupied state or out of the atom into the continuum, as demonstrated in Figure 3.1 (b). This is because until then,
absorption of the X-ray by the core electrons was quantum mechanically prohibited as there was no available state for the photoelectron. A core hole is created in the mean time at the original site of the excited electron (the unfilled marker in Figure 3.1 (b)). At that specific energy (i.e. the edge energy), the incident photons are annihilated in the new absorption channel to promote the electrons, resulting a dramatic sharp rise of $\mu(E)$ that is known as an absorption edge. Figure 3.1 (c) is a sketch of the absorption coefficient against the X-ray energy around an absorption edge.

3.1.2 X-ray absorption spectrum

X-ray absorption spectroscopy (XAS) is a measure of the energy dependence of the absorption coefficient slightly below, at, and above a selected absorption edge of a chosen element in the sample. Since the electrons located in different shells of an atom have individual binding energies, most elements have multiple absorption edges, named according to the corresponding core levels where the electrons are exited from (K, L, M, etc.). The absorption edge energies are well defined for each element as its electron binding energies. Therefore in an XAS measurement, one chooses the interesting element to probe by tuning the X-ray beam energy to one of its edge(s) (i.e. XAS is element-specific.)

Figure 3.2: An X-ray absorption spectrum for crystalline GaAs at As K-edge, pre-edge, edge, and XANES and EXAFS regions are shown schematically. Figure 3.2 is a typical X-ray absorption spectrum before data processing. The gradual trend toward the lower absorption value is the spectral nature of absorption as shown in Equation 3.2 and Figure 3.1 (c), which is treated as the background and is not related
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...to the material properties being examined. The energy region below the absorption edge is the so-called pre-edge of the spectrum. The steep rise of the absorbance is the edge explained above. The remaining structure above the edge is distinguished into two regions, the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS), with the division point at $\sim 50$ eV above the edge. The peaks, shoulders, oscillations and other features additional to the background in these two regions are the X-ray absorption fine structure (XAFS), which carries the information about the local surroundings of the absorbing atoms.

3.1.3 X-ray absorption fine structure

After the incident X-ray causes the photoelectric effect as shown in Figure 3.1 (b), the electron promoted to the continuum state propagates outward in a spherical wave form as a photoelectron. The outgoing photoelectron waves scatter off the electrons of the neighboring atoms and return to the absorbing atom (Figure 3.3). The presence of the waves scattered back alters the absorption coefficient, which is the source of XAFS.

![Figure 3.3: A schematic showing the absorbing atom (yellow), its first nearest neighbors (blue) and an interference pattern created by the outgoing (solid orange circles) and reflected (dashed blue circles) photoelectron waves [99].](image)

According to Fermi’s Golden Rule, when an X-ray enters the region occupied by an atom, the probability of X-ray absorption depends on the similarity of the proposed final state to the indeterminate state prior to the measurement - the more similar, the more likely [101]. For example, when constructive interference is formed by the outgoing and the scattered photoelectric waves at the site of the absorbing atom, there is a high electron density at the site that makes the system more similar to the state before the measurement than in the case where destructive interference is formed. The likelihood of X-ray absorption and the value of the absorption coefficient itself are thereby enhanced and reduced by the constructive and destructive interference in the region of the absorbing
atom, respectively.

The photoelectron radiates in all directions as a spherical wave, thus it can either scatter off one nearby atom and return as shown in Figure 3.3, or scatter with multiple neighboring atoms and then return to the absorbing atom. These two types of events are known as single scattering and multiple scattering, respectively. Both of these effects influence the interference pattern and the resulting absorption coefficient.

Furthermore, the formation of the interference pattern is dominated by the photoelectron wavelength along with the absorber environment. The photoelectron wavelength is controlled by the energy of the incident X-ray, as the photoelectron kinetic energy equals the incident photon energy minus the electron binding energy. Therefore, in an XAS experiment, the X-ray energy-dependent measurement above the edge is actually a scan through a range of wavelengths of the created photoelectrons. The consequently varying interference pattern due to the changing wavelength generates the fine structure of the absorption coefficient. The local environment of the absorbing atom is the other contributor to the formation of the interference pattern (i.e. to the XAFS), so its information can be obtained by analyzing the XAS spectrum.

3.1.4 XANES and EXAFS

XAFS consists of XANES and EXAFS regions. Although they are normally recorded in the same spectrum in a measurement, they are treated differently afterward for several reasons.

The origin of this separation is that the behavior of the photoelectron with a low or a high energy is not the same. The photoelectron is transited to an unoccupied state with a low incident phonon energy, so XANES is sensitive to the coordination chemistry around the absorber, and the three dimensional structural information is obtainable in this region due to the strong photoelectron multiple scattering effect. EXAFS, on the other hand, is more a reflection of the single scattering of the photoelectrons in the continuum, thus it is independent of the chemical bonding but dependent on the atomic arrangement surrounding the absorbing atom. EXAFS is specific to the identification of the neighboring atomic species and the related structural information, like the coordination number, bond length and disorder [99].

The theoretical descriptions are therefore distinct for the two. The EXAFS region can be more easily and precisely defined than the XANES region due to the weak multiple scattering, so its corresponding data analysis and simulation procedures are more mature. The fine structure near the edge is complicated, so more advanced and explicit approaches are essential to produce a theoretical calculation. A match with or a linear combination of known standards are still the typical analysis methods for a XANES spectrum. Simulation accuracy is limited despite significant progress that has been made in recent years [99].
3.2 Theory

3.2.1 Theoretical description of XAFS

XAFS is intrinsically a quantum mechanical phenomenon [97], a transition from the initial electron state, $|\psi_i\rangle$ (with an X-ray and a core electron), to the final state, $|\psi_f\rangle$ (with no X-ray, one core hole and one photoelectron) [100]. According to the time-dependent perturbation theory [102], the probability of a transition per unit time (i.e. the transition rate) is proportional to the squared modulus of the transition amplitude:

$$\frac{2\pi}{\hbar} |\langle \psi_f | H' | \psi_i \rangle|^2 \rho \quad (3.3)$$

where $H'$ is the interaction Hamiltonian between the electromagnetic field and the electrons and $\rho$ is the density of state. $H' \propto \vec{A} \cdot \vec{p}$, where $\vec{A}$ is the vector potential of the wave and $\vec{p}$ is the momentum operator [97]. Assuming only one electron is involved in the transition, and taking only the dipole term in the expansion of the matrix element in Equation 3.3 (dipole approximation) [97], the absorption coefficient, $\mu$, can be described as:

$$\mu \propto |\langle \psi_f | \hat{\epsilon} \cdot \vec{r} | \psi_i \rangle|^2 \rho \quad (3.4)$$

where $\hat{\epsilon}$ denotes the X-ray polarization factor. The quadrupole and higher order terms may need to be taken into account for a high Z element and at L-edges, while the dipole approximation is robust for most cases (e.g. the transmission probability is changed by only 1% with the additional quadrupole term, for Fe at the K-edge) [97]. The matrix element in Equation 3.4 is dependent on the atomic structural orientation with respect to the X-ray polarization, and subjected to the selection rules for transitions. More information about these topics can be found in [97] and [99].

In Equation 3.4, the initial state is very simple in symmetry, and it is highly localized near the center of the absorbing atom. Therefore, the XAFS spectrum is dependent on the value of the final state wavefunction in the small region where the initial state is localized [97]. Constructive photoelectric wave interference in the region results in a high magnitude of the final state wavefunction, consequently leading to an increase of the X-ray absorbency as mentioned in the previous section.

One needs to consider the electron mean free path in the calculation of the final state. The photoelectron interacts dynamically with other electrons in the material during its propagation. These many-body effects lead to inelastic scatterings, excitations (e.g. plasmons) and other effects that result in energy loss. The quasi-particle model employs an energy-dependent self-energy function, $\sum(E_f)$, to account for these inelastic losses, and describes the photoelectron together with others it interacts with collectively:
\[ h' \psi_f = \left[ \frac{p^2}{2m} + V' + \sum (E_f) \right] \psi_f \]  

(3.5)

where the non-Hermitian Hamiltonian \( h' \) of the final state is characterized by the Coulomb potential \( V' \) and the complex valued self-energy \( \sum(E_f) \) \(^\text{99}\). In addition, the excited state decays after its finite lifetime as an electron in a higher orbital falls into and fills the core hole, which the non-hermicity of \( h' \) is responsible for \(^\text{99, 100}\). The mean free path of a photoelectron represents the distance it typically travels before an energy loss occurs or the core hole is filled. The magnitude of the mean free path is energy dependent, having a value of \( \sim 5 - 10 \, \text{Å} \). The limited mean free path length is the primary factor that makes XAFS a local probe. The sensitivity of XAFS to the scattering atoms at a distance greater than \( 10 \, \text{Å} \) from the absorber is negligibly small, only the local environment contributes to the phenomena.

We have discussed the single scattering effect only so far, but all the photoelectron waves that return after they are scattered either single or multiple times contribute to the final state and thereby to the resulting absorption coefficient. The multiple scattering approach separates the potential in Equation 3.6 into individual localized contributions \( v_{\vec{R}} \) from each scattering atom at the positions of \( \vec{R} \) \(^\text{97}\):  

\[ V' + \sum (E_f) = \sum_{\vec{R}} v_{\vec{R}}(\vec{r} - \vec{R}) \]  

(3.6)

The scattering effects of the photoelectron with the neighboring atoms is dependent on the atomic potentials. Most multiple scattering approaches currently employ the muffin-tin approximation, in which the potentials are approximated to be spherically symmetric to a finite radius with a constant interstitial potential between the atomic spheres (as shown in the sketch in Figure 3.4). This approximation method tends to be sufficient for close-packed structures but less so for open structures \(^\text{97}\).

![Figure 3.4: Sketch of a muffin-tin potential](image)

Despite the approximation, an explicit calculation of the final state still turns out to be computationally too demanding. The multiple scattering approach therefore makes use of the photoelectron Green’s function and the propagator \( G \) in real space \(^\text{99}\). The Green’s function separates the contribution from the central atom (i.e. the absorption background) and the contribution from the scattering of the photoelectron with the nearby atoms (i.e.
the fine structure). The later part of the Green’s function is proportional to \((1-G^0T)^{-1}G^0\), where \(G^0\) is the free particle Green’s function and \(T\) is the scattering operator which accounts for all the serial scattering processes off each atom. Herein, a decomposition of the scattering processes from different atoms is carried out by expanding the matrix into a multiple scattering series, if it converges:

\[
(1 - G^0T)^{-1}G^0 = G^0TG^0 + G^0TG^0TG^0 + G^0TG^0TG^0TG^0 + ... \tag{3.7}
\]

The form of this Green’s function expansion implies that the XAFS feature of the absorption coefficient can be expressed as a sum of terms, each of which corresponds to a photoelectron scattering path that begins and ends at the absorbing atom [97].

So far, we are treating XANES and EXAFS within a unified XAFS theory. However, further explanations of the two need to be carried out separately for two main reasons: one is the muffin-tin approximation requires a high photoelectron energy above the absorption threshold to be accurate (in the case of EXAFS); the other is that the convergence of Equation 3.7 is poor in XANES in many cases. Therefore, some alternative methods are developed to interpret the XANES region, which will be discussed later in Section 3.2.3, while the EXAFS region can be described accurately based on the XAFS theory introduced above.

### 3.2.2 EXAFS equation

The EXAFS region of an XAS spectrum can be quantitatively well defined with an EXAFS equation, which is able to be derived from Equation 3.4 with the support of the approximation and expansion approaches described in the last section. Based on [99] and [101], a brief development of the EXAFS equation is demonstrated below with an overview of the underlying theories; Stern [104, 105] and Rehr [120] provide more comprehensive theoretical descriptions of EXAFS.

**Fine structure as a function of wave number**

As discussed above, the Green’s function enables the separation of the absorption contribution from the absorber and that from the scattering of the photoelectron with the neighboring atoms. Thus, the absorption coefficient can be written as \(\mu = \mu_0(1 + \chi)\). Here \(\mu_0\) denotes the absorption background of the absorbing atom (introduced in Section 3.2.1), and \(\chi\) is the absorption fine structure due to the photoelectron scatterings from the environment. An explicit calculation of the final state wavefunction \(\psi_f\) is thereby avoided, and a study of the isolated \(\chi\) is performed instead:

\[
\chi = \frac{\mu - \mu_0}{\mu_0} \tag{3.8}
\]

The wavelength \(\lambda\) of the excited photoelectron is dependent on its kinetic energy \(T\),
3.2. Theory

which is equal to the difference between the incident photon energy $E$ and the absorption edge energy $E_0$ (i.e. the core electron binding energy):

$$E - E_0 = T = \frac{(h/\lambda)^2}{2m_e} \tag{3.9}$$

where $h$ is Planck’s constant, $m_e$ is the mass of an electron. Here the free electron relation between energy and momentum is an approximation. The photoelectron wavenumber $k$ is further defined given that $k = 2\pi/\lambda$ and $\bar{h} = h/2\pi$:

$$k = \frac{1}{\bar{h}} \sqrt{2m_e(E - E_0)} \tag{3.10}$$

A simplified model is built at the beginning. It is assumed that one electron excited from an absorber atom is elastically scattered off only one neighboring atom at a distance of R and returns, as if it is a plane wave bouncing off an ideal “soft boundary”. A preliminary “EXAFS equation” is given as:

$$\chi(k) = f(k) cos(2kR) \tag{3.11}$$

where $f(k)$ denotes the complex scattering amplitude, whose dependence of $k$ is affected by properties of the scattering atom, like its atomic number $Z$. This is the reason why EXAFS is able to distinguish the atomic species nearby the absorbing atom as well as the distance between the two. The $cos(2kR)$ term represents the generated interference pattern at the site of the absorbing atom. Constructive interference is achieved when the condition $2R = n\lambda$ is satisfied, where $n$ is an integer (the round-trip distance is equal to a whole number of the wavelength). This term also describes the oscillation nature of XAFS spectra.

Multiple neighbors and multiple scatterings

The first correction of the equation is made considering that in a more realistic case, multiple neighbors and multiple scatterings are involved. According to the multiple scattering approach described above, the fine structure contribution can be a sum of the modulations from each (single or multiple) scattering path that begins and ends at the absorber atom with one or more scattering atom(s) in between:

$$\chi(k) = \sum_i N_i f_i(k) cos(2kR_i) \tag{3.12}$$

where paths of the same kind are grouped under an index $i$ with the quantity of paths in each group being $N_i$ as the degeneracy. For single scatterings, $R_i$ is still the distance between the absorber and the scattering neighbor with $N_i$ being the coordination number of those neighboring atoms to the absorber, while in multiple scatterings, $R_i$ is the scattering path length divided by two and $N_i$ is the number of paths of the same kind.
Phase shifts
The equations above treat the scattering atoms as ideal elastic boundaries, yet the reality is more complicated. The atomic potentials are usually given by the muffin-tin approximation. The potentials of both the absorbing atom and the scattering atom(s) lead to phase shifts of the photoelectron wave, represented by $\delta_c(k)$ and $\delta_i(k)$, respectively:

$$\chi(k) = \sum_i N_i f_i(k) \sin(2kR_i + 2\delta_c(k) + \delta_i(k))$$ (3.13)

The photoelectron wave experiences phase shift twice from the absorber (once during the way out and once during the way it travels back) and once from the scattering atom. The conversion of a cosine to a sine function is because of historical reasons (the traditional EXAFS equation uses sine function) as well as the introduced phase shifts.

Spherical waves
Furthermore, the photoelectron propagates out in all directions isotropically as a spherical wave instead of a plane wave. When it returns to the absorber atom, its intensity decreases as a function of the square of the scattering path length:

$$\chi(k) = \sum_i N_i f_i(k) \frac{kR_i^2}{kR_i^2} \sin(2kR_i + 2\delta_c(k) + \delta_i(k))$$ (3.14)

Incomplete overlap
A core hole is created on the original site of the ejected photoelectron in the absorbing atom. The appearance of the empty state with lower energy results in orbital adjustments of the other electrons in the atom. The final state of the absorber is not the same as the initial state due to the system relaxation, regardless of the behavior of the photoelectron. This incomplete overlap of the two states reduces the likelihood of the absorption. The amplitude of the fine structure is consequently affected and is phenomenologically modeled by an amplitude reduction factor, $S_0^2$:

$$\chi(k) = S_0^2 \sum_i N_i f_i(k) \frac{kR_i^2}{kR_i^2} \sin(2kR_i + 2\delta_c(k) + \delta_i(k))$$ (3.15)

$S_0^2$ is thereby element dependent and weakly energy dependent, having a typical value of $\sim 0.7 - 1$.

Mean free path
The mean free path of the photoelectron wave, $\lambda(k)$ as discussed above, is also essential here to account for the inelastic interaction the photoelectron undergoes with the surrounding of the absorber and the finite core-hole lifetime. The decay of the photoelectron wave
increases with its travel distance $R_i$ as well, so all these effects are represented by a single factor $e^{-2R_i/\lambda(k)}$, which modifies the equation to:

$$
\chi(k) = S^2 \sum_i N_i f_i(k) e^{-2R_i/kR_i^2} \sin(2kR_i + 2\delta_i(k) + \delta_i(k)) \quad (3.16)
$$

The mean free path decreases as $k$ increases, so EXAFS is less sensitive to multiple scatterings compared to XANES and thus fewer orders of multiple scattering expansion is necessary to carry out a convergent calculation.

### Disorder

In addition, the EXAFS equation we established so far is based on a crucial assumption that only one photon is absorbed by a single atom and exciting one single photoelectron. In an actual experiment, an order of $10^{10}$ absorption events occur within each second and the collected XAS spectra is a sum over all the generated absorption signals. The summed data requires further analysis since the environments of the absorbing atoms are generally not identical or constant over time in a real material:

(1) The absorbing element can be in more than one (or in a gradient) crystallographic environment. For instance, some of the In ion implanted Ge samples in this thesis have a fraction of In atoms precipitated from the Ge lattice. Therefore any In atom can be in three different local environments: surrounded by other In atoms in the precipitation, isolated in the Ge lattice, or where both the In and Ge atoms are involved with a gradual change from the surface to the core of the precipitation. In an XAS measurement of such a sample on an In edge, the generated XAFS signals from all three circumstances are overlapped.

(2) A crystalline sample generally has some intrinsic disorder such as voids and interstitial defects, especially after ion implantation (see Section 2.1.3). These structural variations around the absorbers are scattered by the photoelectrons during a measurement, known as the static disorder.

(3) Thermal disorder exists within a material as well as the static disorder. At room temperature, most chemical bonds have a vibration period of the order of $10^{-13}$ seconds compared to the typical core hole lifetime of $10^{-15}$ seconds in XAS. The absorber - scatterer interatomic distances are thus not constant against time and their variations due to thermal vibrations influence the XAS spectrum.

The issue (1) is commonly handled by a linear combination method, which treats the final $\chi(k)$ as a sum of the products of the individual $\chi_j(k)$ and the fraction of absorbing atoms in the corresponding environment $f_j$ (i.e. $\chi(k) = \sum_j \chi_j(k)f_j$ where normally $\sum_j f_j = 1$).
Because of the static (issue 2) and thermal (issue 3) disorders, the \( N_i \) numbers of "same" paths grouped under index \( i \) defined above are no longer exactly the same. Nevertheless, they are still similar if the disorder level is low (not changing the interference completely). Therefore an assumption can be made that the half path lengths in each group \( i \) have a Gaussian distribution with a mean of \( R_i \) and a standard deviation of \( \sigma_i \). A scattered wave phase difference is created by the varying path lengths in each group, which leads to an XAFS amplitude reduction. The phase difference is dependent on \( k \) with a given \( \sigma_i \), so an \( e^{-2k^2\sigma_i^2} \) term is introduced into the EXAFS equation to account for the damping of its oscillation at high wave number due to these local environment differences:

\[
\chi(k) = S_o^2 \sum_i N_i \frac{f_i(k)}{k R_i^2} e^{-\frac{2R_i}{X(\sigma^2)}} e^{-2k^2\sigma_i^2} \sin(2kR_i + 2\delta_c(k) + \delta_i(k)) \tag{3.17}
\]

In analogy to X-ray diffraction, \( \sigma_i^2 \) is often called the EXAFS Debye-Waller factor, which plays an important role in the sample disorder characterization \[99\].

When the static disorder is large, the linear combination approach used in case (1) can be employed to tackle the problem on certain occasions (i.e. summing over the XAFS contributions from each ordered or disordered lattice configuration).

Cumulant expansion

Last but not least, in a situation where the system presents a significantly asymmetric structure, the Gaussian function is not adequate to approximate the path length distribution. The cumulation expansion method, first proposed by Bunker \[107\], considers the higher moments to describe the distribution. For instance, the EXAFS equation for one group of \( N \) numbers of scattering paths within the fourth cumulants is written as:

\[
\chi(k) = S_o^2 N \frac{f(k)}{k C_1^2} e^{-\frac{2C_1}{X(\sigma^2)}} e^{-\frac{2k^2C_2}{2}+\frac{2k^4C_4}{3}} \sin(2kC_1 - \frac{4}{3}k^3C_3 + 2\delta_c(k) + \delta_i(k)) \tag{3.18}
\]

This expression of the EXAFS equation defines the scattering path length distribution in each group in terms of its cumulants, where \( C_1 = R_i \) is the mean value, \( C_2 = \sigma_i^2 \) represents the variance, and the additional \( C_3 \) and \( C_4 \) are the third and fourth cumulants that denote the asymmetric and symmetric deviations from a Gaussian profile, respectively \[99\]. The \( R_i \) notified here, is a one dimensional distance averaged from its three dimensional distribution.

The local disorder in the samples in this thesis generally obeyed the Gaussian profile, so only the first and second cumulants in Equation \[3.18\] are essential and were applied. For some highly disordered systems, the cumulants higher than the fourth are necessary and this method is no longer a suitable description of EXAFS, and an alternative approach such as the n-body interaction method is more appropriate \[108,109\].

A typical EXAFS equation is developed as above and further refinements are sometimes
made depending on the individual scenarios, such as effects from the polarization of the X-ray beam. The EXAFS equation is fundamental for EXAFS data analysis, simulations and fittings used in the later sections, where the detail of its usage in extracting the structural information from the XAS data is discussed.

### 3.2.3 XANES interpretation

A theoretical explanation of XANES is more complicated than the one for EXAFS. There is no simple analytical description for the region like an “XANES equation”. The EXAFS equation established above breaks down at low-\(k\), due to the \(1/k\) term and the increase of the mean free path\(^{100}\). The latter is caused by the long core-hole lifetime at low photoelectron energy. It results in a more significant multiple scattering effect that requires a very high or a full order of multiple scattering expansions in Equation \(3.7\) for a convergent calculation. In the XANES region, the muffin-tin approximation implemented in the current multiple scattering approach is also less sufficiently accurate for atomic potential modeling\(^{99}\).

However, the near edge fine structure contains important information about the sample, some of which EXAFS is not able to provide. Due to its high sensitivity to multiple scattering, the three dimensional geometry of the sample structure (compared to one dimensional in EXAFS) can be determined. XANES also has the potential to identify chemical bonding to the absorber, like oxidation states, since the core electrons are transited to the unoccupied states instead of the continuum. Another key advantage of XANES over EXAFS is that it is a larger signal (thereby has a greater signal to noise ratio), which enables measurements on the absorber diluted samples or on highly damaged samples\(^{100}\).

Considering that XANES is a useful tool, several alternative approaches were proposed in recent years in this area to address problems in XANES. For the high \(Z\) elements whose deep core electrons are excited, the multiple expansion method still works with a satisfying convergence due to the short core-hole life time\(^{99}\). In other cases, an explicit matrix inversion is essential to solve the \((1 - G^0T)^{-1}G^0\) term mentioned in Section \(3.2.1\). This procedure is able to achieve a full order expansion but unfortunately it is very computationally demanding. Fast parallel Lanczos algorithms can be applied to speed up the calculations\(^{110}\). Some full potential approaches have been reported that are able to provide a more precise atomic potential, replacing the muffin-tin approximation\(^{97,99,110}\).

Despite the great efforts that have been made in the field, the theoretical interpretation of XANES is still less mature and satisfying than that of EXAFS. Precise simulations of the XANES spectral features are usually time-consuming and difficult to achieve. To obtain the sample structural properties, a fingerprinting and linear combination fitting of the spectrum with empirical standards are generally the most reliable and common methods, while in some cases theoretical standards are calculated to assist. To achieve a direct quantitative description of the theory like the one in the EXAFS region, further progress
of the XANES explanation in the future is needed.

3.3 Experimental aspects

Acquisition of high quality XAS data is dependent upon many factors, including a properly prepared sample, an intense X-ray beam with a variable monochromatized energy, a well designed experimental setup, etc. This section discusses the sample preparation procedures, the generation of X-rays by a synchrotron, the X-ray beam control within a beamline, and other details of the XAS measurements performed in this thesis.

3.3.1 Sample preparation

It is possible to perform an XAFS analysis on nearly any type of material, but that does not mean all samples work equally well or are equally easy to deal with [101]. The first prerequisite for a high signal-to-noise ratio XAS measurement is a sample preparation procedure that considers both the sample characteristics and the experimental conditions. Calvin [101] thoroughly reviews the preparation techniques for a variety of samples under different measurement environments. Bunker [97] also underlines the key points in the design of an XAS sample preparation method. In this section, we focus on XAS sample preparation for thin films.

As described in Section 2.2, the dopant atoms were implanted into thin films of the samples with bulk substrates. Since local structures around the implanted atoms are desired, the implanted atoms are the element of interest in the XAS experiment. Considering most samples are dilute (absorbing atoms $< \sim 1$ at. %), the fluorescence XAS measurement mode is employed instead of the more straightforward transmission mode (details will be given in Section 3.3.4). When using fluorescence XAS to investigate the samples, the bulk substrates generate a large amount of noise like fluorescence, diffracted and scattered X-rays, while only the low concentration absorbers within the thin films contribute the desired local environment related fluorescence signals. Therefore, stand-alone thin films are preferred for a fluorescence XAFS study, and a unique lift-off protocol was developed to isolate the thin films from the bulk substrates.

The lift-off method achieved an intact thin film separation from the bulk substrate. A schematic protocol for the ion implanted GOS sample is shown in Figure 3.5 (a). The Si substrate was thinned to 50 $\mu$m by mechanical grinding and completely removed after $\sim$ 48 hrs KOH etching at room temperature. The substrate removal procedure for the SOI sample was slightly different as demonstrated in Figure 3.5 (b). The Si thin film on the surface was firstly coated by black wax and then a HF etching process was followed until the SiO$_2$ layer in between was completely removed. The isolated Ge thin film, or the Si thin film after a TCE (Trichloroethylene) rinse, was stacked into multiple layers before mounting on a sample holder with two kapton windows. The stacked isolated thin films is
able to enhance the signal-to-noise ratio in the measurement. This approach is generally based on the work of Decoster et al., who presented EXAFS data quality improvements by using these lift-off protocols, and showed that the similar selective etching method can be utilized on the preparation of other types of thin films [111].

Figure 3.5: Schematic representation of the lift-off procedure for thin films of crystalline (a) Ge and (b) Si [111].

An alternative substrate removal protocol was developed for the SOI sample in this thesis. After a 1 µm thick SiO₂ layer was deposited on the sample surface by PECVD, the same mechanical grinding and KOH etching procedures as for the GOS samples were applied for the Si thin film separation. This new method avoided the long HF etching time (up to a few days) and reduced the possibility of the thin film being attacked by HF.
when the dopant concentration is high. Both methods were used in this thesis to prepare the SOI samples and the difference between the resulting data was not obvious. For the preparation of the Si$_{1-x}$Ge$_x$ sample, the procedure of a SiO$_2$ layer deposition with a KOH etching of the substrate Si was carried out for its thin film isolation. The sample mounting and stacking processes were the same as for the other two types of samples.

### 3.3.2 Synchrotron radiation

Synchrotron radiation sources are the preferred sources of X-rays for XAS experiments, since the measurement requires an intense X-ray beam (on an order of $10^{10}$ photons per second) to obtain the data in a reasonable time frame, as well as a continuous X-ray energy spectrum [97]. The XAS measurements in this thesis were hence performed at the Australian Synchrotron, which is a third-generation synchrotron light source designed as sketched in Figure 3.6.

![Design of a modern synchrotron facility](image)

Figure 3.6: Design of a modern synchrotron facility [112].

At the Australian Synchrotron [112], electrons are produced in bunches every two nanoseconds by a thermal tungsten matrix cathode operating at 500 MHz. The linear accelerator charges the generated electrons to 100 MeV over 10 meters, whose velocities are already higher than 99.99% the speed of light. The electron beam potential is further increased to 3 GeV in the 130 meter long circular booster ring, by means of synchronously ramping the strength of both the magnetic and the electric fields. The storage ring is the final destination for the accelerated electrons, which is 216 meters in circumference and holds a 200 mA current with a beam lifetime over 20 hours. The electrons are forced to travel inside the ring by a series of powerful bending magnets, and complete over one million laps per second. Intensive electromagnetic radiation is thereby created by the almost light-speed circulating electrons, with a continuous energy spectrum over a wide range of wavelengths (from infrared to hard X-rays). The radiation serves as a light source for the individual experiments.

The generated synchrotron light is usually optimized for different beamlines via the “insertion devices” that are placed in the long straight sections incorporated into the
3.3. Experimental aspects

storage ring. The device can be a wiggler or a undulator that uses alternating magnetic fields to create a strong or gentle oscillation of the electron beam, respectively. The former emits a broad but intense beam of incoherent light at a continuous energy extended to a very high X-ray energy region, while the latter creates a narrow beam of coherent radiation at a certain energy but whose intensity can be amplified by up to $10^4$ times. Individual beamlines are positioned to capture the synchrotron radiation given off by the storage ring, and perform a fine tuning of the light beam using filters, monochromators and mirrors etc [112]. The experiments are conducted at the end sections of each beamline with their own customized facilities. Employing the delivered and specified synchrotron light, imaging, scattering, absorption and other research techniques can be carried out.

3.3.3 XAS beamline setup

An XAFS study of a sample not only requires the X-ray beam to be intense, but also to be able to scan a range of energy refined to a narrow bandwidth ($\sim 1$ eV) to resolve the XAFS features with high stability and accuracy [97]. In this thesis, these demands were reached by the XAS beamline at the Australian Synchrotron.

Figure 3.7: Components of the XAS beamline in the Australian Synchrotron [113].

A schematic setup of the XAS beamline is illustrated in Figure 3.7. The beam of light is transfered to the beamline by a wiggler from the storage ring, so it is broad with a wide range of wavelengths. The double crystal monochromator in the middle of the figure is thus the key component, which selects the desired X-ray energy within a narrow band from the incident broad beam using the criterion of Bragg diffraction, $n\lambda = 2dsin\theta$ [99]. Here $n$ is an integer, $\lambda$ denotes the X-ray wavelength, $d$ stands for the lattice spacing of the diffracting crystal and $\theta$ represents the angle under which the beam is incident on the crystal [99]. The incident photons that have wavelengths meeting the Bragg condition are
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diffracted by the first crystal, including the X-rays with the desired energy \( (n = 1, \text{ the fundamental}) \) and the harmonics \( (n \geq 2) \). The removal of the harmonic contamination is achieved by a harmonic rejection system in the XAS beamline. The optimal X-ray energy range and the energy resolution are crystal lattice spacing dependent. Si (311) oriented crystal sets were employed in this thesis, providing an available X-ray energy region from 5.5 to 37 keV with a resolution of \( \Delta E / E \) up to \( 4 \times 10^{-5} \) \[113]. The radiation other than that diffracted are absorbed by the monochromator, so the device is cooled by liquid nitrogen to remove the generated heat. The beamline is also composed of two sets of mirrors for beam collimation and focusing and two sets of slits for beam size defining, on each side of the monochromator, as well as shutters and other optics for the radiation control. With such an arrangement, a highly monochromatic X-ray beam with a variable energy is delivered to the experimental station for the absorption coefficient measurements.

3.3.4 Experimental setup - fluorescence mode

XAS spectrum is normally measured in three modes: transmission, fluorescence or electron yield. The transmission mode is the most straightforward among the three. It simply detects the X-ray flux of the beam using ion chambers, both before \( (I_0) \) and after \( (I_t) \) it passes through the sample. \( I_0 \) and \( I_t \) thereby have a common energy \( (E) \) dependence, the absorption coefficient \( \mu(E) \) can be easily calculated by Equation 3.1. However, this measurement mode requires the samples to be homogeneous and have a constant thickness. And most important of all, the absorbing elements have to be concentrated enough such that the difference between \( I_0 \) and \( I_t \) is significantly larger than the variation due to counting statistics \[99\].

Figure 3.8: Decay of the excited state: X-ray fluorescence (left) and Auger effect (right) \[100\].

Dilute or non-homogeneous samples can be investigated in either the fluorescence or
the electron yield mode, where the emitted fluorescent X-rays or the emitted electrons due to X-ray absorption are detected respectively to calculate the $\mu(E)$ value. The emissions of both fluorescence X-rays and Auger electrons are caused by the decay of the core hole after its finite life time. The core hole is filled by an electron at the higher orbital within $\sim 10^{-15}$ seconds after the photoelectric event described in Section 3.1.1 occurs. The transition of the electron leads to two types of phenomena as sketched in Figure 3.8. In X-ray fluorescence, an X-ray with a well-defined energy is emitted, which is named according to the levels the electron transmits from and to. For example, a $K_\alpha$ fluorescence line is created by the electron that drops from the L to the K shell of an atom. In the Auger effect, a second electron is emitted into the continuum when the core hole is filled. Both of the effects are related to the X-ray absorption of the sample in some manner, thus the two corresponding XAS measurement modes, fluorescence and electron yield, are found. The likelihood of the two mechanisms to occur in a decay are energy dependent, X-ray fluorescence and Auger effect dominate the high ($> 3 \text{ keV}$) and low energy ($< 3 \text{ keV}$) regions, respectively [101].

Considering most of the samples in this thesis are dilute (absorbing atoms $< 1$ at. %) and the absorption edge selected in this thesis is In K-edge (27.94 keV [114]), the X-ray fluorescence mode was setup in the Australian synchrotron XAS beamline. Herein, we intuitively treat $\mu(E) \propto I_f/I_0$, where $I_f$ is the monitored intensity of a fluorescence line that is associated with the absorption process [100]. The actual calculation of $\mu(E)$ utilizing $I_f$ is certainly more complicated, details of which can be found in References [100] and [101].

In order to detect the X-ray fluorescence signal and measure the supplemental X-ray fluxes, the experimental section of the XAS beamline in Australian Synchrotron is configured as in Figure 3.9. All the components are in an interlocked and radiation-protected hutch, into which the monochromatic X-ray beam enters. The incoming X-ray intensity ($I_0$) is firstly measured by an ion chamber filled with Helium before interacting with the sample. The sample is mounted on a vibration minimized cryostat and maintained at a
temperature of 18 K to reduce thermal disorder, with a tilt of \(45^\circ\) respect to the incoming X-ray beam. When the X-ray beam hits the sample, the fluorescence yield is normally highest in a direction perpendicular to the incident beam, where the \(10 \times 10\) pixel-array Ge solid state detector is positioned. The flux of the transmitted radiation is detected in the second ion chamber, noted as \(I_1\), mainly used for sample alignment in the fluorescence mode. For the energy calibration in the subsequent data analysis, the XAS spectrum of the reference sample is simultaneously measured in a transmission mode utilizing the third ion chamber (with an X-ray intensity of \(I_2\)). In this thesis, a uniform In foil was the reference sample material used for the XAS measurements. Multiple scans (3 - 6 times) were carried out for each sample and averaged afterward to maximize the signal to noise ratio.

With an experimental setup as in Figure 3.9, the Ge fluorescence detector not only receives the characteristic X-ray signal but also a significant amount of noise:

1. a peak due to the elastic scattering of the incident X-ray beam with the sample,
2. a Compton (inelastic) scattered radiation from the weakly bound electrons,
3. \(K_\alpha, K_\beta, L_\alpha, L_\beta\) etc. lines from all the elements with edges below the incident photon energy in the sample, kapton tape, sample substrate, contamination in the cryostat, etc.

Figure 3.10 shows a spectrum of the recorded X-ray intensity in an actual experiment, where the In \(K_\alpha\) fluorescent line is present together with large Compton and elastic scattered X-ray signals. The fluorescence X-rays from the atoms other than In are also visible in the low energy channels.

The sample preparation procedure described previously is for the purpose of reducing this noise, but in most cases, additional approaches are necessary to isolate the desired fluorescent line from the background. The Si or Ge solid state detectors have the advantage of being able to record a wide energy range X-ray fluorescence spectrum. The X-ray signals from individual origins can be identified and quantified as shown in Figure 3.10. With the detector resolution of \(\sim 200\) eV, a region of interest can be set on the fluorescence spectrum to isolate the desired fluorescence signal (e.g. the In \(K_\alpha\) in Figure 3.10) from the background. One of the drawbacks of this type of detector is that determining the energy of each photon takes the detector a finite amount of time, during which another X-ray hitting the detector is not registered as a separate X-ray. This “deadtime” effectively limits the count rate. It is common to couple independent detectors to form multiple-element detectors to improve the signal to noise ratio. The one in the XAS beamline of Australian Synchrotron, for instance, is a 100 element detector in a \(10 \times 10\) array.

This signal isolating approach is sufficient for samples with concentrated absorbers, but less so for the dilute sample whose region of interest is heavily contaminated by the tail of the Compton scattering signal, as in Figure 3.10. The situation can be improved by introducing a \(Z - 1\) or \(Z - 2\) filter between the sample and the detector, where \(Z\) is
the atomic number of the element under investigation. The filter preferentially absorbs the Compton and elastic peak and passes the desired florescence line. To avoid the re-radiation from the filter itself, a set of Soller slits is often placed behind the filter to block the secondary emissions \[100\]. In this thesis, a silver filter was used for low concentration samples.

![Emission Spectrum](image)

Figure 3.10: An emission spectrum of a highly diluted In doped in Si sample above the In K edge \[115\].

### 3.4 Data processing

Calibration and normalization of the XAS data are the prerequisites for a spectral comparison or a linear combination fit. Data reduction and transformation also play important roles in the subsequent EXAFS simulations. There are a number of ways to prepare the data before analysis, the selection of which depends on the individual sample and measurement. The following is a general data processing procedure for dilute samples in a fluorescence mode experiment, which was used in this thesis and carried out via the Athena code \[116\][117\] within the Ifffit package \[119\].
3.4.1 Data averaging

The first step of the procedure is to average the multiple XAS spectra recorded in the multiple element detector into one \( \mu(E) \) for each scan of the sample, de-selecting the obvious outliers in the meantime if one or a few of the element(s) in the detector did not function effectively. Spurious points occasionally exist in the data due to monochromator crystal defect(s), X-ray diffraction, electronic flaws or other unexpected reasons. A deglitching or truncation of the data is necessary in these cases. Energy calibration is achieved by selecting an energy point in the data as the standard edge energy, \( E_0 \). That energy point is defined by the \( E \) that gives a maximum value of the first derivative \( \mu(E) \), and is matched to \( E_0 \) by applying an energy shift to the data. Using this method, multiple numbers of spectra from repeated measurements for the same sample are aligned, before being merged into a single \( \mu(E) \). Figure 3.11 (a) demonstrates such a spectrum after merging six aligned spectra of one sample that are previously calibrated to \( E_0 \) as indicated at the absorption edge.

3.4.2 Normalization

After the preprocessing of the data, each sample has one averaged spectrum. At this stage the spectra cannot be directly compared with each other because of the effects of different sample thicknesses and concentrations. In order to make the \( \mu(E) \) value represent only the chemical and structural properties around the absorbers, a spectral normalization is essential. To that end, the pre-edge and post-edge regions are approximated by a linear and a quadratic function, respectively. With each region determined between two markers, Figure 3.11 (a) shows the fitting lines. The step height \( \Delta \mu_0 \) is then defined by the difference between the pre-edge and post-edge fitting values at \( E_0 \) as illustrated in Figure 3.11 (a). The spectrum is normalized after being subtracted by the pre-edge approximating function and divided by \( \Delta \mu_0 \). This leads to a spectrum as shown in Figure 3.11 (b), which has a zero pre-edge amplitude and a flattened structure above the absorption threshold oscillating around a value of 1. The spectral differences of the individual data on the pre-edge and post-edge slopes and the \( \mu \) scales are now removed. Herein, unless the data requires extra care like a correction for self-absorption when the sample is concentrated \[101\], its XANES region is fully prepared for analysis. Further manipulation is applied to EXAFS only.

3.4.3 Background subtraction

As discussed in Section 3.2.2, the EXAFS equation is presented as the fine structure contribution, \( \chi \). Thus, the absorption background \( \mu_0(E) \) is removed by subtracting the normalized spectrum with a spline function that approaches \( \mu(E) \) from the edge to the post-edge as drawn in Figure 3.11 (b). The resulting spectrum is \( \chi(E) \) as plotted in Figure 3.11 (c). After the photoelectron energy \( (E) \) is converted to the wavenumber \( (k) \) using Equation 3.10, the isolated \( \chi(k) \) is usually multiplied by a weighting factor \( k, k^2 \)
Figure 3.11: (a) The XAS spectrum for the 0.6 at. % In in Ge sample measured at the In K-edge with fitted pre-edge and post-edge lines, (b) the normalized $\mu(E)$ obtained from the one in (a), and (c) the fine structure isolated $\chi(E)$ after subtracting the data by the background function as shown in (b).
or $k^3$. This is necessary because the spectral oscillations decay with an increasing $k$ due to the $1/k$ and $e^{-k^2}$ terms in the EXAFS equation (Equation 3.17). A spectrum with a greater amplitude consistency can be obtained with a weighting factor, as shown in Figure 3.12 (a) in comparison with the one in Figure 3.11 (c). Depending on the individual XAFS spectrum and analysis approach, different $k$-weightings may be selected. The weighted $\chi(k)$ can already be used for fingerprinting the sample absorbers’ environment by comparing to known standards, and is able to be described by the EXAFS equation, but it is common to take an additional step in the data processing procedure as follows.

3.4.4 Fourier transformation

There is an important concept in the EXAFS equation that the lengths of a group of similar scattering paths can be approximated by a Gaussian distribution. We are able to visualize this distribution from an experimental spectrum by performing its Fourier transformation (FT), as plotted in Figure 3.12 (b). This procedure was firstly proposed by Sayers et al. [118], an explanation of which, in a simplified way, is that a FT of Equation 3.17 can be written as:

$$|\chi(R)| = S_o^2 \sum_i N_i f_i e^{-2R_i/\lambda} e^{\left(\frac{(R-R_i-\delta_i)^2}{2\sigma_i^2}\right)}$$

where $|\chi(R)|$ is the magnitude of FT of $k \cdot \chi(k)$, $R$ is half of the scattering distance, whose mean value and standard deviation for each group under index $i$ are $R_i$ and $\sigma_i$ respectively, and $\delta_i$ accounts for all the phase shifts. The rest of the terms retain the same meaning as in Equation 3.17 except a crucial assumption is made that $f_i(k)$, $\lambda(k)$ and $\delta_i(k)$ are not $k$ dependent, but are $f_i$, $\lambda$ and $\delta_i$ constants, respectively.

A considerable advantage of this step is that each scattering group $i$ produces a peak on $R$-space, which can be charcterized by a Gaussian-like term $e^{(R-R_i-\delta_i)^2/2\sigma_i^2}$ and an effective amplitude term $S_o^2 N_i f_i e^{-2R_i/\lambda}$, independently. When the difference in $R_i$ is large and $\sigma_i^2$ have small values, the peaks are distinguishable. $|\chi(R)|$ is approximately a radial distribution function if multiple scattering can be disregarded (which is weak in EXAFS anyway). $R$ is thereby often called the radial distance. In such a case, each peak can be identified as a distribution of the bond lengths between a shell of local neighboring atoms and the absorbing atom.

After applying a smooth Hanning window to select a finite range of data on the isolated EXAFS spectrum in Figure 3.12 (a), Figure 3.12 (b) demonstrates the benefits of a FT. By fingerprinting the $|\chi(R)|$ of the sample to those of the In metal standard and a known sample with substitutional In atoms in a Ge lattice, the sample spectrum shown in the figure is determined to be a combination of the two standards. The peaks in positions around 2 Å, 3.6 Å and 4.2 Å correspond to photoelectron scattering from the In atoms to their 1st, 2nd and 3rd nearest neighbors (NNs) of the Ge lattice, while the ones around
3.4. Data processing

Figure 3.12: (a) The fine structure as function of photoelectron wavenumber $\chi(k)$ with $k^2$ weighting, converted from Figure 3.11 (c), (b) the magnitude of FT of $k^2\chi(k)$ using the data and window plotted in (a), and (c) the real part of back-transformed data with the window drawn in (b).
2.6 Å and 3 Å are In-In bond-related. The actual bond lengths are not represented here in the R range because the correction of phase shift is not employed.

However, we must remember that the $k$-independent assumption made in Equation 3.19 never stands in reality. The $k$ dependence of the terms is complicated, and yields no simple analytical form of FT of EXAFS \[104]. Equation 3.19 is far from accurate enough to be used as a complete theoretical description; it is used for explanation convenience since it is presented in a simple Gaussian function form. Therefore, $|\chi(R)|$ differs from a radial distribution function. The mean value for each Gaussian distribution in $|\chi(R)|$ is affected by a complex phase shift function $\delta_i(k)$, and the amplitude involves the $k$-related $f_i(k)$ and $\lambda(k)$ terms, besides the other constants. Among them, $f_i(k)$ is responsible for the coordinating atomic species identification, which partially accounts for the strong photoelectron scattering signal from In-In bonds compared to that from the In-Ge bonds as shown in Figure 3.12 (b). Furthermore, different $k$-weights and window functions can be used in the FT, which makes $\chi(R)$ a more complicated function. Despite an analytical representation of $\chi(R)$ being difficult, a FT of an experimental spectrum is easy to achieve and is commonly applied on the data analysis, since it still represents the path length distributions in the R-range, similar to a radial distribution function.

A back-FT of $\chi(R)$ can be carried out to investigate the XAFS contribution from a single group of paths. With the isolation using a Hanning window as drawn in Figure 3.12 (b), the In-In bond-corresponding peak in radial distance is back-transformed. The real part of the result is plotted in Figure 3.12 (c). The spectrum is presented versus the photoelectron wavenumber as in the previous $k$-range and with the same $k$-weighting. To differentiate the two ranges, an alternative name, $q$-space, is usually given for the back-transformed spectrum.

### 3.5 Fittings and simulations

#### 3.5.1 EXAFS - path fitting

The path fitting method employed to study the EXAFS part of the data in this thesis was carried out with the *Artemis* program \[117] in the *Iffeffit* package \[119]. The analysis started with a model as the input, which consists of an absorbing atom and a cluster of surrounding scattering atoms. According to the species and positions of the atoms specified in the given model, the multiple scattering approach described in Section 3.2.1 was applied to generate a variety of single and multiple scattering paths. Paths of the same kind were rearranged into one group, whose effective scattering amplitude and phase shift were calculated by the *FEFF* code (version 8.4 for this thesis \[116,120\]), considering the degeneracy, photoelectron scattering distance, mean free paths and atomic potential etc. The series of scattering path groups were sorted afterward with respect to their half scattering path lengths, $Reff$. Table 3.1 lists all the scattering path groups with $Reff$ within
3.5. Fittings and simulations

5 Å of a model, and the degeneracy and the calculated effective scattering amplitude of each group.

The next step was to choose a combination of the predicted scattering paths to fit the experimental $|\chi(R)|$. The selection of paths is case dependent upon the system under investigation, quality of the data, aim of the study, etc. Generally speaking, the more paths used, the higher the fit accuracy that is able to be realized. However, that also requires a larger number of independent variables to be described, which leads to an increase of the uncertainties or even a breakdown of the fitting algorithm. Thanks to the finite length of the mean free path in EXAFS, the scattering amplitude converges towards zero after $Reff$ reaches a few Å, where the contributions of the paths are negligible. It is thereby justified to de-select the paths that are longer than a certain radial distance. Besides, the single scattering paths are usually more intense than the multiple ones of similar lengths, thus the former are often included while the latter are not essential in many cases unless they are intense.

Table 3.1: A list of single and multiple scattering paths for the model of one substitutional In atom in a crystalline Ge lattice, where the absorbing In atom and its first, second and third NNs Ge atoms are labeled as In$_0$, Ge$_1$, Ge$_2$ and Ge$_3$ respectively. In$_0$Ge$_1$In$_0$, for example, means the path that the photoelectron travels from atom In$_0$ to Ge$_1$ and returns to In$_0$. The properties of each scattering path group used in the fit are also tabulated, including the degeneracy (N), effective scattering amplitude (amp), mean half path length ($R = Reff + \Delta r$) and Debye-Waller factors (DWF).

<table>
<thead>
<tr>
<th>No.</th>
<th>Path</th>
<th>N</th>
<th>Amp</th>
<th>$R$ (Å)</th>
<th>DWF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>In$_0$Ge$_1$In$_0$</td>
<td>4</td>
<td>100</td>
<td>2.50 + $\Delta r_1$</td>
<td>$\sigma^2$</td>
</tr>
<tr>
<td>2</td>
<td>In$_0$Ge$_2$In$_0$</td>
<td>12</td>
<td>62</td>
<td>4.00 + $\Delta r_2$</td>
<td>$\sigma^2$</td>
</tr>
<tr>
<td>3</td>
<td>In$_0$Ge$_3$Ge$_1$In$_0$</td>
<td>12</td>
<td>3.2</td>
<td>4.45 + 1.87$\Delta r_1$</td>
<td>$2\sigma^2$</td>
</tr>
<tr>
<td>4</td>
<td>In$_0$Ge$_2$Ge$_1$In$_0$</td>
<td>24</td>
<td>16.6</td>
<td>4.45 + 0.33$\Delta r_1$ + 0.91$\Delta r_2$</td>
<td>$\sigma^2$</td>
</tr>
<tr>
<td>5</td>
<td>In$_0$Ge$_3$In$_0$</td>
<td>12</td>
<td>37.4</td>
<td>4.70 + $\Delta r_3$</td>
<td>$\sigma^2$</td>
</tr>
<tr>
<td>6</td>
<td>In$_0$Ge$_1$In$_0$Ge$_1$In$_0$</td>
<td>4</td>
<td>3.6</td>
<td>4.90 + 2$\Delta r_1$</td>
<td>$4\sigma^2$</td>
</tr>
<tr>
<td>7</td>
<td>In$_0$Ge$_1$Ge$_2$Ge$_1$In$_0$</td>
<td>12</td>
<td>2.7</td>
<td>4.90 + 0.67$\Delta r_1$ + 0.82$\Delta r_2$</td>
<td>$\sigma^2 + \sigma^2$</td>
</tr>
</tbody>
</table>

Since each peak in the experimental $|\chi(R)|$ represents the length distribution of a group of scattering paths in $R$-space, the distribution can be approximated using the cumulant expansion method explained in Section 3.2.2. A Gaussian distribution with $C_1 = R_i$, $C_2 = \sigma^2_i$ is an example here of such an approximation. A modification of the input model is carried out, assuming the path lengths of each of the chosen path groups is Gaussian distributed in $R$, which is characterized by a mean value of $R_i = Reff_i + \Delta r_i$ and a variance of $\sigma^2_i$. Here $\Delta r_i$ accounts for the difference between the $R_i$ used in the fit and the calculated $Reff_i$ from the input model. Table 3.1 demonstrates such an adjustment of the selected paths to simulate the actual path distributions.

When a least-squares fit to the experimental $|\chi(R)|$ is performed using the modeled path distribution of the selected path groups, $\Delta r_i$ and $\sigma^2_i$ are the structural variables to be refined in the fit. $S^2_0$ and $E_0$ (explained in Section 3.2.2) are commonly determined from the
spectral fitting process of the reference sample and kept constant for other samples with the same absorbing element. For samples with certain defects, \( N_i \) can be considered as a variable as well (e.g. a degeneracy of \( \sim N-1 \) instead of \( N \) is expected in a fit when a vacancy defect is a nearest neighbor to the absorber atom). These parameters can float freely, be restrained or be fixed to make the generated \( |\chi(R)| \) match the experimental data. This process is usually performed with multiple \( k \)-weights to minimize the correlation between the parameters \([99]\). A high quality fit (e.g. Figure 3.13) is indicated by a small R-factor (the relative error between the fit and the data, a value below 0.05 generally means a good fit \([117]\)). It also produces \( R_i, \sigma_i^2 \) and \( N_i \) values with small uncertainties, representing the sample absorbers’ local environmental information: the interatomic distances, disorders and coordination numbers, respectively.

In a fit of the data of a crystalline sample, the effective scattering amplitude of some multiple scattering paths can be relatively large due to their high \( N \) and must be taken into account (as shown in Table 3.1). It is not practical to have individual \( \Delta r_i \) and \( \sigma_i^2 \) variables for each multiple scattering path group, resulting in too many degrees of freedom in the fit. The problem can be resolved by approximating these values with the ones in the single scattering paths, utilizing the known geometrical location of the atoms of the input model \([121, 122]\). The multiple scattering path \( \text{In}_0\text{Ge}_1\text{Ge}_1\text{In}_0 \) in Table 3.1 for example, is a triangle trip that the photoelectron travels (from \( \text{In}_0 \) to the first \( \text{Ge}_1 \) and second \( \text{Ge}_1 \) and returns to the original \( \text{In}_0 \)) with two legs identical to the single scattering path \( \text{In}_0\text{Ge}_1\text{In}_0 \). Using the existing bond angles in the model, the \( \Delta r \) and \( \sigma^2 \) values of the path are approximated with a triangular function of \( R_1 \) and \( \sigma_1^2 \), respectively. The approximation results for the other multiple scattering paths of the model are shown in the same table.

Another variable number reduction approach is to assume the scattering path groups of similar lengths to have an identical \( \Delta r_i \) to \( \text{Reff}_i \) ratio, \( \alpha \), which makes \( R_i = \text{Reff}_i \times (1+\alpha) \). The first method was used on the data of all the investigated samples and the second one was applied to fit the reference spectra in this thesis.

When the absorber atoms of a sample are in more than one crystallographic surrounding, a linear combination fit utilizing the EXAFS contributions from each environment is necessary, as discussed in Section 3.2.2. One more parameter, \( f_j \), is introduced in the fitting process, denoting the fraction of absorbers in each environment under index \( j \). That leads to a final fitting spectrum \( |\chi(R)| = \sum_j |\chi_j(R)|f_j \), where \( f_j \) varies freely from 0 to 1 and \( \sum_j f_j = 1 \). With a window to define the region of interest in the fit, Figure 3.13 demonstrates the result of such a fit, which shows 63% of In absorbers are in an In metal environment while 27% are substitutional in the Ge lattice. \( f_j \) can also be used as a random fraction to account for the absorbers in highly disordered surroundings that make a negligible contribution to EXAFS, and in that case the amplitude of the fitting spectrum is reduced by a factor of \( f_j \) \([121]\).

The accuracy of the simulation is obviously dependent on two factors, one is the theoretical calculation, the other is the input model. The former is no longer a major problem
due to the progress made on the area in recent years [99]. The model dependence of the technique makes some pre-existing knowledge about the system under investigation become essential [99]. The knowledge can be experimentally obtained by analyzing the XAFS data itself (e.g. comparing it with the known standards) or conducting supplementary experiments such as RBS and TEM. Based on the structural understanding of the sample, the model can be built in different ways. In the case where the absorbers are the dopant atoms in the substitutional site of the substrate lattice, (as is the case with most of the samples in this thesis,) the model can be generated easily by substituting one of the substrate atoms in its bulk material with one absorber atom. Positions of the atoms in the original substrate lattice can be created by computer programs, like Atoms [123]. The model in Table 3.1 was generated in this way. This direct replacement of different species of atoms leads to incorrect bond lengths in the initial model. The floating parameters \( \Delta r_i \) are adjusted to account for that in the fit and provide the corrected interatomic distances afterward. This advantage exists when the difference between the actual \( R_i \) and the modeled \( \text{Reff}_i \) is not significant, so the required range of variation of \( \Delta r_i \) is affordable by the fitting algorithm. The fit may not be able to work equally well when the local environment is defective or involves another one or more dopant atom(s). This issue can be addressed by performing a structural relaxation of the model before it is input to the fit, which provides \( \text{Reff}_i \) values closer to the actual \( R_i \) values. Using this method, a comparison can also be carried out between the theoretically relaxed structure and the EXAFS fitted structure, which achieves a more convincing result. In this thesis, the path fittings of the data of the C + In co-implanted samples as well as the implanted SiGe samples
took advantage of using input models whose geometries were optimized with the *ab initio* modeling technique described in Section 2.7.

### 3.5.2 XANES

After the XAS measurement data is calibrated and normalized, its near edge region can be extracted for analysis (as in Figure 3.14). Comparing the XANES spectrum of the sample with the known standards already yields some qualitative assessment of the chemical and structural environment of the absorbing atoms, provided that the spectra of the standards are sufficiently different from each other [99]. For instance, it is reasonable to predict that the data in Figure 3.14 contains an In metal XANES spectral fraction and certain contributions from the In atoms in the substitutional sites of the Ge lattice, by comparing its oscillation features with those of the standards. The linear combination fit method introduced before is employed here to quantify the fractions of absorbing atoms in each environment, with \( \mu(E) = \sum_{j} \mu_j(E)f_j \). Here \( f_j \) is the fraction of contribution from the standard spectrum \( \mu_j(E) \) used to fit the experimental data. By minimizing the difference between the linear combined spectrum and the measured spectrum, the \( f_j \) values are approximated. A precise fit to the data is shown in Figure 3.14 using this approach with the fraction values calculated.

![Figure 3.14: A linear combination fit of the XANES data of the 0.6 at. % In doped Ge sample, using the spectra of an In metal standard and an In atom in substitutional site of Ge lattice (In subs Ge) standard simulated in the FEFF code.](image-url)
The quality of this analysis is significantly dependent on the standards. First of all, the standards must not be similar to each other. Furthermore, only a limited number of standards are needed to be considered in a fit, which again requires some pre-existing knowledge about the investigated system. Last but not least, the sources of the standard spectra are crucial, the understanding of the sample is totally based on that of the standards. The standard spectra can be obtained either experimentally or via simulations. Generally, the XAS measurement data of the reference samples and the well-studied absorber local environment samples serve as the high quality standards. When these spectra are not available or the sample of interest has a more complex structure surrounding the absorbing atoms due to disorder or other reasons, the standard spectra need to be simulated.

The simulation of XANES is more complicated than that of EXAFS. This thesis employed the FEFF 9 \cite{124,125} code to perform an \textit{ab initio} XANES calculation. Similar to the simulation process of the EXAFS region above, the first step was to input a model containing a specified absorbing atom and some surrounding scattering atoms. A full multiple scattering calculation was then carried out for all the scattering paths within a radius up to 10 Å depending on the convergence of the result of the particular model. The calculation was based on the muffin-tin approximation of the atomic potential that was obtained from the self-consistent calculation using the Hedin Lundqvist exchange function \cite{126}. Figure 3.14 shows the simulated XANES spectra of the In metal model and the model of an In atom in a substitutional site of a Ge lattice. Since the muffin-tin approximation is not sufficiently accurate in some cases, as discussed in Section 3.2.3, a complementary XANES calculation was performed utilizing the finite difference method within the FDMNES program \cite{127}. The difference between the results from the two methods was minor in this thesis. The XANES calculations were thus mainly performed using the muffin-tin approximation as it is less computationally demanding.

The XANES simulations in both FEFF and FDMNES codes are model dependent, which leads to the same issue as in the EXAFS calculation above: it is essential to have some pre-existing knowledge about the local structural information of the sample absorbing atoms. The XANES simulation input model can be built in the same way as in the EXAFS simulation. However, since there is no $\Delta r$ variable in the XANES simulation as in an EXAFS fitting, the interatomic distance corrections need to be taken into account in the model before it is input into the calculation. As a consequence, the model development approach plays an even more important part here. In this thesis, all the generated models used for the XANES simulations were structurally relaxed beforehand, utilizing the DFT modeling technique described in Section 2.7.
In this chapter, we report on the effects of dopant concentration on the structural and electrical properties of In-implanted Ge. For In concentrations of $\leq 0.2$ at. %, XANES and EXAFS measurements demonstrate all In atoms occupy a substitutional lattice site while metallic In precipitates are apparent in transmission electron micrographs for In concentrations $\geq 0.6$ at. %. Evidence of the formation of In-vacancy complexes deduced from EXAFS measurements is complimented by DFT simulations. Hall effect measurements of the conductivity, carrier density and carrier mobility are then correlated with the substitutional In fraction. This chapter is based on our published work [128].

4.1 Introduction

As introduced in Chapter 1, Ge has increasingly important applications in the fabrication of semiconductor devices, due to a high hole mobility [129] and low dopant activation temperature in comparison with Si [130]. For this reason, Ge is likely to replace Si in future high-mobility complementary metal oxide semiconductor (CMOS) devices [131], where the channel of the $n$-type field-effect transistor (NFET) is based on InGaAs while that of the $p$-type field-effect transistor (PFET) is formed from Ge. It is noted that un-doped Ge naturally shows $p$-type conductivity, and this is related to Fermi level pinning at the surface [133].

The $p$-type dopants in Ge have element-specific advantages. The low intrinsic diffusion
of B in Ge is ideal for ultra-shallow junction formation \cite{134,135} while Ga exhibits a
very high solid solubility limit in Ge \cite{136}. Recently, In has been reconsidered as a p-type
dopant in Ge given it introduces a shallow acceptor level 0.0112 eV above the Ge valence
band \cite{137}. Given that the presence of dopants and disorder in a semiconductor lattice
influences the electrical properties of a device \cite{129}, a comprehensive understanding of
such influences calls for a detailed study, as presented herein, of In-doped Ge at both the
micro and macro scale.

Dopant diffusion and electrical defects in In-doped Ge have previously been inves-
tigated as a function of annealing conditions using secondary ion mass spectrometry
(SIMS) \cite{138} and deep level transient spectroscopy (DLTS) \cite{139}, respectively. The lat-
ter demonstrated that Ge point defects are not In-related and recover after annealing
at 600 °C. Previous studies have shown that most dopant species in Ge tend to occupy
substitutional lattice sites and most defect processes are mediated by vacancies (V) (since
interstitials (I) have significantly higher formation energy) \cite{138,140,141}. DFT calculations
were performed to predict the binding energy and migration enthalpies of different types
of In-vacancy (In$_{m}$V$_{n}$) clusters \cite{96,142}. Recent lattice-site location studies using the
emission channeling technique \cite{143} concluded that In preferentially occupies Ge bond-
centered sites before annealing for low In implantation fluences ($2.9 \times 10^{12}$ ions/cm$^2$)
as is consistent with earlier perturbed angular correlation spectroscopy (PAC) measure-
ments \cite{144,146} and DFT calculations \cite{147}. After annealing at 300 °C, In atoms then
redistribute to substitutional sites. For In concentrations in the range used for impurity
doping, complementary information about the local atomic environment around an In
atom, including coordination numbers, structural disorder and bond lengths, is lacking.
Such knowledge could enable one to correlate subtle changes in atomic environment to the
electrical properties as a function of In concentration.

In this thesis, we have used the synchrotron-based analytical techniques of XANES and
EXAFS to study the atomic-scale environment of In-doped Ge over a broad In concen-
tration range. Previously, XANES and EXAFS were utilized to investigate In complexes
in Si, demonstrating that In atoms were substitutional at low concentrations and pre-
cipitated at high concentrations \cite{148,149}. The current literature is lacking information
about In-doped Ge examined with XANES and EXAFS, which we address in this thesis.
Complementary measurements of the structural properties using TEM and Raman spec-
troscopy were also performed as were DFT calculations. Finally, the electrical properties
were characterized with Hall effect measurements to enable the correlation of structural
and electrical properties of In-doped Ge at concentrations appropriate for semiconductor
doping technologies.
4.2 EXAFS analysis

Isolated EXAFS spectra of the In doped Ge samples were Fourier-transformed over a k range of 2.2 - 11 Å\(^{-1}\) with an adaptive Hanning window and back FT over a non-phase-corrected radial distance R range of 1.6 - 4.65 Å (2.3 - 4 Å for the In standard) [150]. The experimental data were fitted using k-weights of 2, 3 and 4 simultaneously, with a complete multiple scattering analysis. The parameters used in the triple k-weight fit are listed in Table 4.1 while the spectra are plotted with k-weight of 2 in Figure 4.2 and 4.3.

Four different models were used to characterize the atomic-scale environment of implanted In atoms as shown schematically in Figure 4.1:

1. All In atoms occupying a substitutional lattice position in Ge;
2. All In atoms are in an environment of metallic In;
3. A combination of (1) and (2);
4. As per (3) but with the addition of a vacancy in the first shell surrounding an In atom in Ge.

![Structural models used in the EXAFS fitting showing (a) a substitutional In atom in a Ge lattice, (b) a metallic In (c) a substitutional In atom in a Ge lattice with a vacancy in the first nearest neighbor shell.](image)

Figure 4.1: Structural models used in the EXAFS fitting showing (a) a substitutional In atom in a Ge lattice, (b) a metallic In (c) a substitutional In atom in a Ge lattice with a vacancy in the first nearest neighbor shell.

The amplitude reduction factor \(S_0^2\) was determined for the In metal standard (0.7) and then fixed for the subsequent fitting of all spectra [150]. The energy shift parameter \(E_0\) was fixed to be 1.52 eV for model (1) and 2.15 eV for model (2), according to the fitting quality. For model (1), three different Debye-Waller Factors (DWFs) and bondlengths were used for the single scattering paths. DWFs and bondlengths of the multiple scattering paths were calculated from single scattering paths to reduce the number of variables (Section 3.4). Since the two main scattering paths of In metal are similar (3.245 and 3.370 Å),
Chapter 4. In doped Ge

analysis using model (2) floated all the bondlengths by multiplying the theoretical values by a factor \((1 + \alpha)\), \(R = R_{\text{eff}} \times (1 + \alpha)\) and a single DWF variable was used. Model (3) was achieved by combining the scattering amplitude of model (2) multiplied by a metal fraction \(f_m\) and model (1) multiplied by a substitutional fraction, \(1 - f_m\). Model (4) is the same as model (3) but with a reduced coordination number (CN) of the first shell surrounding an In atom in Ge.

Table 4.1: EXAFS fitting results as a function of In concentration and model. \(\alpha\) is the factor of difference between the calculated and theoretical In path lengths; \(\sigma^2_{\text{In}}\) is the DWF used in the fittings with model (2); \(r_1\), \(r_2\), \(r_3\) and \(\sigma^2_1\), \(\sigma^2_2\), \(\sigma^2_3\) are the radial distances to the first, second and third NNs and their corresponding DWFs, respectively; \(f_m(\%)\) is the In metal fraction and 1st NN CN\(_{\text{Ge}}\) is the coordination number of Ge surrounding In in the first shell; R-factor represents the fit quality; uncertainties on the least significant digit(s) of the values are given in brackets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Model</th>
<th>(\alpha) (%)</th>
<th>(\sigma^2_{\text{In}}) (Å(^2))</th>
<th>(r_1) (Å)</th>
<th>(r_2) (Å)</th>
<th>(r_3) (Å)</th>
<th>(\sigma^2_1) (Å(^2))</th>
<th>(\sigma^2_2) (Å(^2))</th>
<th>(\sigma^2_3) (Å(^2))</th>
<th>(f_m) (%)</th>
<th>1st NN CN(_{\text{Ge}})</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 at.%</td>
<td>1</td>
<td>—</td>
<td>2.558(2)</td>
<td>4.042(4)</td>
<td>4.683(8)</td>
<td>0.0032(3)</td>
<td>0.0041(4)</td>
<td>0.0064(9)</td>
<td>0</td>
<td>4</td>
<td>0.0093</td>
<td></td>
</tr>
<tr>
<td>0.06 at.%</td>
<td>1</td>
<td>—</td>
<td>2.559(2)</td>
<td>4.046(3)</td>
<td>4.685(7)</td>
<td>0.0034(2)</td>
<td>0.0046(4)</td>
<td>0.0071(9)</td>
<td>0</td>
<td>4</td>
<td>0.0078</td>
<td></td>
</tr>
<tr>
<td>0.2 at.%</td>
<td>1</td>
<td>—</td>
<td>2.563(1)</td>
<td>4.053(3)</td>
<td>4.689(7)</td>
<td>0.0036(2)</td>
<td>0.0051(3)</td>
<td>0.0074(7)</td>
<td>0</td>
<td>4</td>
<td>0.0055</td>
<td></td>
</tr>
<tr>
<td>0.2 at.%</td>
<td>3</td>
<td>-7.36(24)</td>
<td>0.0293(17)</td>
<td>2.565(1)</td>
<td>4.052(3)</td>
<td>4.690(5)</td>
<td>0.0026(1)</td>
<td>0.0043(3)</td>
<td>0.0067(7)</td>
<td>14(7)</td>
<td>4</td>
<td>0.0038</td>
</tr>
<tr>
<td>0.6 at.%</td>
<td>3</td>
<td>-2.15(12)</td>
<td>0.0052(5)</td>
<td>2.561(7)</td>
<td>4.037(9)</td>
<td>4.711(29)</td>
<td>0.0042(8)</td>
<td>0.0031(10)</td>
<td>0.0069(19)</td>
<td>72(7)</td>
<td>4</td>
<td>0.0188</td>
</tr>
<tr>
<td>0.6 at.%</td>
<td>4</td>
<td>-2.12(9)</td>
<td>0.0041(4)</td>
<td>2.561(5)</td>
<td>4.044(8)</td>
<td>4.712(14)</td>
<td>0.0036(5)</td>
<td>0.0055(8)</td>
<td>0.0071(13)</td>
<td>63(4)</td>
<td>3.1(4)</td>
<td>0.0118</td>
</tr>
<tr>
<td>1.2 at.%</td>
<td>3</td>
<td>-2.13(11)</td>
<td>0.0050(5)</td>
<td>2.561(14)</td>
<td>4.034(17)</td>
<td>4.759(36)</td>
<td>0.0044(12)</td>
<td>0.0027(15)</td>
<td>0.0047(25)</td>
<td>81(6)</td>
<td>4</td>
<td>0.0174</td>
</tr>
<tr>
<td>1.2 at.%</td>
<td>4</td>
<td>-2.13(9)</td>
<td>0.0041(3)</td>
<td>2.561(10)</td>
<td>4.033(12)</td>
<td>4.752(21)</td>
<td>0.0039(7)</td>
<td>0.0056(11)</td>
<td>0.0068(15)</td>
<td>72(5)</td>
<td>2.6(5)</td>
<td>0.0130</td>
</tr>
<tr>
<td>In foil</td>
<td>2</td>
<td>-0.46(6)</td>
<td>0.0040(2)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>100</td>
<td>—</td>
<td>0.0046</td>
</tr>
</tbody>
</table>

Figure 4.2 shows EXAFS spectra as a function of In concentration. The 0.02, 0.06 and 0.2 at. % samples share a similar EXAFS spectrum while the 0.6 and 1.2 at. % samples are comparable to the In standard. This implies In atoms have a common atomic environment for In concentrations \(\leq 0.2\) at. % and begin to precipitate to form metallic In for concentrations of \(> 0.6\) at. %. Fittings of the FT EXAFS spectra, as shown in Figure 4.3, confirm this argument. For samples with In concentration \(\leq 0.2\) at. %, In atoms occupy a four-fold coordinated substitutional site in a crystalline Ge matrix, consistent with model (1). For these three samples, the In-Ge nearest neighbor (NN) distances (Figure 4.4) increases with increasing In concentration. The surrounding Ge lattice expands by \(\sim 0.1\) and 0.05 Å at the first and second shells, respectively, due to the presence of substitutional In. The fitted DWFs (Figure 4.5) for these three samples also increase as a function of In concentration, indicative of increasing disorder. Fitting the 0.2 at. % sample spectrum with model (3) yielded no evidence of a two component system comprised of substitutional In and metallic In. A non-physical DWF (0.0293 Å\(^2\)) was obtained with a low metallic fraction \((f_m = 14\%).\)
4.2. EXAFS analysis

Figure 4.2: $k^2$-weighted EXAFS spectra as a function of photoelectron wavenumber for In concentrations of 0.02-1.2 at. %. Spectra are offset vertically for clarity. Dashed line shows the $k$-range window used for the data fitting.

Figure 4.3: FT EXAFS spectra as a function of radial distance for In concentrations of 0.02-1.2 at. %. Spectra are offset vertically for clarity. Dashed lines show the $R$-range windows used for the data fitting. Symbols represent the data while solid lines are best fits using model (1) for 0.02, 0.06 and 0.2 at. %, model (2) for the In standard and model (4) for 0.6 and 1.2 at. %.
For 0.6 and 1.2 at. % samples, the FT EXAFS spectra appear to be comprised of substitutional In and metallic In components. However, application of model (3) to the EXAFS analysis, where a substitutional In atom is four-fold coordinated with Ge atoms, yielded non-physical DWFs (relatively high for the first shell but unrealistically low for the 2nd and 3rd shells) (Figure 4.5). Given the DWF and CN are highly correlated and both influence the FT EXAFS magnitude, model (4) was invoked where the CN for In atoms in the non-metallic environment was floated such that CN \( \leq 4 \) atoms. The resulting R values were much improved, attesting to the higher validity of this model compared to that of model (3).

The fittings of 0.6 and 1.2 at. % samples with model (4) yielded metallic fractions of 63 and 72 %, respectively, with substitutional In atom CNs of 3.1 and 2.6 atoms, respectively. The dashed lines of Figure 4.5 demonstrate that the fitted DWFs for the non-metallic In component of these two samples with model (4) are, within experimental error, effectively constant as a function In concentration, as is the In-Ge NN distance, while the distances to second and third NNs (Figure 4.4) decrease and increase, respectively, at 0.6 at. % and beyond. We speculate that the reduced CN and reduced second NN distance are evidence of an In-V complex. Comparing the fitting of the metallic component to the In standard, the In-In NN distance in the former is reduced by 2 %. This implies that the In precipitates in the 0.6 and 1.2 at. % samples are compressed by the Ge matrix. The CN for the In precipitates and In standard were equal indicating that finite-size effects were negligible and thus the In precipitates must be of a significant size (>\(\sim\) 10 nm). The detailed EXAFS spectra-fitting results are listed in Table 4.1.
4.2. EXAFS analysis

Figure 4.4: Radial distances from the In atom to the first (circles), second (squares) and third (triangles) NN determined with EXAFS. For 0.02, 0.06 and 0.2 at. % samples, fitting results with model 1 are shown, for 0.6 and 1.2 at. % samples, fitting results with models 3 (open symbols) and 4 (solid symbols) are shown. Dashed lines are the NN radial distances in bulk Ge.

Figure 4.5: DWFs for the first (circles), second (squares) and third (triangles) NNs determined with EXAFS. For 0.02, 0.06 and 0.2 at. % samples, fitting results with model 1 are shown, for 0.6 and 1.2 at. % samples, fitting results with models 3 (open symbols) and 4 (solid symbols) are shown.
4.3 XANES analysis

The XANES spectra of the samples were normalized from 15 eV below to 55 eV above the In K-edge and are shown in Figure 4.6(a). As the In concentration increases, the absorption edges are shifted to lower energy, toward the metallic state, as expected. The XANES spectra of the 0.6 and 1.2 at. % samples exhibit an oscillation characteristic of In metal but with lower amplitude given the metallic In fraction in these samples is < 100 %. The XANES spectra for samples with lower In concentrations (0.02 - 0.2 at. %) are by comparison much smoother.

Ab-initio XANES calculations were performed using both FEFF9 and FEMNES codes for comparison with the experimental results. The simulated spectra of substitutional In in a Ge lattice, with and without vacancies, and In metal were normalized and aligned to the experimental spectra. The simulated spectra then served as standards to perform linear combination fitting (LCF) of the experimental results. A LCF was also performed with the ATHENA program using the experimental XANES spectra of the 0.02 at. % and In standard. The calculated In metal fractions are listed in Table 4.2. Figure 4.6(a) shows the experimental results are well described by the combination of substitutional In in Ge and In metal models, and the two simulation methods agree well. Figure 4.6(b) shows that the simulated XANES spectra are insensitive to the presence of a vacancy in the first NN shell surrounding a substitutional In atom. The variation from one simulation code to another (FEFF9 and FDMNES) is greater than the variation with and without a vacancy using one of the two given codes. As shown in Table 4.2, the calculated In metal fractions from the Athena LCF based on experimental spectra generally agree with the fitting based on simulated spectra from FDMNES and FEFF9 and also the results from EXAFS fitting.

Table 4.2: In metal fractions as a function of In concentration comparing results from experimental XANES (ATHENA), simulated XANES (FDMNES and FEFF9) and experimental EXAFS. The first NN shell surrounding an In atom is comprised of Ge atoms with the coordination number designated "1st NN CN_{Ge}". Uncertainties on the least significant digit of the values are given in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1st NN CN_{Ge}</th>
<th>Athena</th>
<th>FDMNES</th>
<th>FEFF9</th>
<th>EXAFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 at. %</td>
<td>4</td>
<td>0 %</td>
<td>0(3) %</td>
<td>0(2) %</td>
<td>0 %</td>
</tr>
<tr>
<td>0.06 at. %</td>
<td>4</td>
<td>0(2) %</td>
<td>0(1) %</td>
<td>3(1) %</td>
<td>0 %</td>
</tr>
<tr>
<td>0.2 at. %</td>
<td>4</td>
<td>15(1) %</td>
<td>11(1) %</td>
<td>16(1) %</td>
<td>0 %</td>
</tr>
<tr>
<td>0.6 at. %</td>
<td>4</td>
<td>62(2) %</td>
<td>61(3) %</td>
<td>61(2) %</td>
<td>72(7) %</td>
</tr>
<tr>
<td>0.6 at. %</td>
<td>3</td>
<td>—</td>
<td>59(2) %</td>
<td>60(3) %</td>
<td>63(4) %</td>
</tr>
<tr>
<td>1.2 at. %</td>
<td>4</td>
<td>70(1) %</td>
<td>69(3) %</td>
<td>70(1) %</td>
<td>81(6) %</td>
</tr>
<tr>
<td>1.2 at. %</td>
<td>3</td>
<td>—</td>
<td>66(2) %</td>
<td>67(3) %</td>
<td>72(5) %</td>
</tr>
</tbody>
</table>

\(^a\)The 1st NN CN_{Ge} value determined with EXAFS is 3.1 for this sample.

\(^b\)The 1st NN CN_{Ge} value determined with EXAFS is 2.6 for this sample.
4.3. XANES analysis

Figure 4.6: (a) XANES spectra (circles) and their best fits with FDMNES (dashed lines) and FEFF9 (dot dashed lines) using the LCF method. Metal fractions are listed in Table 4.2. The fittings of the 0.6 at. % and 1.2 at. % samples are based on In metal and In substitutional in Ge with 1st NNs coordination number of 3. (b) the comparison of simulated XANES spectra with coordination number of 3 and 4 in the In to Ge first NNs and the simulated XANES spectra from EXAFS modeling and DFT structure relaxation. All spectra were vertically offset for clarity.
Figure 4.6(b) shows that the XANES spectra simulated from the DFT relaxed structure are in good agreement with the structure from the models derived with EXAFS. The In-Ge NN distance calculated by DFT, with and without a vacancy, agrees with the EXAFS results, within 2% difference. The high quality of the XANES fitting also implies that the models are physically realistic. Other models such as two vacancies or an In atom in the first NN shell were also investigated with DFT but were not compatible with either the EXAFS or XANES results.

4.4 Supplementary results and discussion

Figure 4.7 shows the TEM images as a function of In concentration. No structural disorder or metallic In precipitates are observed at low In concentration (0.06 at. %) while precipitates are apparent for In concentrations of > 0.6 at. %. The precipitate density and size are greater for the 1.2 at. % sample. The crystalline nature of the precipitates is confirmed by the Moiré patterns formed as a result of the overlap of the In and Ge lattices. The TEM images thus confirm the synchrotron-based measurements showing that In precipitates at > 0.6 at. %. At these concentrations, line defects (dislocations) are also visible in the dark-field TEM image (inset in Figure 4.7 (b)).

Raman spectra were also recorded across the In concentration range, focusing on the Ge TO band. (Metallic In is not Raman active.) Figure 4.8 shows normalized Ge TO spectra fitted with Lorentzian functions. The spectra of the low concentration samples (0.02-0.2 at. %) are similar to bulk crystalline Ge while the high concentration samples (0.6 and 1.2 at. %) have much lower amplitude and are shifted to lower wavenumber. Figure 4.8 (b) and (c) show the Raman shift and FWHM. A significant change is observed between samples with In concentrations of 0.2 at. % and 0.6 at. % (without and with In precipitates). The shift to lower wavenumbers results from the Ge lattice expansion while the increase in FWHM (and decrease in peak height) results from increasing disorder. The Raman shift and FWHM both scale with the In concentration. We also note that no broad features from an amorphous component are observable.
Figure 4.7: Cross section TEM images for (a) 0.06 at. %, (b) 0.6 at. % and (c) 1.2 at. % samples. The inset in (b) is a dark field image while that in (c) shows a high resolution image of a metallic In precipitate.
Chapter 4. In doped Ge

Figure 4.8: (a) Raman spectra with data and fits shown as symbols and lines, respectively, (b) peak position shift and (c) FWHM (ratio of the data from the samples to a Ge wafer) as a function of In concentration.

Hall effect measurements are shown in Figure 4.9. All samples exhibited p-type conductivity and the sample geometry did not significantly influence the results. As the In concentration increases, the resistivity decreases while the carrier density increases as expected. The carrier mobility decreases as the In concentration increases due to the increase in both disorder and ionized impurity scattering. For high In concentrations (> 0.6 at. %), the In atom active fraction drops significantly. The increase in carrier density continues with increasing In concentration despite our observation of In precipitates in these samples. We would anticipate a saturation of the carrier density once the In concentration exceeds the solid solubility limit and In precipitates begin to form. This result may indicate that disorder in the Ge lattice can potentially enhance the carrier density, as proposed by Romano et al [151].

Figure 4.9: (a) Resistivity and (b) carrier density and Hall mobility as a function of In concentration where squares and circles represent square and clover leaf measurement geometries, respectively. The number under the carrier density is the ratio of active to total implanted In atoms (according to measurements on samples with clover leaf patterns).

Our results agree well with previous experiments performed by Decoster et al. [139, 143] for low fluence ($10^{12}$ In/cm$^2$) In-doped Ge samples implanted at room temperature.
Utilizing DLTS and emission channeling, they showed that defects in the Ge lattice were removed and In atoms occupied a substitutional lattice site after annealing above 500 °C. Rutherford backscattering spectrometry/channeling measurements also demonstrated that most In atoms occupied a substitutional lattice site after annealing in these low fluence samples. Finally, PAC experiments showed In atoms occupied substitutional lattice sites with perfect cubic symmetry after annealing at 600 °C.

Table 4.3: Calculated binding energies of a substitutional In atom and vacancy with the vacancy as either the first, second or third NN of an In atom. The binding energy difference (\(\Delta E\)) between a split (\(E_{\text{split}}\)) and a substitutional vacancy as the first NN (\(E_{\text{subs}}\)) is also shown.

<table>
<thead>
<tr>
<th></th>
<th>1st NN</th>
<th>2nd NN</th>
<th>3rd NN</th>
<th>(\Delta E = E_{\text{split}} - E_{\text{subs}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our calculation</td>
<td>-0.88</td>
<td>-0.74</td>
<td>0.22</td>
<td>-0.03</td>
</tr>
<tr>
<td>Chroneos</td>
<td>-0.96a</td>
<td>-0.16a</td>
<td>0.14a</td>
<td>0.01b</td>
</tr>
<tr>
<td>Höhler</td>
<td></td>
<td></td>
<td></td>
<td>-0.47c</td>
</tr>
</tbody>
</table>

\(a\) Reference [142].
\(b\) Reference [96].
\(c\) Reference [147].

Using DFT, we also calculated the binding energy of a substitutional In atom and a vacancy, with the vacancy as either the first, second or third NN of an In atom. Results are listed in Table 4.3 and agree well with earlier calculations from Chroneos et al [142]. The negative binding energy is indicative of greater stability when an In atom and vacancy are bound together compared to isolated In and vacancy. Our results, and those of Chroneos et al. [142], show that the binding energy increases when the vacancy is either a second or third NN, demonstrating that an In-V cluster is most stable with the vacancy as the first NN. This finding clearly supports our EXAFS results, where we presented evidence of such an In-V cluster.

Figure 4.10: Schematics of (a) a substitutional vacancy coordinating with an In atom and (b) a split vacancy coordinating with an In atom.

Another controversial issue about an In-V cluster is its lattice location in Ge. Höhler et al. [147] proposed that the configuration of two half-vacancies coordinating an In atom (a split vacancy, Figure 4.10 (b)) is more stable than that of a substitutional In-V cluster (a substitutional vacancy, Figure 4.10 (a)). The former had a binding energy 0.47 eV lower than the latter (Table 4.3). However, Chroneos et al. [96] reported that the binding energy
difference between the two was 0.01 eV, and hence the formation of the two structures are of an equal energetic preference. Our calculation provided a $\Delta E$ value of -0.03 eV, in agreement with that of Chroneos et al. [96]. Our EXAFS analysis showed no evidence of In bonding with six Ge atoms as the first NN (which split vacancy can lead to), and vacancies were found occupying substitutional sites as in Figure 4.10(a).

4.5 Summary

Our detailed investigation of the atomic-scale environment surrounding an In atom in In-implanted Ge has demonstrated that In atoms occupy a substitutional site at low concentrations and precipitate to form metallic In at high concentrations. In addition, EXAFS measurements yielded evidence of an In-V complex and this result was supported by complementary DFT calculations, showing that In-V pairing is energetically favorable. The synchrotron-based structural characterization was supplemented by TEM and Raman measurements which showed that lattice disorder increases with the implanted ion fluence or, equivalently, In concentration. Finally, electrical characterization demonstrated that lattice disorder may enhance the carrier density as suggested in previous reports [151].
\section{Summary}
Chapter 4. In doped Ge
Enhanced Electrical Activation in In-implanted Ge by C Co-doping

At high dopant concentrations in Ge, electrically activating all implanted dopants is a major obstacle in the fulfillment of high-performance Ge-channel CMOS devices. In this chapter, we demonstrate a significant increase in the electrically-active dopant fraction in In-implanted Ge by co-doping with the isovalent element C. Electrical measurements have been correlated with X-ray absorption spectroscopy, Raman spectroscopy and transmission electron microscopy results in addition to density functional theory simulations. With C + In co-doping, the electrically active fraction was doubled and tripled at In concentrations of 0.2 and 0.7 at. %, respectively. This dramatic improvement was the result of C-In pair formation such that In-induced strain in the Ge lattice was reduced while the precipitation of In and the formation of In-V clusters were both suppressed. This chapter is based on our published works [154,155].

5.1 Introduction

Source and drain regions in CMOS devices necessitate high dopant concentrations to reduce contact resistance and improve device performance [156]. Attaining a sufficient electrically-active dopant fraction is a substantial challenge at high dopant concentrations. In the first instance, the maximum electrically-active dopant fraction is limited by the solid solubility. As this threshold is approached, the formation of electrically-inactive dopant-atom clusters (D\textsubscript{n}) and/or dopant-vacancy complexes (D\textsubscript{n}V\textsubscript{m}) is triggered [135,157,160].
When the threshold is exceeded, dopants may also precipitate.

While Ge is considered a promising candidate to replace Si in future high-mobility CMOS devices [131, 132], the low solid solubility of dopants in Ge is a major obstacle [161]. In has attracted recent interest as a potential p-type dopant in Ge due to a low activation energy of 0.0112 eV [138, 139, 143]. In the last chapter, we reported a decrease in the electrically-active dopant fraction for In concentrations > 0.2 at. % as a result of the formation of electrically-inactive In metal precipitates and In-V clusters [128] as is consistent with earlier density functional theory (DFT) calculations [96, 142]. The solid solubility of In in Ge was found to be between 0.2 and 0.6 at. % at a maximum annealing temperature of 550 °C [128], yet the source and drain regions in future CMOS device require dopant concentrations above 1 at. % [156]. To meet a more aggressive electrical activation target at advanced device dimensions, an above-equilibrium, metastable solid solubility limit for In in Ge is required [156]. To this end, several methods to enhance the electrically-active dopant fraction have been considered: rapid thermal annealing [162], excimer laser annealing [163] and flash annealing [164] have all been successfully utilized to achieve an electrically-active B concentration in Ge in excess of the solid solubility limit, as has preamorphization followed by solid phase epitaxy [161, 165]. An important alternative is co-doping including double donor doping [166] and F co-doping [167], both of which were beneficial for n-type dopant activation in Ge. Chronos [168] recently reviewed co-doping strategies for Ge, concluding that co-doping (with double donors, F or isovalent atoms) is advantageous for controlling the vacancy (V) concentration. As above, this point defect is a key component of the electrically-inactive dopant cluster D\textsubscript{n}V\textsubscript{m}.

As an isovalent element to Ge, C is a promising option for co-doping with In. C + In co-doping in Si has been previously studied with both experiment and simulation: Rutherford backscattering spectroscopy (RBS) [169], spreading resistance profiling [170], x-ray absorption spectroscopy (XAS) [148, 149] and DFT calculations [171, 172] demonstrated that C and In atoms have a preference for pairing such that In precipitation was suppressed and high electrically-active dopant fractions were achieved. Intuitively, a similar effect can be anticipated in Ge. Supporting evidence includes perturbed angular correlation (PAC) [173] measurements that indicated 34% of In probes paired with C atoms on substitutional sites after 600 °C annealing (which has been attributed to strain compensation between undersized C atoms and oversized In atoms [173]), and recent DFT calculations that C-In pair formation in Ge was energetically favorable (with a binding energy of -0.46 eV) [174].

In this chapter, we correlate electrical and structural measurements in C + In co-doped Ge to not only demonstrate C-In pairing but to identify the mechanisms by which a three-fold enhancement of electrically-active dopant fraction has been obtained. We also examine a range of C and In concentrations, the latter at device-appropriate levels, to establish the concentration-dependent effectiveness of this approach. A direct comparison of the measurement results between In doped Ge in the last chapter and C + In doped Ge in this chapter are provided.
5.2. Detail of XAS fitting

Isolated EXAFS spectra (see Figure 5.2 (b) later) of the C + In doped Ge samples were Fourier-transformed over a k range of 2.2 - 11 Å$^{-1}$ with an adaptive Hanning window and back FT over a non-phase-corrected radial distance R range of 1.5 - 4.65 Å (2.3 - 4 Å for the In standard, Figure 5.2 (d)). The experimental data were fitted using k-weights of 2, 3 and 4 simultaneously with parameters listed in Table 5.1. The comparison spectra of In doped Ge samples (from Chapter 4) are shown later in Figure 5.2 (a) and (c). Two models were involved in the fits of the C + In doped Ge EXAFS spectra after DFT geometry optimization:

1. All In atoms occupying a substitutional lattice position in Ge;
2. All In atoms occupying a substitutional lattice position in Ge and paired with C as first nearest neighbor (NN);

The fitting detail of model (1) was given in the last chapter. The structural relaxation of model (2) showed that the second and third shells of Ge were separated into 3 sub-shells each as shown in Table 5.1. To reduce the number of variables, the three sub-shells share one DWF and one ΔR (bond length difference between the EXAFS fits and the DFT relaxed input model) values. The coordination number (CN) of C to In was floated in the fit, considering not all In atoms formed pairs with C. The CNs of Ge to In were calculated accordingly using the geometry relations between C and Ge atoms with the following equations, as in Table 5.1:

\[
CN_{\text{In-Ge}_1} = 4 - CN_{\text{In-C}_1}
\]  
(5.1)

\[
CN_{\text{In-Ge}_2-1} = CN_{\text{In-Ge}_2-3} = 3 \times CN_{\text{In-C}_1}
\]  
(5.2)

\[
CN_{\text{In-Ge}_2-2} = 12 - CN_{\text{In-Ge}_2-1} - CN_{\text{In-Ge}_2-3}
\]  
(5.3)

\[
CN_{\text{In-Ge}_3-2} = CN_{\text{In-Ge}_3-3} = 3 \times CN_{\text{In-C}_1}
\]  
(5.4)

\[
CN_{\text{In-Ge}_3-1} = 12 - CN_{\text{In-Ge}_3-2} - CN_{\text{In-Ge}_3-3}
\]  
(5.5)

where $CN_{\text{In-Ge}_m-n}$ means the coordination number of the mth NN Ge to In in the nth sub-shell.

The amplitude reduction factor $S_0^2$ was determined for the In metal standard (0.7) and then fixed for the subsequent fitting of all spectra [150]. The energy shift parameter (E$_0$) was fixed to be 1.52 eV for model (1) and 4.31 eV for model (2), according to the fitting quality.

Linear combination fits (LCF) of the XANES spectra were performed using the experimental data of the lowest concentration sample and that of the In standard, as in Figure 5.3 (shown later).
In 3 sub-shells each, the parameters are labeled 1, 2, 3. CN

The scattering path. Since the second and third shells of Ge neighbors were separated into

R

coordination number of the second NN Ge to In in the first sub-shell.

Ge). CN

subs Ge) and In and C in substitutional sites of the Ge lattice as the 1st NN ( C + In subs

Table 5.1: EXAFS fitting variables for samples of different In/C concentrations and DFT

calculation results on models with one In atom in a substitutional site of the Ge lattice (In

sub Ge) and In and C in substitutional sites of the Ge lattice as the 1st NN ( C + In subs

Ge). CN

of the first, second and third nearest Ge neighbors to the substitutional In and their corresponding DWFs, respectively; CN

In-C

1

and σ

In-C

1

are the coordination number and distance of C to In and the DWF of

the scattering path. Since the second and third shells of Ge neighbors were separated into

3 sub-shells each, the parameters are labeled 1, 2, 3. CN

In-Ge

2

− 1, for example, means the coordination number of the second NN Ge to In in the first sub-shell.

<table>
<thead>
<tr>
<th>Sample Parameters</th>
<th>0.07 at.% DFT (In subs Ge) EXAFS</th>
<th>0.2 at.% EXAFS</th>
<th>0.65 at.% EXAFS</th>
<th>1.3 at.% EXAFS</th>
<th>DFT (C + In subs Ge)</th>
</tr>
</thead>
</table>
| R

In-C

1

(A) | — | — | 2.04±0.06 | 2.02±0.06 | 2.02±0.07 | 2.08 |
| CN

In-C

1

| — | — | × 0.35±0.17 | × 0.55±0.11 | × 1.29±0.11 | × 1 |
| σ

In-C

1

(A) | — | — | 0.0046±0.0013 | 0.0042±0.0015 | 0.004±0.0009 | — |
| R

In-Ge

2

(A) | 2.56±0.002 | 2.61 | 2.60±0.002 | 2.59±0.002 | 2.59±0.004 | 2.63 |
| CN

In-Ge

2

| × 4 | × 4 | × 3.65±0.17 | × 3.45±0.11 | × 2.71±0.11 | × 3 |
| σ

In-Ge

2

(A) | 0.0033±0.0003 | — | 0.0035±0.0004 | 0.0038±0.0004 | 0.0042±0.0005 | — |
| R

In-Ge

2

− 1(A) | 4.05±0.004 | 4.12 | 3.48±0.005 | 3.48±0.008 | 3.46±0.006 | 3.51 |
| CN

In-Ge

2

− 1 | × 12 | × 12 | × 1.05±0.51 | × 1.65±0.33 | × 3.87±0.33 | × 3 |
| R

In-Ge

2

− 2(A) | 4.08±0.005 | 4.08±0.008 | 4.05±0.006 | 4.10 |
| CN

In-Ge

2

− 2 | × 9.9±1.02 | × 8.7±0.66 | × 4.26±0.66 | × 6 |
| R

In-Ge

2

− 3(A) | 4.36±0.005 | 4.36±0.008 | 4.34±0.006 | 4.38 |
| CN

In-Ge

2

− 3 | × 1.05±0.51 | × 1.65±0.33 | × 3.87±0.33 | × 3 |
| σ

In-Ge

2

(A) | 0.0042±0.0005 | — | 0.0049±0.0008 | 0.0055±0.0006 | 0.0063±0.001 | — |
| R

In-Ge

2

− 1(A) | 4.68±0.009 | 4.80 | 4.42±0.007 | 4.40±0.012 | 4.38±0.02 | 4.45 |
| CN

In-Ge

2

− 1 | × 12 | × 12 | × 9.9±1.02 | × 8.7±0.66 | × 4.26±0.66 | × 6 |
| R

In-Ge

2

− 2(A) | 4.79±0.007 | 4.78±0.012 | 4.75±0.02 | 4.82 |
| CN

In-Ge

2

− 2 | × 1.05±0.51 | × 1.65±0.33 | × 3.87±0.33 | × 3 |
| R

In-Ge

2

− 3(A) | 5.06±0.007 | 5.04±0.012 | 5.02±0.02 | 5.09 |
| CN

In-Ge

2

− 3 | × 1.05±0.51 | × 1.65±0.33 | × 3.87±0.33 | × 3 |
| σ

In-Ge

2

(A) | 0.0067±0.0009 | — | 0.0073±0.0009 | 0.0077±0.0001 | 0.0094±0.0002 | — |
5.3 C-In pairing not found at low concentration (∼0.06 at. %)

Figure 5.1 compares the resistivity, carrier density and carrier mobility of In and C + In implanted Ge samples as a function of In concentration. All samples exhibited p-type conductivity. At low In concentrations (∼0.06 at. %), the effect of co-doping was negligible with the vast majority of In atoms electrically active either with (80.6 % In active) or without C present (84.9 % In active). The EXAFS spectra in both k and R range (Figure 5.2) implied that the two samples have the same In lattice locations, and this is consistent with the XANES spectra in Figure 5.3. The FT spectrum of the co-doped sample was fitted with model (1), with the fitting parameters in Table 5.1. A good agreement was reached between the In-Ge bondlengths calculated from DFT and those obtained from the EXAFS fit. The XAS analysis result in Table 5.2 shows that In atoms occupied substitutional lattice sites and were four-fold coordinated with Ge atoms, with or without C present, thus corroborating with the electrical measurements. Clearly the low concentration (∼0.06 at. %) of both C and In atoms yielded a low probability for C-In pair formation. Also, no evidence of electrically-inactive configurations (In metal precipitates or In-V clusters) was apparent with XAS. Finally, the TEM images of Figures 5.4 (a) and (d), In and C + In co-doped samples, respectively, show no significant differences in structural disorder. The difference in Ge lattice strain and disorder levels is also not obvious for the singly doped and co-doped samples, as the Raman spectra show in Figure 5.5.

Table 5.2: The In metal fraction and coordination numbers of the 1st nearest neighbor Ge and C to In (CN_{Ge} and CN_{C}, respectively) of the In doped Ge and C + In doped Ge samples.

<table>
<thead>
<tr>
<th>In (and C) concentration (at. %)</th>
<th>In metal fraction (%)</th>
<th>CN_{Ge}</th>
<th>CN_{C}</th>
</tr>
</thead>
<tbody>
<tr>
<td>In doped Ge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>0</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>0.06</td>
<td>0</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>0</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>0.6</td>
<td>63 ± 4</td>
<td>3.1 ± 0.4</td>
<td>-</td>
</tr>
<tr>
<td>1.2</td>
<td>72 ± 5</td>
<td>2.6 ± 0.5</td>
<td>-</td>
</tr>
<tr>
<td>C + In doped Ge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.07</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>0.2</td>
<td>0</td>
<td>3.65 ± 0.17</td>
<td>0.35 ± 0.17</td>
</tr>
<tr>
<td>0.65</td>
<td>0</td>
<td>3.45 ± 0.11</td>
<td>0.55 ± 0.11</td>
</tr>
<tr>
<td>1.3</td>
<td>0</td>
<td>2.71 ± 0.11</td>
<td>1.29 ± 0.11</td>
</tr>
</tbody>
</table>
Figure 5.1: (a) Resistivity, (b) carrier density and (c) carrier mobility as a function of In concentration. Squares and circles represent In-doped Ge and C + In co-doped Ge, respectively. In panel (b), unbracketed and bracketed numbers are the electrically-active fractions for In-doped Ge and C + In co-doped Ge, respectively.
5.4 In activation enhanced by C-In pairing and strain compensation (at 0.2 at. %)

As Figure 5.1 demonstrates, the influence of co-doping was more significant at higher In concentrations. At 0.2 at. %, the carrier density of the C + In implanted sample doubled from the In implanted sample (activation ratio increased from 42.3 % to 85.9 %). While the carrier mobility decreased (by 30 %) as a result of increased lattice disorder and ionized impurity scattering, the resistivity was halved in the co-doped sample.

Evidence of C-In pairing was found in the DFT-guided EXAFS analysis of the 0.2 at. % co-doped sample. As demonstrated in Table 5.1, the DFT calculations showed that a substitutional C-In pair in Ge splits the Ge second and third shells (with distances of 4.05 and 4.68 Å, respectively) surrounding an In atom into six different shells (with distances of 3.51, 4.10, 4.38, 4.45, 4.82 and 5.09 Å). This increase of disorder surrounding an In atom was manifested as smearing of the second and third nearest neighbor peaks of the corresponding FT EXAFS spectrum (Figure 5.2(d)), compared to that without C (Figure 5.2(c)). Using model (2), a high quality fit to the EXAFS spectrum was obtained as in Figure 5.2(d). Note that not all In atoms were paired: on average, one In atom was coupled to 0.35 ± 0.07 C atoms as shown in Table 5.2, a result in agreement with earlier PAC measurements [173]. Small ∆R values were used in the fit (≤ 0.04 Å) as shown in Table 5.1 attesting to the high validity of this model. Our DFT calculations also supported the result by showing C-In pairing is energetically favorable in Ge, the binding energy of the cluster is -0.27 eV, in agreement with a previous DFT study (-0.46 eV) [174].

The C-In pairing-induced disorder enhancement in the second and third Ge shells did not have an apparent effect on the EXAFS spectra in k-range by comparing Figure 5.2(a) and (b), as well as on the XANES spectra as shown in Figure 5.3. The XANES spectra of three structurally-relaxed models were simulated with the FEFF9 code ( inset of Figure 5.3(b)), including: an In atom in a substitutional site of the Ge lattice (InGe3, model (1)), a C-In pair in substitutional sites of Ge lattice (InCGe3, model (2)) and a C atom in the bond center of In-Ge (InCGe4). The introduction of C did not affect the fine structure ossification feature significantly. Furthermore, XANES is insensitive to the presence of C and the disorder increase of the surrounding Ge atoms. The XANES spectrum of the 0.2 at. % C + In doped Ge sample was fitted with only the experimental data of the 0.06 at. % sample, since the In metal component was not detected. The enhanced Ge lattice disorder due to C co-doping was observed by Raman spectroscopy, as shown in Figure 5.3(d). A higher FWHM of the Ge Raman peak in the co-doped samples compared with the singly doped sample at this concentration (0.2 at. %).

At this concentration, we attribute the enhanced carrier density in the C + In implanted sample to strain compensation by C-In pairing and not the suppression of In precipitation or In-V cluster formation. This was further validated by (i) Raman Spectroscopy that indicated strain in the Ge lattice was reduced with C co-doping, Ge Raman
peak position shift decreased with the presence of C (Figure 5.5 (c)); and (ii) the XAS results for In-doped Ge without C, where the two electrically-inactive configurations were not apparent (Figure 5.2 (a) and (c), discussed in Chapter 4).

To verify that the enhancement of the carrier density is a result of C-In pairing but not simply induced by C implantation alone, test measurements were performed on C only implantation in Ge samples. According to Hall effect measurements (not shown), the electrical properties of Ge are independent of C doping (C concentration up to 1.2 at. %). The Raman spectroscopy results in Figure 5.5 also show that the effect on the Ge lattice from C only implantation is negligible.

Figure 5.2: $k^2$-weighted EXAFS spectra as a function of photoelectron wavenumber for (a) In-doped Ge and (b) C + In co-doped Ge. (c) and (d) are the Fourier-transformed EXAFS spectra of (a) and (b), respectively, as a function of radial distance. Symbols are data points and solid lines are best fits. Spectra are offset for clarity.
5.5 In activation enhancement by C-In pairing in suppression of formation of electrically-inactive configurations (at ∼ 0.6 at. %)

The greatest effect of C + In co-doping was observed at an In concentration of 0.6 at.%. Without C, the electrically-active dopant fraction was only 21% (Figure 5.1) as a result of the formation of electrically-inactive configurations (discussed in Chapter 4). For example, the corresponding EXAFS and XANES spectra (Figure 5.2 (a) (c) and Figure 5.3 (a), respectively) were dominated by a metallic In component (apparent upon comparison with the In metal standard). As shown in Table 5.2, 63% ± 4% of In atoms are in the metallic phase, those In atoms still in solution (the peak at a non-phase-corrected radial distance of ∼ 2 Å) were on average surrounded by 0.9 ± 0.4 vacancy (an In-V cluster) and 3.1 ± 0.4 Ge atoms. Metallic In precipitates were evident in the corresponding TEM image (Figure 5.4 (b)) while line defects (dislocations) were observable in the associated dark-field image (inset).

Figure 5.3: The XANES spectra (symbols) and their best fits (solid lines) using the LCF method of (a) In-doped Ge and (b) C + In co-doped Ge samples. The inset in (b) is the simulated XANES spectra from three DFT structurally-relaxed models, with 4 Ge atoms (InGe₄), 3 Ge atoms and 1 C atom (InCGe₃) as first NNs of In as well as a C atom in the bond center of In and Ge (InCGe₄).

At the similar concentration (0.65 at. %), C + In co-doping yielded a three-fold improvement in electrically-active fraction (∼ 63%, from Figure 5.1). The corresponding EXAFS spectra (Figure 5.2 (b) and (d)) remain similar to that of substitutional, four-fold coordinated In with no evidence of metallic In or In-V clusters. This result is consistent with the co-doping strategies proposed by Chroneos [168] that the V concentration can be controlled by isovalent element co-doping in Ge. This result was also supported by XANES, where no In metal-related fine structure was observed in Figure 5.3 (b), which
was confirmed by the LCF (In metal fraction not used). Note that no In precipitates were observed in the TEM image of Figure 5.4 (e), demonstrating the effectiveness of co-doping as a means of achieving an above-equilibrium solid solubility limit.

Figure 5.4: Cross-section TEM images for (a) 0.06 at. %, (b) 0.6 at. % and (c) 1.2 at. % In-doped Ge. The insets in (b) and (c) are a dark-field image and a high-resolution image of an In precipitate, respectively. Panels (d), (e) and (f) are comparable images for C + In co-doped Ge.

The smearing of the second and three peaks in the FT EXAFS spectrum (Figure 5.2 (d)) is again an indication of C-In pairing. Applying the same EXAFS analysis method (above) to the spectrum of this sample (0.65 at. % C + In doped Ge), we found that one In atom was on average paired with 0.55 ± 0.11 C atoms as shown in Table 5.2. The bondlengths from the EXAFS fit are also in good agreement with those from the DFT model (Table 5.1). For this sample (0.65 at. % C + In doped Ge), the three-fold enhancement of the electrically-active dopant fraction is mainly a result of C co-doping in suppressing the formation of In metal and In-V clusters, leading to a recovery of In atoms back to an electrical active, four-fold coordinated local environment.
5.6. In activation not enhanced due to the significant lattice disorder caused by high implant concentration (\(\sim 1.2\) at. %)

At the highest In concentration of 1.2 at. %, co-doping yielded no improvement to the electrical properties (Figure 5.1). The EXAFS and XANES spectra for In-doped Ge (Figure 5.2 (a) (c) and Figure 5.3 (a), respectively) were again dominated by the metallic component (discussed in Chapter 4). As shown in Table 5.2, 72\% \pm 5\% of In atoms are in the metallic phase. For C + In-doped Ge, the In metallic components of both EXAFS and XANES spectra (Figure 5.2 (b) (d) and Figure 5.3 (b), respectively) were clearly damped relative to lower In concentrations. For the co-doped sample (1.3 at. %), one In atom was paired with 1.29 \pm 0.11 C atoms as shown in Table 5.2. In precipitates were readily apparent in the TEM image of the sample without C (Figure 5.4 (c)), and the high-resolution image shown in the inset shows a metallic In precipitate. Amazingly, In precipitates were again not visible in the TEM image for the C + In co-doped sample.
Chapter 5. C + In doped Ge

(Figure 5.4 (f)), demonstrating the above-equilibrium solid-solubility limit in this sample was increased at least two-fold with C present. A fit of the C + In doped 1.3 at. % sample EXAFS spectrum with an additional In metal fraction was also tested, and yielded no evidence of a two component system (non-physical DWFs obtained). Hence, the metallic In amount is lower than the limit that is detectable by EXAFS.

The low amplitude of the EXAFS spectra of the 1.3 at. % co-doped sample in both k or R range (Figure 5.2 (b) and (d), respectively) indicated the high concentration implantations of both C and In ions caused significant lattice disorder. Quantitative confirmation of this increase in disorder is manifested by an increase in the DWFs as shown in Table 5.1. The Raman spectra in Figure 5.5 shown that, although C co-doping is able to realize strain compensation, it also led to a more dramatic disorder increase when the dopant concentration increases, in agreement with the DWFs. The high level of Ge lattice disorder was considered to be responsible for the poor electrical properties of this sample, given that electrically inactive clusters were not found.

5.7 Summary

In conclusion, we have characterized the electrical and structural properties of C + In co-doped Ge, demonstrating this approach can yield a significant three-fold increase in carrier density relative to a conventional dopant-only implantation protocol. We attribute the enhanced carrier density in the 0.2 at. % sample to strain compensation, and that in the 0.6 at. % sample to the suppression of In precipitation and In-V cluster formation. An above-equilibrium solid solubility limit for In in Ge was achieved. Our experimental identification of C-In pairing is in excellent agreement with theoretical predictions and demonstrates that co-doping with isovalent elements is an effective strategy for attaining the high electrically-active dopant fractions required for advanced devices.
5.7. Summary
Chapter 5. C + In doped Ge
In this chapter, we report on the effects of dopant concentration and substrate stoichiometry on the electrical and structural properties of In-implanted Si$_{1-x}$Ge$_x$ alloys. Correlating the fraction of electrically-active In atoms from Hall effect measurements with the In atomic environment determined by XAS, we observed the transition from electrically-active, substitutional In at low In concentration to electrically-inactive metallic In at high In concentration. The In solid-solubility limit has been quantified and was found to be dependent on the Si$_{1-x}$Ge$_x$ alloy stoichiometry. The solid-solubility limit increased as the Ge fraction increased. This result was consistent with DFT calculations of two In atoms in a Si$_{1-x}$Ge$_x$ supercell that demonstrated In-In pairing was energetically favorable for $x < \sim 0.7$ and energetically unfavorable for $x > \sim 0.7$. TEM imaging further complemented the results described above, with the In concentration and Si$_{1-x}$Ge$_x$ alloy stoichiometry dependencies readily visible. We have demonstrated that low resistivity values can be achieved with In implantation in Si$_{1-x}$Ge$_x$ alloys and this combination of dopant and substrate represents an effective doping protocol. This chapter is based on our published work \cite{175}.

6.1 Introduction

In is a promising p-type dopant in both Si \cite{171} and Ge \cite{143}, with substrate-specific advantages and disadvantages towards the application to CMOS devices. In Si substrates,
the low diffusion coefficient of In enables the formation of a super-steep retrograde channel profile (SSRCP) to boost device scaling [148,169,171], yet In has a low solid-solubility limit (0.0036 at.%) [176] and a deep acceptor level (0.150 eV above the valence band) [177]. In Ge substrates, device electrical performance can be significantly advanced. As discussed in Chapter 4, Ge has a superior carrier mobility [138], a higher In solid-solubility limit (>0.02 at.%) [128] and a shallower In acceptor level (0.0112 eV above the valence band) [137]. Relative to Si, the narrow bandgap of Ge can however yield higher off-state leakage due to band-to-band tunneling (BTBT) [178].

$\text{Si}_{1-x}\text{Ge}_x$ alloys have the potential to combine the positive aspects of Si and Ge substrates to produce a reasonably steep In profile with high electrical activation, and furthermore, relieve the BTBT problem in Ge. While the carrier mobility in $\text{Si}_{1-x}\text{Ge}_x$ decreases rapidly as the Si fraction increases, strain engineering in $\text{Si}_{1-x}\text{Ge}_x$ is regularly utilized to maintain a high carrier mobility [178,179]. To optimize the trade-off between In concentration and Ge fraction in In-doped $\text{Si}_{1-x}\text{Ge}_x$, a systematic study of the electrical activation/deactivation kinetics is thus necessary and forms the basis of this chapter.

For In-doped Si and Ge, as described in Chapter 4, earlier work has shown that In atoms were electrically active and located on substitutional lattice sites when the In concentration was below the solid-solubility limits [143,148]. The formation of electrically inactive In metal precipitates [128,171,176] and In-V pairs [96,128,142] (where V denotes a vacancy) was observed when these thresholds were exceeded. While the electrical and structural properties of In-doped Si and Ge have been studied, those of In-doped $\text{Si}_{1-x}\text{Ge}_x$ have yet to be reported. Hence, in this thesis we used Hall effect measurements to determine the electrical properties of In-doped $\text{Si}_{1-x}\text{Ge}_x$ which were then correlated with the structural properties determined by XAS and TEM. The dependencies on both In concentration (from 0.02 to 1.2 at. %) and $\text{Si}_{1-x}\text{Ge}_x$ stoichiometry ($x = 0, 0.65, 0.9$ and $1$) were investigated, with the aim to examine these effects at device-appropriate levels. We also used DFT to perform a theoretical study of In-In pairing as a function of $\text{Si}_{1-x}\text{Ge}_x$ stoichiometry and then correlated theoretical and experimental results.

### 6.2 Electrical properties of In-implanted $\text{Si}_{1-x}\text{Ge}_x$

Figure 6.1 shows results of the three measured electrical parameters; resistivity, carrier density and mobility; as a function of In concentration and $\text{Si}_{1-x}\text{Ge}_x$ stoichiometry. All samples exhibited $p$-type conductivity.

We first consider the In concentration dependence. In general, as the In concentration increased, the resistivity, carrier density and mobility decreased, increased and decreased, respectively, for each $\text{Si}_{1-x}\text{Ge}_x$ substrate (as anticipated). The exception is Si which we discuss below. The increased carrier density was simply the result of the increased In dopant concentration while the decreased mobility was due to the increased ionized impurity scattering. The trend in resistivity is determined by that of the carrier density and mobility,
where the first is inversely proportional to the product of the second and third. For the In-doped Si samples, the three electrical parameters saturated beyond an In concentration of 0.004 at. %, indicative that the solid-solubility limit had been exceeded (as confirmed below). For our annealing conditions, we thus estimate a solid-solubility limit for In in Si between 0.002 and 0.006 at. %, a result in excellent agreement with that of Solmi et al. [176] (0.0036 at. %). The electrically-active fraction of implanted In atoms is shown in Table 6.1 again as a function of In concentration and Si$_{1-x}$Ge$_x$ stoichiometry. Clearly the electrically-active fraction decreased as the In concentration increased. In addition to In atom precipitation, we will identify and discuss additional reasons for this deactivation of In atoms below.

Table 6.1: The electrically-active fraction of In atoms as a function of In concentration in different substrates.

<table>
<thead>
<tr>
<th></th>
<th>0.02 at. %</th>
<th>0.06 at. %</th>
<th>0.2 at. %</th>
<th>0.6 at. %</th>
<th>1.2 at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>In doped Si</td>
<td>1.9%</td>
<td>0.65%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In doped Si$<em>{0.35}$Ge$</em>{0.65}$</td>
<td>80.7%</td>
<td>60.1%</td>
<td>23.1%</td>
<td>9.1%</td>
<td></td>
</tr>
<tr>
<td>In doped Si$<em>{0.1}$Ge$</em>{0.9}$</td>
<td>100%</td>
<td>73.1%</td>
<td>35.1%</td>
<td>17.6%</td>
<td></td>
</tr>
<tr>
<td>In doped Ge</td>
<td>94.8%</td>
<td>84.9%</td>
<td>42.3%</td>
<td>21.0%</td>
<td>17.3%</td>
</tr>
</tbody>
</table>

We now consider the Si$_{1-x}$Ge$_x$ stoichiometry dependence. As the Ge fraction in the Si$_{1-x}$Ge$_x$ alloy increased, the resistivity is decreased while both the carrier density and mobility are increased. This increased carrier density was the result of an increased In solid-solubility as the Ge fraction is increased. The increased mobility is consistent with the higher carrier mobility in Ge relative to Si$_{1-x}$Ge$_x$ and Si. This is consistent with an earlier study of Si$_{1-x}$Ge$_x$ [180]. We note that the high mobility we measured for In-doped Si was in part due to the very low carrier density, and hence low level of ionized impurity scattering in this sample. The Hall mobility as a function of carrier concentration is in agreement with earlier studies [181][182]. From Table 6.1, the electrically-active fraction of implanted In atoms increased as the Ge fraction in the Si$_{1-x}$Ge$_x$ alloy increased due to the corresponding increase of the In solid-solubility. Figure 6.1 readily demonstrates that, relative to Si, low resistivity values have been achieved with In dopants in Si$_{1-x}$Ge$_x$ alloys.
Chapter 6. *In doped SiGe*

Figure 6.1: (a) Resistivity, (b) carrier density and (c) carrier mobility as a function of In concentration. Squares, diamonds, triangles and circles represent In doped Si, In doped Si$_{0.35}$Ge$_{0.65}$, In doped Si$_{0.1}$Ge$_{0.9}$ and In doped Ge, respectively.
6.3 Structural properties of In-implanted Si$_{1-x}$Ge$_x$

To better understand the mechanism(s) by which In atoms were electrically activated/deactivated in Si$_{1-x}$Ge$_x$ alloys, we probed the atomic-scale environment around the In atoms with EXAFS (Figure 6.2 (a) - (d)) and XANES (Figure 6.2 (e) - (h)). The EXAFS experimental data were simultaneously fit using k-weights of 2, 3 and 4, with the input models structurally-relaxed by DFT. The bondlengths derived from the EXAFS fittings agreed well with those calculated by DFT. Linear combination fits of the XANES spectra were performed using the data of the lowest concentration samples (where EXAFS showed the In atoms were substitutional) and that of metallic In as standards. The EXAFS results are summarized in Figure 6.3 as a function of both In concentration and Si$_{1-x}$Ge$_x$ alloy stoichiometry, supplemented by a lattice structural analysis performed with TEM (Figure 6.4).

As above, we begin with the In concentration dependence. The FT EXAFS spectra were generally comprised of several components, typically In in a substitutional lattice position (with a peak at a non-phase-corrected radial distance of $\sim 2.3$ Å) and In in a metallic In precipitate (with a peak at a non-phase-corrected radial distance of $\sim 3.2$ Å). The relative fraction of these two components was clearly In-concentration dependent, the substitutional (S) and metallic (M) fractions decreased and increased, respectively, as the In concentration increased. The substitutional fractions (listed on Figure 6.2) determined by EXAFS were well correlated with the electrically-active fractions determined by Hall Effect measurements (Table 6.1) and thus the substitutional In atoms were indeed responsible for the production of charge carriers, not structural disorder as suggested by others [151]. Note that to achieve improved EXAFS fittings, it was at times necessary to introduce a third component, either In in a random location (R), with no contribution to the EXAFS spectra [121], or an In-vacancy pair, as described in detail in a previous report [128] and in Chapter 4. XANES analysis complemented the EXAFS results. Linear combination fitting of the XANES spectra (Figure 6.2 (e) - (h)) with substitutional and metallic spectra (listed on the figure) yielded metallic fractions in excellent agreement with those determined by EXAFS.
Figure 6.2: (a) (b) (c) and (d) are the FT EXAFS spectra as a function of radial distance for the In implanted Si, Si$_{0.35}$Ge$_{0.65}$, Si$_{0.1}$Ge$_{0.9}$, and Ge samples, respectively. Dashed lines show the R-range windows used for the data fitting. (e) (f) (g) and (h) are the XANES spectra as a function of the incident photon energy for the In implanted Si, Si$_{0.35}$Ge$_{0.65}$, Si$_{0.1}$Ge$_{0.9}$, and Ge samples, respectively. Spectra are offset vertically according to In concentration for clarity. Symbols represent the data while solid lines are best fits.
6.3. Structural properties of In-implanted $\text{Si}_{1-x}\text{Ge}_x$

Figure 6.3: A summary of the fractions of the implanted In atoms in substitutional sites of $\text{Si}_{1-x}\text{Ge}_x$ (S), in a metallic In environment (M), in a random lattice location (R) and in substitutional sites paired with vacancy (V). The lattice locations were determined by EXAFS as in Figure 6.2.

We now consider the $\text{Si}_{1-x}\text{Ge}_x$ stoichiometry dependence. The appearance of the metallic In component in the EXAFS spectra enabled us to make quantitative estimates of the In solid-solubility limit in the $\text{Si}_{1-x}\text{Ge}_x$ alloys. Results are listed in Table 6.2. Clearly the In solid-solubility limit increased as the Ge fraction in the $\text{Si}_{1-x}\text{Ge}_x$ alloy increased. This result was well explained by our DFT calculations, as described below.

The EXAFS results are summarized in Figure 6.3 as a function of both In concentration and $\text{Si}_{1-x}\text{Ge}_x$ alloy stoichiometry. As above, this figure demonstrated the metallic fraction increased as the In concentration increased. Furthermore, the solid-solubility of In in the $\text{Si}_{1-x}\text{Ge}_x$ alloy increased as the Ge fraction increased (and hence the onset of precipitation was observed at higher In concentrations as the Ge fraction increased). The figure shows that substitutional In atoms were electrically active at low In concentrations and In metal precipitation was the process by which In atoms become electrically inactive at high In concentrations.

TEM analysis was entirely consistent with EXAFS and XANES results. Figure 6.4 shows cross-sectional images for several In concentrations as a function of $\text{Si}_{1-x}\text{Ge}_x$ alloy stoichiometry. The limited field of view inhibited quantification but clearly the number of In precipitates increased as the In concentration increased.
Table 6.2: The estimated In solid solubility in Si$_{1-x}$Ge$_x$ as a function of the Si$_{1-x}$Ge$_x$ stoichiometry.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>In solid solubility (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.002 - 0.006</td>
</tr>
<tr>
<td>Si$<em>{0.35}$Ge$</em>{0.65}$</td>
<td>0.02 - 0.06</td>
</tr>
<tr>
<td>Si$<em>{0.1}$Ge$</em>{0.9}$</td>
<td>0.06 - 0.2</td>
</tr>
<tr>
<td>Ge</td>
<td>0.2 - 0.6</td>
</tr>
</tbody>
</table>

Figure 6.4: Cross section TEM images for the samples of different implantation concentration (horizontal) and substrates stoichiometry (vertical). The inset in (h) shows a high resolution image of a metallic In precipitate.
6.4 A theoretical study of the structural properties of In-implanted $\text{Si}_{1-x}\text{Ge}_x$

The experimental results presented above demonstrated a clear dependence on $\text{Si}_{1-x}\text{Ge}_x$ alloy stoichiometry. To identify and understand the reasons for this behavior, we used DFT calculations for two substitutional In atoms in a 64-atom $2 \times 2 \times 2$ $\text{Si}_{1-x}\text{Ge}_x$ super-cell over the entire stoichiometry range from $x = 0$ to 1. Calculations were performed for four In cluster configurations, with the second In atom positioned as either the first, second or third nearest neighbor (NN) of the central In atom in addition to an In atom at the super-cell vertex, the maximum possible separation.

Figure 6.5: The binding energies of two In atoms in substitutional sites of $\text{Si}_{1-x}\text{Ge}_x$ as a function of Ge composition. Circles, diamonds, triangles represent the binding energies for the two In atoms as first, second and third nearest neighbors (NN), respectively; squares are those of two In atoms in diagonal locations (one In atom in the center and the other in the vertex of the supercell, the furthest distance the two atoms can be positioned). Dashed lines are the best fits of the data with an exponential function.

Figure 6.5 shows binding energies of In clusters as a function of $\text{Si}_{1-x}\text{Ge}_x$ alloy stoichiometry and the separation between the two In atoms. In general, the binding energies trended downward (more favorable) as the Ge fraction decreased. The binding energies also trended downward as the separation between the two In atoms decreased. Equivalently, the In atoms preferred to pair. The difference in binding energies as a function of
the separation became more pronounced as the Ge fraction decreased. Equivalently, there was a greater driving force for In atoms to pair as the Ge fraction decreased. For In clusters in Si, the calculated binding energies were -0.62 (1st NN), -0.40 (2nd NN), -0.31 (3rd NN) and -0.26 (diagonal) eV for the four configurations, agreeing well with the results previously reported by Yamauchi et al \[171\]. The negative binding energies indicated that In atoms tend to aggregate spontaneously \[171\] for $x \sim < 0.7$. This approximate stoichiometry marked the transition from energetically favorable ($x \sim < 0.7$) to energetically unfavorable ($x \sim > 0.7$) conditions for In-In pair formation. This theoretical result has identified the reason for the increased In solid-solubility limit as the Ge fraction in $\text{Si}_{1-x}\text{Ge}_x$ increased.

### 6.5 Summary

We have characterized the electrical and structural properties of In-implanted $\text{Si}_{1-x}\text{Ge}_x$. Both the In concentration and $\text{Si}_{1-x}\text{Ge}_x$ alloy stoichiometry dependencies have been examined. The In solid-solubility limit has been quantified and was found to increase as the Ge fraction in the $\text{Si}_{1-x}\text{Ge}_x$ alloy increases. In metal precipitation (at In concentrations in excess of the solid-solubility limit) was the primary reason for the electrical deactivation of In atoms. A complementary theoretical study of In-In pairing in $\text{Si}_{1-x}\text{Ge}_x$ alloys demonstrated pairing was energetically favorable for $x \sim < 0.7$ and identified the reason for the trend in the In solid-solubility limit as a function of $\text{Si}_{1-x}\text{Ge}_x$ alloy stoichiometry. Our results have clearly demonstrated that In implantation in $\text{Si}_{1-x}\text{Ge}_x$ alloys is an effective means of achieving the low resistivity values necessary for advanced electronic devices.
Enhanced electrical activation in In-implanted Si$_{0.35}$Ge$_{0.65}$ by C co-doping

In this chapter, we demonstrate a significant increase in the electrically-active dopant fraction of In-implanted Si$_{0.35}$Ge$_{0.65}$, by co-doping with the isovalent element C. Electrical measurements have been correlated with X-ray absorption spectroscopy to determine the electrical properties and the In atom lattice location, respectively. With C + In co-doping, the solid solubility of In in Si$_{0.35}$Ge$_{0.65}$ was at least tripled from between 0.02 and 0.06 at. % to between 0.2 and 0.6 at. % as a result of C-In pair formation, which suppressed In metal precipitation. The most dramatic improvement of electrical properties was attained in the 0.06 and 0.2 at. % co-doped samples, whose dopant electrically-active fractions increased from approximately 60% and 23% to 90% and 40%, respectively. This chapter is based on our published work [183].

7.1 Introduction

As discussed in Chapter 6, In is a promising $p$-type dopant in both Si and Ge with substrate-specific advantages and disadvantages. Using Si$_{1-x}$Ge$_x$ alloys has the potential to combine the positive aspects of both towards the application to CMOS devices. In Chapter 6, we found that the solid solubility of In in Si$_{1-x}$Ge$_x$ decreased rapidly as a function of the substrate Si composition, from that of In in Ge ($\sim$ 0.2 at. %) [175] towards that of In in Si ($\sim$ 0.0036 at. %) [176]. For instance, in the In implanted Si$_{0.35}$Ge$_{0.65}$ samples, the formation of electrically-inactive In metal precipitates was triggered at an In concentration...
as low as 0.06 at. %, which affected the electrical activation of In significantly. Source and drain regions of advanced CMOS devices necessitate high dopant concentrations as well as high electrically-active dopant fractions to reduce contact resistance and improve device performance [156]. To this end, an above-equilibrium, metastable solid solubility limit for In in Si$_{1-x}$Ge$_x$ is required.

Co-doping C with In is one of the most promising approaches to meet such a requirement. It has been reported that in both Si [148, 149, 169, 170] and Ge [154, 173, 174] (Chapter 5), enhancement of In electrical activation was realized by C co-doping. Above-equilibrium solid solubility was attained in both substrates as a consequence of C-In pair formation that suppressed In precipitation. Intuitively, similar effects can be anticipated in Si$_{1-x}$Ge$_x$, despite earlier studies that found C did not bring a beneficial impact to B activation in Si$_{1-x}$Ge$_x$ [184–186].

C co-doping has unique advantages over other co-doping or dopant reactivation strategies such as double acceptor doping [171], flash annealing [164], pre-amorphization with solid phase epitaxy [161, 165], and so on. As an isovalent element to Si and Ge, C has played important roles in modifying Si$_{1-x}$Ge$_x$ properties. By introducing C into Si$_{1-x}$Ge$_x$, dopant diffusion confinement can be achieved [187, 189] and an extra degree of freedom can be added to the strain [190, 192] and bandgap engineering [193, 195] of Si$_{1-x}$Ge$_x$. The effect of C on the Si$_{1-x}$Ge$_x$ bandgap expansion is crucial, since the narrow bandgap of high Ge composition Si$_{1-x}$Ge$_x$ is a substantial issue that causes a high off-state leakage due to band-to-band tunneling (BTBT) [178]. (The bandgap of Si and Ge are 1.12 and 0.66 eV, respectively, while that of diamond is 5.5 eV.) In fact, as C-doped Si$_{1-x}$Ge$_x$ outperforms Si$_{1-x}$Ge$_x$ in many areas, the Si$_{1-x-y}$Ge$_y$C$_y$ ternary semiconductor was proposed to replace Si$_{1-x}$Ge$_x$ in advanced electronic device fabrication [196, 197]. The material is now even more promising, given that this work shows C also has the capability of enhancing the solid solubility of In in Si$_{1-x}$Ge$_x$, which improves the In electrical activation.

In this chapter, Hall effect measurements demonstrate a significant increase of In electrically-active fraction in Si$_{0.35}$Ge$_{0.65}$ in the presence of C. Correlating that with the structural characterization performed using X-ray absorption spectroscopy, such an electrical activation increase was found to be the result of In solid solubility enhancement in Si$_{0.35}$Ge$_{0.65}$ due to C co-doping. We examined a range of C and In concentrations (0.02 - 0.6 at. %), the latter at device-appropriate levels, to establish the concentration-dependent effectiveness of this approach.
7.2 Results and discussion

Figure 7.1 compares the resistivity, carrier density and carrier mobility of In and C + In implanted Si$_{0.35}$Ge$_{0.65}$ samples as a function of In concentration. All samples exhibited p-type conductivity. The EXAFS and XANES spectra of the In and C + In co-doped samples are compared in Figure 7.2, and results are summarized in Table 7.1. The EXAFS experimental data were simultaneously fit using k-weights of 2, 3 and 4, with the input models structurally-relaxed by DFT. The bondlengths derived from the EXAFS fittings agreed well with those calculated by DFT. Linear combination fits of the XANES spectra were performed using the data of the lowest concentration samples (where EXAFS showed the In atoms were substitutional) and that of metallic In as standards.

At low In concentration (0.02 at. %), co-doping leads to a minor increase and decrease of carrier density and Hall mobility, respectively, yielding a similar resistivity to the sample without C (as shown in Figure 7.1). The effect of C co-doping on the electrical properties was negligible at this concentration (0.02 at. %). The analysis of the EXAFS spectra (Figure 7.2 (a) and (c)) show that all implanted In atoms occupied substitutional lattice sites (S sites) and were four-fold coordinated in both the singly doped and co-doped samples (Table 7.1). Thus, with or without C present, no evidence of electrically-inactive In metal precipitates (In atoms in M site) was apparent in both EXAFS and XANES spectra (Figure 7.2). This correlates well with the electrical measurements, where the vast majority of In atoms were electrically active in both the 0.02 at. % In doped and C + In co-doped samples.

As Figure 7.1 demonstrates, the influence of co-doping was more significant at higher In concentrations. At 0.06 at. %, the In activation ratio increased from 60.1% to 90.4% due to C co-doping, while the carrier mobility decreased as a result of increased lattice disorder and ionized impurity scattering. An obvious resistivity reduction was observed. This improvement of the electrical activation is a result of C-induced In solid solubility enhancement in Si$_{0.35}$Ge$_{0.65}$. The EXAFS fits (Figure 7.2 (a)) and XANES linear combination fits (Figure 7.2 (b)) show that without C, ~26% of the implanted In atoms in Si$_{0.35}$Ge$_{0.65}$ formed In metal precipitates at this concentration (0.06 at. %, in Table 7.1). However, with C present (0.06 at. % C + In), the In metal contribution to EXAFS scattering peak (Figure 7.2 (c)) and In metal related XANES fine structure oscillation (Figure 7.2 (d)) are not visible. The fits of the spectra confirmed all implanted In are in S sites (as shown in Table 7.1). Evidence of C-In pairing was not found in this sample, where the concentration of the C-In pairs is expected to be lower than the detectable limit of EXAFS.
Figure 7.1: (a) Resistivity, (b) carrier density and (c) carrier mobility as a function of In concentration. Squares and circles represent In-doped Si$_{0.35}$Ge$_{0.65}$ and C + In co-doped Si$_{0.35}$Ge$_{0.65}$, respectively. In panel (b), un-bracketed and bracketed numbers are the electrically-active fractions for In-doped Si$_{0.35}$Ge$_{0.65}$ and C + In co-doped Si$_{0.35}$Ge$_{0.65}$, respectively.
7.2. Results and discussion

In doped Si\(_{0.35}\)Ge\(_{0.65}\) (a) and (b) are the Fourier-transformed, \(k^2\)-weighted EXAFS spectra as a function of radial distance for the In-doped Si\(_{0.35}\)Ge\(_{0.65}\) and C + In co-doped Si\(_{0.35}\)Ge\(_{0.65}\) samples, respectively. (b) and (d) are the corresponding XANES spectra as a function of the incident photon energy. Spectra are offset vertically according to In concentration for clarity. Symbols represent the data while solid lines are best fits.

The greatest effect of C + In co-doping was observed at an In concentration of 0.2 at. %. According to the EXAFS and XANES analysis (Figure 7.2 (a) and (b), respectively) of the 0.2 at. % In singly doped Ge sample, \(\sim 67\%\) of the In dopants in Si\(_{0.35}\)Ge\(_{0.65}\) were in an In metal environment (M site), only \(\sim 33\%\) and \(\sim 23\%\) of the In atoms were in S site and electrically-active (Table 7.1 and Figure 7.1), respectively. The suppression of In metal precipitate formation was achieved with C co-doping at this In concentration (0.2 at. %). The corresponding EXAFS spectrum (Figure 7.2 (c)) remains similar to that of substitutional, four-fold coordinated In with no evidence of metallic In. A high quality fit was obtained using a DFT relaxed model of a C-In pair in a substitutional site of Si\(_{0.35}\)Ge\(_{0.65}\), showing that one In atom was on average paired with 0.75 ± 0.13 C atoms. Thus, we expected that \(\sim 75\%\) of the implanted In atoms formed C- In pairs (in C site), and 25% remained in a S site without C bonding (Table 7.1). A fit of the C + In doped 0.2 at. % sample EXAFS spectrum, with additional In metal fraction, was also tested, but yielded no evidence of In atoms in M sites (non-physical DWFs were obtained). C-In pair formation was supported by our DFT calculations, with the calculated value for C-In binding energy...
in a substitutional site in Si$_{0.35}$Ge$_{0.65}$ of -0.35 eV. This effectively shows that C-In pairing is indeed energetically favorable in Si$_{0.35}$Ge$_{0.65}$. Although the linear combination fit of XANES spectrum of the 0.2 at. % C + In sample (Figure 7.2 (d)) proposed that 25% of the In were in M sites (Table 7.1), no sign of In metal related oscillation feature was observed, in agreement with the EXAFS analysis. The reduction of the In metal fraction due to C co-doping resulted in a dramatic increase of the 0.2 at. % C + In sample dopant activation ratio (from 23.1% to 40.2%), along with a resistivity decrease from about 5 to 3.5 mΩ × cm as shown in Figure 7.1. The low amplitude of the 0.2 at. % co-doped sample EXAFS spectrum implied (high Debye-Waller factors values were used in the fit) a high level of disorder in the In local environment. This is responsible for the relatively low In electrically active fraction (40.2 %), given that In metal precipitation was not found in the sample. C-In pair formation as well as its similar effects on In solid solubility and electrical activation enhancement were observed in both C + In co-doped Si [148,149,169,170] and Ge [154,173,174], consistent with our results here with Si$_{0.35}$Ge$_{0.65}$.

Table 7.1: A summary of the quantified fractions (from Figure 7.2) of In atoms in substitutional sites (S), metallic In (M), random lattice location (R) and substitutional sites paired with C (C) for the In and C + In implanted Si$_{0.35}$Ge$_{0.65}$ samples.

<table>
<thead>
<tr>
<th>In (and C) concentration (at. %)</th>
<th>In (and C) concentration (at. %)</th>
<th>EXAFS</th>
<th>XANES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>S fraction (%)</td>
<td>M fraction (%)</td>
</tr>
<tr>
<td>In doped SiGe</td>
<td>0.02</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>74 ± 4</td>
<td>26 ± 4</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>33 ± 2</td>
<td>67 ± 2</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>-</td>
<td>81 ± 4</td>
</tr>
<tr>
<td>C + In doped SiGe</td>
<td>0.02</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>25 ± 13</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>-</td>
<td>67 ± 3</td>
</tr>
</tbody>
</table>

At the highest In concentration of 0.6 at. %, In metal precipitation was found in both the In implanted (Figure 7.2 (a) and (b)) and C + In co-implanted (Figure 7.2 (c) and (d)) samples. This indicated that even with the introduction of C, 0.6 at. % was still beyond the solid solubility threshold of In in Si$_{0.35}$Ge$_{0.65}$. C co-doping enhanced the In solid solubility limit of Si$_{0.35}$Ge$_{0.65}$ from between 0.02 and 0.06 at. % to between 0.2 and 0.6 at. %, which is (at least) a three-fold increase. At this concentration (0.6 at. %), the EXAFS analysis show that ~ 81% and ~ 67% (Table 7.1) of the doped In atoms were on M sites of Si$_{0.35}$Ge$_{0.65}$ for the singly implanted and co-implanted samples, respectively.
The lower metal fraction in the co-doped sample was also an indication of the enhanced solid solubility. Note that to achieve improved EXAFS fittings, a fitting component of In atoms in a random location (R site) with no contribution to the EXAFS spectra [121], was introduced. As shown in Figure 7.1, the formation of electrically-inactive In metal precipitates in the (0.6 at. %) co-doped sample caused a low In active ratio (12.7%). Hence, only a minor improvement was obtained from the one without C (9.1%), along with a slightly lower resistivity and Hall mobility.

7.3 Summary

In conclusion, we have characterized the electrical and structural properties of C + In co-doped Si$_{0.35}$Ge$_{0.65}$, demonstrating this approach can yield a significant increase in carrier density relative to a conventional single dopant implantation protocol. An above-equilibrium solid solubility limit of In in Si$_{0.35}$Ge$_{0.65}$ was achieved with C-In pairing, which was at least three times greater than that without C. As a consequence, the formation of In precipitates was effectively suppressed and the carrier density was enhanced. Our experimental identification of the In atom lattice site and electrically-active fraction demonstrates that co-doping with C is an effective strategy for obtaining the high electrically-active dopant fractions required for advanced devices.
8 Conclusion and Future Work

8.1 Conclusion

This thesis performed systematic studies on the structural and electrical properties of In-doped Si, Si$_{1-x}$Ge$_x$, and Ge, and demonstrated that C co-doping is an effective strategy to achieve significant improvements in the electrical properties of these systems. We provided the field of semiconductor device fabrication crucial information about these materials. Such a knowledge can play important roles in their application to future CMOS devices beyond the 7 nm technology node, to maintain the pace of Moore’s Law in the semiconductor industry.

C and In atoms were incorporated into the Si, Si$_{1-x}$Ge$_x$, and Ge substrates using ion implantation, with a wide range of concentrations (the values of which were confirmed by RBS). The In lattice location and ion implantation-induced substrate disorder were identified using EXAFS and XANES, and complemented by TEM, Raman spectroscopy, and DFT calculation. DFT calculations also provided theoretical investigations of the In atom clustering characteristics, which supported the experimental results. Hall effect measurements of the dopant electrical activation fraction, conductivity, carrier density and carrier mobility of the samples were correlated with the structural properties.

Firstly, we performed a systematic study of the structural and electrical properties of In-doped Ge. As shown in Figure 8.1, In atoms occupy a substitutional site in Ge at low concentrations and precipitate to form metallic In when the solid solubility is exceeded. In addition, EXAFS measurements yielded evidence of In-V complex formation along with that of metallic In, and this result was supported by complementary DFT calculations,
which showed that In-V pairing is energetically favorable. XAS, TEM, and Raman measurements showed Ge lattice disorder increases with implanted In concentration. Electrical characterization demonstrated that the electrical deactivation of the In atoms was caused by the formation of In precipitates and In-V clusters, and lattice disorder may enhance the carrier density of the In implanted Ge samples.

With the aim to enhance the In solid solubility and electrical activation in Ge, we co-implanted C with In in Ge. We found that this approach can yield a significant three-fold increase in carrier density relative to a conventional dopant-only implantation protocol. As shown in Figure 8.1 C - In pairs were found at high (C and In) concentrations, which effectively suppressed the formation of electrically-inactive In precipitates and In-V clusters. An above-equilibrium solid solubility limit of In in Ge was achieved. Raman spectroscopy demonstrated a reduction of In-induced strain in the Ge lattice, which also improved the In electrical activation. Our experimental identification of C-In pairing is in excellent agreement with theoretical predictions and demonstrates that co-doping with the isovalent element C is an effective strategy for attaining the high electrically-active dopant fractions required for advanced CMOS devices.

![Figure 8.1](image-url)

**Figure 8.1:** A summary of the fractions of the implanted In atoms in substitutional sites of Si$_{1-x}$Ge$_x$ (S), in a metallic In environment (M), in a random lattice location (R), and in substitutional sites paired with vacancy (V) or Carbon (C). The lattice locations were determined by EXAFS as shown in Chapter 4-7.
8.2. Future work

Using Si\textsubscript{1−x}Ge\textsubscript{x} alloys as the In doping substrate has the potential to combine the positive aspects of In-doped Si and In-doped Ge. Hence, we characterized the electrical and structural properties of In-implanted Si\textsubscript{1−x}Ge\textsubscript{x}. Both the In concentration and Si\textsubscript{1−x}Ge\textsubscript{x} alloy stoichiometry dependencies have been examined. EXAFS and XANES measurements showed that In atoms occupy a substitutional site in Si\textsubscript{1−x}Ge\textsubscript{x} at low concentrations and start to form metallic In precipitates when the solid solubility was exceeded (as shown in Figure 8.1). The solid-solubility limit of In in Si\textsubscript{1−x}Ge\textsubscript{x} has been quantified by XAS and TEM and was found to increase as the Ge fraction in the Si\textsubscript{1−x}Ge\textsubscript{x} alloy increases. The reason for such an In solid-solubility limit dependence on Si\textsubscript{1−x}Ge\textsubscript{x} stoichiometry was identified by a DFT study, which demonstrated that the In-In pairing preference decreases as a function of the Ge composition in the Si\textsubscript{1−x}Ge\textsubscript{x} alloy. Correlating the fraction of electrically-active In atoms from Hall effect measurements with the In atomic environment determined by XAS, it was found that In metal precipitation (at In concentrations in excess of the solid-solubility limit) is the primary reason for the electrical deactivation of In atoms. Our results have clearly demonstrated that In implantation in Si\textsubscript{1−x}Ge\textsubscript{x} alloys is an effective means of achieving the low resistivity values necessary for advanced CMOS devices.

Last but not least, we successfully enhanced the solid solubility of In in Si\textsubscript{1−x}Ge\textsubscript{x} by C co-doping, which improved the electrical properties of In-doped Si\textsubscript{1−x}Ge\textsubscript{x}. As shown in Figure 8.1, the formation of In metal precipitates in the 0.06 at. % and 0.2 at. % In-doped Si\textsubscript{0.35}Ge\textsubscript{0.65} samples was effectively suppressed by co-doping C with In. The solid solubility of In in Si\textsubscript{0.35}Ge\textsubscript{0.65} was at least tripled from between 0.02 and 0.06 at. % to between 0.2 and 0.6 at. %, as a result of C-In pair formation. The In electrical activation fractions of the co-doped samples increased significantly, as the In atoms recovered a substitutional, four-fold coordinated structure.

8.2 Future work

The present studies of this thesis demonstrated a promising future for (C +) In doped Ge and Si\textsubscript{1−x}Ge\textsubscript{x}, towards the application on advanced CMOS devices. However, a number of details about the systems are still lacking, and hence further work is required before they can be applied to device fabrication. First of all, In implanted Si, Si\textsubscript{0.35}Ge\textsubscript{0.65}, Si\textsubscript{0.10}Ge\textsubscript{0.90}, and Ge were studied in this thesis, yet an investigation of the full range of stoichiometry is essential to find the optimum point that is the most device-appropriate. In addition, the diffusion profile of In in Si\textsubscript{1−x}Ge\textsubscript{x} is not determined, which can play a key role in the realization of shallow junctions and subsequent device scaling. The effect of C co-doping on In diffusion is also not clear. To fully characterize these aspects, a systematic secondary ion mass spectrometry (SIMS) study in correlation to DFT calculation is necessary. In the case of C + In co-doping, the effect of higher C to In implantation concentration ratios (higher than 1 : 1) has not yet been investigated, which may result in an even higher In
solid solubility in Ge and Si\(_{1-x}\)Ge\(_x\). Moreover, there is still no available literature about the effects of annealing conditions on In atom activation in Ge and Si\(_{1-x}\)Ge\(_x\). With a more advanced annealing technique replacing the three steps annealing used in this thesis (such as flash annealing, rapid thermal annealing or pulsed laser annealing), a further increased In solid solubility and carrier density can be expected in Ge and Si\(_{1-x}\)Ge\(_x\).

In addition, some other characterization techniques that were not employed in this thesis could be useful in obtaining supplementary information about the systems. For example, spreading resistance profiling (SPR) can provide the charge-carrier depth distribution of the implanted samples, an atomic probe study can identify the 3D geometrical locations of the atoms, the substrate strain and disorder conditions can be further investigated by x-ray diffraction (XRD) and so on.

In the future, alternative group III elements in group IV semiconductors other than In in Si, Si\(_{1-x}\)Ge\(_x\) and Ge could also be considered and applied in future CMOS devices. For instance, both Ga doped Si \[198\] and Ga doped Ge \[199\] were found to exhibit superconducting features, yet a systematic study of their electrical and structural properties is still lacking. In addition, the effect of C co-doping on these materials has not yet been examined, which has the potential to further improve their electrical performance. Co-doping with other elements instead of, or together with, C can be another efficient approach to further enhance dopant activation. According to published literature, both B \[171\] and F \[166\] are primary candidates. One of the most promising future projects to succeed this thesis is to implant In into Si\(_{1-x-y}\)Ge\(_x\)C\(_y\) ternary semiconductors. Because of the superior properties of Si\(_{1-x-y}\)Ge\(_x\)C\(_y\) in strain and bandgap engineering as well as dopant diffusion confinement, it has been proposed as a replacement for Si\(_{1-x}\)Ge\(_x\) in advanced electronic devices \[196\], \[197\]. Since this thesis has shown that C has the capability to enhance the solid solubility of In in Si\(_{1-x}\)Ge\(_x\), and to improve the In electrical activation, remarkable electrical properties can be anticipated using this dopant - substrate combination (In in Si\(_{1-x-y}\)Ge\(_x\)C\(_y\)). Alternatively, In implanted Si\(_{1-x}\)C\(_x\) and Ge\(_{1-x}\)C\(_x\) binary semiconductors are also attractive topics that worthy of detailed investigations.
8.2. Future work
Chapter 8. Conclusion


[64] V. A. Fock, Z. Phys. **61**, 126 (1930);


