Study of Si-Ge Interdiffusion with Highly N-type Doping

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Abstract

Silicon photonics has emerged as an effective solution to overcome the wiring limit imposed on electronic device (e.g. transistors) density and performance with continued scaling. In the past few decades, researchers all over the world have invested extensive effort on finding solutions to a Si-compatible lasing material system. Recently, Ge-on-Si lasers were demonstrated as promising candidates. Heavy n-type doping in Ge is the key technique to realize Ge lasing.

However, Si-Ge interdiffusion during high-temperature growth or fabrication steps changes the distribution of Ge fraction and increases atomic intermixing, which degrades the device performance. Studies on the Si-Ge interdiffusion with high Ge fraction and P doping effects are not available. The subject is of technical significance for the structure, doping and process design of Ge-on-Si lasers and Ge based MOSFET.

In this work, Si-Ge interdiffusion under high n-type doping was investigated both by experiments and by theoretical analysis.

1) Si–Ge interdiffusion with different P doping configurations was investigated. Significant interdiffusion happened when the Ge layer was doped with P at $10^{19}$ cm$^{-3}$ after defect annealing cycles, which resulted in a SiGe-alloy region at the Si-Ge interface. The thickness of this SiGe alloy was more than 150 nm. With high P doped Ge, Si–Ge interdiffusivity is enhanced 10–20 times in the $x_{Ge} > 0.7$ region compared with the control sample without P doping. The phenomenon is attributed to the Fermi-level effect. Due to the high P concentration peak in the Si-Ge interdiffusion region, the concentration of negatively charged vacancy was greatly increased and thus the interdiffusivity of Si–Ge.
Next, the impact of the Fermi-level effect on Si-Ge interdiffusion was further investigated by theoretical modeling.

2) Ge/Si0.25Ge0.75/Ge multilayered structures with no P doping and high P doping were investigated. A model of Si-Ge interdiffusion under high n-type doping was proposed to describe the impact of the Fermi-level effect. By fitting to the SIMS data from experiments with different anneal temperatures, it was found out that the Fermi-enhancement factor of Si-Ge interdiffusion was quadratically dependent on the ratio of electron concentration over intrinsic electron concentration \( (n/n_i) \). This suggests that for Ge fractions from 0.75 to 1 under high n-type doping, Si-Ge interdiffusion is dominated by vacancies with double negative charge \( (V^{2-}) \). This is the first work on the quantitative modeling of Si-Ge interdiffusion with high n-type doping.
Preface

The work in this thesis was funded by Natural Science and Engineering Research Council of Canada (NSERC) and Crosslight Software Inc. (Vancouver, BC). Most of the work was done in the Department of Materials Engineering at UBC during the past two years, including the designs of experiments, etch pit density characterization, the thermal annealing with Linkam heating stage and the Matlab™ simulations. All the theoretical modeling and simulations were conducted by the author. Experimentally, the author designed the sample structures and all the annealing conditions, prepared samples for secondary ion mass spectrometry (SIMS), performed etch pit density and X-ray diffraction characterization, deposited silicon oxide layer by plasma-enhanced chemical vapor deposition (PECVD), and data analysis of the experiment results. Without the contributions from the collaborators, however, this thesis could not have been accomplished.

The samples used in Chapter 3 were grown by Dr. Yew Heng Tan in Prof. Chuan Sheng Tan’s group at Nanyang Technological University. Moreover, the samples used in Chapter 4 were fabricated by Dr. G. Riggott at Microsystems Technology Laboratories of Prof. J. L. Hoyt’s group at Massachusetts Institute of Technology (MIT).

TEM measurements and analysis in Chapter 4 were performed by Dr. Dalaver H. Anjum in King Abdullah University of Science and Technology. The sample preparation was performed by the author.

The SIMS measurements were performed by Mr. S. Smith in Evans Analytical Group (EAG), a provider of commercial material characterizations. The sample preparation and the analysis of the SIMS data were performed by the author.
XRD measurements in Chapter 3 were performed by Dr. Yuanwei Dong upon a PANalytical X’Pert PRO MRD tool in Semiconductor Defect Spectroscopy Laboratory. Moreover, XRD measurements in Chapter 4 were performed by Mr. Yiheng Lin and the author together. All the data analysis and simulations with software Epitaxy were carried out by the author.

In addition, one journal article has been published based on the work in Chapter 3.

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Dedication

To my father and my mother.
Chapter 1: Introduction

1.1 Industry Background and Motivation

1.1.1 Moore’s law and the Interconnect Bottleneck

Silicon (Si) based integrated circuits (ICs) have revolutionized the world ever since they were invented in the mid-20th-century. Driven by the huge demand, the semiconductor industry has improved the productivity of ICs by 25% ~ 30% annually [1]. According to the observations of Gordon Moore, the number of transistors per square centimeter on Si-based ICs doubles approximately every two years, also known as Moore’s law [2]. The most important and sophisticated transistors are metal-oxide-semiconductor field effect transistors (MOSFETs) as shown in Figure 1-1, products based on which count for 60-70% of the total semiconductor market [3]. For decades, the device performance of MOSFETs has been improved when the gate length, junction depth, and gate dielectric thickness are scaled.

![Figure 1-1 Illustration of an n-type MOSFET structure](image)

However, this scaling trend has reached the physical limit of the thickness of gate dielectrics, where further reduction in the gate dielectrics thickness is not possible due to the
unwanted high leakage current [4]. Meanwhile, the scaling of the transistors also leads to the increasing resistance-capacitance (RC) delay of metal interconnects [5]. Therefore, in the past decade, the semiconductor industry has slowed down the scaling pace greatly. For example, the scaling factor of the physical gate length from 2004 to 2010 is ~0.9 per year [6] compared to the predicted scaling factor of 0.7 [2]. Tremendous efforts have been made to extend Moore’s law. One approach is to use three-dimensional structures such as fin-based field effect transistors (FinFETs) to replace the conventional planar MOSFETs [7], [8]. Another approach is to use high mobility channel materials like Germanium (Ge) or compound semiconductors [9], [10].

As the speed of transistors improves, the delay and power consumption of the metal interconnects that connect them is getting longer and higher. As shown in Figure 1-2 [11], when the technology node (gate length) decreases, the RC delay of 1mm wire increases drastically, whereas the intrinsic gate delay decreases slowly. The delay due to metal interconnects has become the limiting factor of IC performance, known as the interconnect bottleneck. In analogy,
the problem that we are facing for transistors and interconnects is like that of “fast cars on slow roads”.

1.1.2 Optical Interconnects and Si Photonics

As we know, photons have been used in communications for decades, such as in optical fibers for long-distance communications. Optical communication has a few advantages: 1) photons are immune to the RC delay problem; 2) photons of different wavelengths do not interact with each other, and they can be transmitted simultaneously; and 3) the transmission medium such as silica costs less than metals [12]. Optical interconnects are already available for short distance applications such as rack-to-rack (1-100m) and board-to-board (0.5-1m) interconnects. One of most popular products is optical thunder cables that were originally developed by Inter Inc. [13]–[15].

Can we communicate on-chip or intra-chip with optical interconnects? The field of Si photonics answers this question. Si photonics refers to the field of using silicon as an optical medium for photonic systems. This field is gaining significant momentum because it allows optical devices to be made cheaply using standard semiconductor fabrication techniques and to be integrated into microelectronic chips. It provides a promising solution to cost-effectively meeting the ever-increasing demands on data speed and bandwidth [16]. To transfer data through light signals, a light source is the key component in optical interconnects. However, it is also the most challenging device to achieve. As Si is an indirect band gap material, it is not an efficient light emitter. Besides, the integration of traditional III-V laser materials with Si has
always be a problem due to the lattice mismatch, thermal expansion coefficient mismatch and process incompatibility [17], [18]. In the past few decades, researchers all over the world have invested extensive efforts on finding solutions to a Si-compatible lasing material system [19]–[23].

1.2 Ge-on-Si Lasers and N-type Doping Technique

Ge is the most Si-compatible semiconductor because they have the same crystalline structure (diamond cubic structure), close lattice constant and similar physical properties such as self-diffusivity, Young’s modulus, Poisson ratio, etc. It plays an important role in Si photonics, such as in light sensing and modulation [24], [25]. However, Ge is an indirect bandgap semiconductor as Si, which is inferior in light emitting applications than direct bandgap semiconductors, such as Gallium Arsenide (GaAs) and Indium Phosphide (InP).

Figure 1-3 (a) illustrates the band structure of Ge [26]. Ge has the lowest energy point of its conduction band at the L valley, and the energy difference between the L valley and the top of the valence bands is called the indirect bandgap, which is 0.66 eV at room temperature [27]. When an electron in an L valley recombines with a hole in the heavy hole (HH) or the light hole (LH) band, a third particle, normally a phonon, is needed to maintain the momentum conservation principle, which makes the transition ineffective for light emitting. Fortunately, the direct bandgap at the Γ valley is only 136 meV higher than the indirect bandgap at the L valley at room temperature. To turn Ge into an efficient light emitter, people can compensate the difference between the direct and the indirect bandgaps of Ge.
In 2007, researchers from MIT demonstrated that Ge can become a direct bandgap material by adding tensile strain or high n-type (i.e. phosphorus) doping [28]. As shown in Figure 1-3 (b), with an additional tensile strain applied to Ge, the Γ valley in Ge shrinks faster than the L valleys due to the smaller effective mass in the Γ valley. For Ge to become a direct band gap material, according to calculations, the additional tensile strain need to be at least 1.8% for biaxial strain or 4.6% for uniaxial strain [26]. However, such high tensile strain narrows the bandgap too much so that the lasing wavelength will be larger than two microns [29]. Besides, it is technically hard to achieve such high tensile strain in Ge [30]–[32]. At the time of writing this thesis, no successful efforts have been reported in making Ge-on-Si lasers with only tensile strain.

To lower the requirement of tensile strain and keep the Ge lasing wavelength at around 1550 nm (within the telecommunication C-band wavelength range), researchers proposed to use n-type doping to raise the Fermi level and thus raise the effective bottom of the indirect L valley to the Γ valley or even higher [28]. As shown in Figure 1-3 (c), n-type dopants provides free electrons to occupy the energy states in the bottom of the L valley. According to calculations and experiments, to turn Ge into a direct bandgap material, n-type doping concentration has to be
on the order of $10^{19}$ cm$^{-3}$ with 0.2% tensile strain Ge. Previously many efforts have been made on adding large concentration of n-type dopants into Ge. In 2009, Kurdi et. al. used gas immersion laser doping technique and achieved up to $5 \times 10^{19}$ cm$^{-3}$ of P doping concentration in Ge [33]. In 2012, same doping level was achieved by Camacho et. al. with P delta-doped layer [34]. In addition, spin-on dopant process and multiple implantation were also successful in doping Ge up to about $1 \times 10^{20}$ cm$^{-3}$ [35], [36].

By using the n-type doping technique, in 2010, an optically pumped Ge-on-Si laser was demonstrated using 0.24% biaxial tensile strain [23]. It operated at room temperature with a gain of 50 cm$^{-1}$ at n-type doping level of $1 \times 10^{19}$ cm$^{-3}$. The lasing was in a wavelength range from 1590 to 1610 nm. In 2012, an electrically pumped Ge-on-Si laser was demonstrated by researchers from MIT and APIC Corporation with $4 \times 10^{19}$ cm$^{-3}$ n-type doped Ge and 0.2% biaxial tensile strain, as shown in Figure 1-4. The lasing wavelengths were between 1520 nm and 1700 nm with a variation consistent with different clamping condition and an output power up to 7 mW at room temperature [34].

In the first demonstrated Ge laser, the threshold current density was too high (280 kA/cm$^2$), and the quantum efficiency was too low for any practical uses [34]. Xia’s group recently
performed two-dimensional laser simulations to investigate this problem [37]. The reasons for the poor performance are from three factors: 1) small optical confinement factor due to the laser structure design, which can be easily optimized, 2) small carrier lifetime due to the material quality and processing imperfections and 3) Si-Ge interdiffusion at the Ge/Si interface due to high P doping. Although the data of Si-Ge interdiffusion from the demonstrated Ge laser device is not available, according to the work of the laser simulation, it is clear that Si-Ge interdiffusion is one of the key reasons for the poor performance. From the prototype structure of Ge laser in Figure 1-4, the thickness of Ge layer is on the order of $10^2$ nm, which is in the range of typical diffusion lengths of Si-Ge interdiffusion. Therefore, it is important to understand the Si-Ge interdiffusion in the Ge-on-Si laser structures.

1.3 Literature Review on Si-Ge Interdiffusion

Significant Si-Ge interdiffusion research efforts started in the 1990s. To measure interdiffusion at Si/SiGe interfaces, various techniques were utilized by researchers, such as Rutherford backscattering spectrometry [38], [39], photoluminescence, X-ray diffraction (XRD) [40]–[43], secondary ion mass spectrometry (SIMS) [44]–[46] and Raman spectroscopy [47]. Typical interdiffusion structures studied in the 1990s were Si/Si$_{1-x}$Ge$_x$ superlattices with the thickness from 30 nm to a few microns and with $x_{Ge} < 0.3$. Due to the scaling of electronic and optoelectronic devices and the change in structures and fabrication techniques, typical diffusion lengths of Si-Ge interdiffusion during thermal annealing in current technologies are comparable to the thickness of SiGe thin films in the devices, which is in the range of $10^0$ nm~$10^2$ nm. The
range of current interest has expanded to the whole range of Ge. Therefore, since the last
decade, Si-Ge interdiffusion has been revisited by many groups.

For Si-Ge interdiffusion in Ge-on-Si laser structures, Ge layers are typically under the
conditions of: 1) 0.2% tensile strain, 2) high dislocations density, and 3) high P doping
concentration. To summarize the prior art in this area, accordingly, previous research efforts on
the Si-Ge interdiffusion were discussed in the four aspects below:

1) Si-Ge interdiffusivity in relaxed crystals with low dislocation density,

2) Impact of the strain on Si-Ge interdiffusivity,

3) Impact of dislocations on Si-Ge interdiffusivity,

4) Impact of n-type dopants on Si-Ge interdiffusivity.

1.3.1 Si-Ge Interdiffusivity in Fully Relaxed Crystals with Low Dislocation Density – the Base Line

SiGe single crystals with low defect density are the commonly used materials for industry
device applications. Point defects, i.e. interstitials (I) and vacancies (V), contribute to dopant
diffusion in SiGe is now generally accepted based on both experimental observations and
theoretical calculations. According to literature, in Si and Si-rich SiGe alloys, Si and Ge self-
diffusion are via both interstitials and vacancies [48]–[53]. Cowern et al. [45] demonstrated that
for small values of Ge composition, diffusion at low temperature (T < 400 °C) is mostly mediated
by vacancies. As the Ge fraction increases, the vacancy mechanism becomes more and more
dominant [52]–[55]. Strohm et al. [53] concluded that when $x_{Ge} > 0.25$, Ge self-diffusion is
completely via vacancies. Moreover, with atomistic kinetic Monte Carlo simulations, Castrillo et
al. [56], [57] showed that both Si and Ge self-diffusion is controlled by vacancies over the medium Ge fraction range.

The interdiffusivity of Si-Ge has a strong concentration dependence. As summarized in Figure 1-5, the interdiffusivity increases almost exponentially with Ge fraction [58]–[63]. Previously, utilizing XRD technology, people focused on the interdiffusion in multiple quantum wells (MQW) with $x_{Ge} < 0.50$ [58], [64]. In 2007, based on SIMS technology and the Boltzmann-Matano method, Xia et al. [60] built a $D_MDC$ model to describe the Si-Ge interdiffusivity with $x_{Ge} < 0.6$. Recently, Dong et al. [61] established a benchmarking value for Si-Ge interdiffusivity over the full Ge fraction range. Based on Darken’s law and thermodynamics theory, Dong et al. considered Si-Ge alloys as regular solutions and expressed the Si-Ge interdiffusivity as follows:

$$D = D_{Si}^* \left(1 + \frac{\partial \ln y_{Si}}{\partial \ln x_{Si}}\right) x_{Ge} + D_{Ge}^* \left(1 + \frac{\partial \ln y_{Ge}}{\partial \ln x_{Ge}}\right) x_{Si}, \quad (1.1)$$

where $D_{Si}^*$ and $D_{Ge}^*$ are the self-diffusivity of Si and Ge; $y_{Ge}$ ($y_{Si}$) stands for the chemical coefficient of component Ge (Si), which can be expressed as:

$$\frac{\partial \ln y_{Si}}{\partial \ln x_{Si}} = \frac{(1-x_{Ge})x_{Ge}(4017x_{Ge}-17574)}{R_g T} \quad (1.2)$$

$$\frac{\partial \ln y_{Ge}}{\partial \ln x_{Ge}} = \frac{(1-x_{Ge})x_{Ge}(4017x_{Ge}-17574)}{R_g T} \quad (1.3)$$

where $R_g$ is the ideal gas constant and $T$ is the absolute temperature.
1.3.2 Impact of Strain on Si-Ge Interdiffusion

Two decades ago, the first Si n- and p-MOSFETs with biaxial stress induced by Si$_{1-x}$Ge$_x$ buffer layers were demonstrated by Welser et al. [65] and by Nayak et al. [66] respectively. A 2.2 times enhancement in electron mobility and a 1.5 times enhancement in hole mobility were reported. Since then, strain, especially compressive strain, has been widely applied in SiGe devices to enhance their performance.

It has been shown that compressive strain can significantly accelerate Si-Ge interdiffusion. Theiss et al. demonstrated in 1995 interdiffusion was enhanced in amorphous Si/Ge multi-layers under hydrostatic pressure similar to that under lattice mismatch strain [67]. However, due to the strong concentration dependence of the activation energy of diffusion under the
pseudomorphic condition, it was hard to separate the strain impact from the concentration impact. In 2002, using Ge self-diffusivity as the reference line, Aubertine et al. successfully separated strain and Ge concentration effects on Si-Ge interdiffusion [64]. Xia et al. built a $D_rD_C$ model that obtained the Si-Ge interdiffusivity with the Boltzmann-Matano method under a relaxed condition, and then modeled the impact of compressive strain as an exponential factor without any temperature dependence [60]. Recently, in 2014, Dong et al. built a compressive strain enhanced interdiffusion model via thermodynamics theory that extends the studied Ge molar fraction range from $0 < x_{Ge} < 0.56$ to $0 < x_{Ge} < 0.75$ [61].

Tensile strain has, however, according to the observation by Xia et al. [60], for the range of $0 < x_{Ge} < 0.56$, a negligible impact on Si-Ge interdiffusivity.

1.3.3 Impact of dislocations on Si-Ge Interdiffusion

For crystals in reality, it is extremely hard to eliminate all the dislocations no matter how perfect the crystals are. In the devices based on SiGe thin films, the most important extended defects are threading dislocations (TDs) and misfit dislocations (MDs). Threading dislocations can degrade the performance of electronic devices, which is undesirable. TDs can accelerate diffusion as rapid diffusion short circuits, which will be discussed in more detail in Section 2.1.2. However, the impact of TDs is dependent on their density and Ge fraction. In 2007, Xia et al. demonstrated that when the threading dislocation density (TDD) is on the order of $10^7$ cm$^{-2}$, the impact of TDs on Si-Ge interdiffusion is only significant in the low Ge region ($x_{Ge} < 0.05$), compared to samples with TDD on the order of $10^5$ cm$^{-2}$. When the TDD is on the order of $10^{10}$ cm$^{-2}$, reported by Gavelle
et al. [68], for \( x_{Ge} < 0.8 \), the interdiffusion is found to be strongly increased by the presence of dislocations.

Normally in electronic devices, TDs are minimized to the range of \( 10^4 \sim 10^6 \text{ cm}^{-2} \) [69]. For Ge lasers with Ge-on-Si structure, however, TDs are often larger than \( 10^8 \text{ cm}^{-2} \) [70], which suggests that the impact of TDs cannot be neglected when considering Si-Ge interdiffusion in Ge-on-Si structure.

1.3.4 Impact of Dopants on Si-Ge Interdiffusion

In 2002, Takeuchi and Ranade et al. [71], [72] studied the Ge-Si interdiffusion in a polycrystalline Ge/Si structure under arsenic (As) doping. They reported that the interdiffusion was enhanced by about five times when the As doping level was \( 1 \times 10^{21} \text{ cm}^{-3} \). In 2008, Gavelle et. al. [68] studied the impact of boron on Si-Ge interdiffusion in a Ge on Si structure. The interdiffusion is retarded when boron is doped in Ge layer. In 2011, Py et al. [73] studied the P impact on Si-Ge interdiffusion in a SiGe/Si supperlattice structure. P enhanced interdiffusion has been reported for SiGe alloys with a low Ge faction \( (x_{Ge}) \) of 0.265. He attributed the enhanced interdiffusivity to the indirect interaction between Ge and point defects released by P-defect clusters formed at high P concentration.

1.4 Problem Definition and Thesis Goal

The interdiffusion of Si-Ge can change the Ge layer into a SiGe alloy, which delays the lasing of the laser device. Ge-on-Si lasers are commonly built with crystalline Ge/Si structure under P doping. For Si-Ge interdiffusion in SiGe materials system, the interdiffusivity of undoped
SiGe has been well studied. However, for Si-Ge interdiffusion with P doping, literature only shows that P can accelerate Si-Ge interdiffusion with low Ge fraction [73]. Studies on the Si-Ge interdiffusion with high Ge fraction and P doping are not available.

In this thesis, the interdiffusion of Si-Ge under high P doping condition is investigated both by experiments and by theoretical analysis, and a model that predicts Si-Ge interdiffusion with P doping is also proposed. The goal is to shed some light on the mass transfer phenomena in Ge-on-Si structures. This subject is of technical significance for the structure, doping and process design of Ge-on-Si lasers and other Ge based MOSFET [74], [75].
Chapter 2: Si-Ge Interdiffusion Theories, Material Characterization, and Modeling Techniques

After introducing the progress made in Ge-on-Si lasers and reviewing the prior-art on SiGe interdiffusion, we need to discuss the interdiffusion theories, experiment and modeling methods that were used in the studies in Chapter 3 and 4.

2.1 Mechanisms of Diffusion in Si-Ge Material System

Diffusion, on a macroscopic scale, is described by Fick’s laws for common cases. On a microscopic scale, however, it is a complicated many-body physics problem. When dealing with problems in this thesis, a constant diffusivity in Fick’s laws is no longer in effect. Only by investigating the microscopic mechanisms can we explain or predict the macroscopic behavior of diffusion.

In the semiconductor industry, the common form of semiconductor materials is crystalline. For high-performance devices, such as bipolar transistors, Ge modulators, Ge photodetectors, Ge lasers and SiGe MOSFETs, Si$_{1-x}$Ge$_x$ ($0 \leq x \leq 1$) materials are single crystalline. In SiGe crystals, defects play crucial roles in impurity diffusion and interdiffusion. Although there is a mechanism of diffusion that requires no defects, i.e. the direct exchange mechanism, where the diffusing atoms or ions simply exchange places with their neighboring host atoms/ions, it is usually regarded to be negligible due to the high activation energy needed [76].

Normally, in crystalline solids, defects can be categorized as point defects, line defects (dislocations) and area defects (grain boundaries and stack faults). In correspondence to these defects, there are three types of diffusion paths [77]:
1) Lattice diffusion mediated by point defects,
2) Dislocations-mediated short-circuit diffusion,

In this work, type 3) diffusion is not relevant as the SiGe samples in our studies are single crystalline. Previously, it was established that the diffusion in the SiGe system is mainly through lattice diffusion, i.e. point defects, when the threading dislocation density is on the order of $10^5$ to $10^6 \text{ cm}^{-2}$ [61]. Recently, according to Gavelle et al. and Dong et al.’s work [68], [78], dislocations-mediated short-circuit diffusion is significant when the threading dislocation density is above $10^7 \text{ cm}^{-2}$. For our samples, the threading dislocation densities are in the range of $10^7$ to $10^8 \text{ cm}^{-2}$. Therefore, in the follow, we discuss only the first and second diffusion paths.

2.1.1 Point Defects: Vacancy and Interstitial

For Si (Ge) crystalline, point defect, in definition is constituted by anything other than a Si (Ge) atom on a lattice site. However, there are two principal types of point defects that act as vehicles for diffusion. One is simply a missing Si (Ge) lattice atom or vacancy, which we designate as V. The other is an extra Si (Ge) atom or interstitial, which we designate as I. The corresponding diffusion processes with Vs and Is are illustrated in Figure 2-1 and 2-2.

The idea that diffusion in Si (Ge) happens through vacancy-assisted and interstitial-assisted mechanisms has been widely accepted based on both experimental observations and theoretical calculations [76]. As shown in Figure 2-1, a vacancy adjacent to a moving atom provides a mechanism for the moving atom to hop to the adjacent site. This is precisely the diffusion mechanism that dominates in metals. However in Si (Ge) crystalline, a Si (Ge) interstitial
can also “kick out” a substitutional atom from its lattice site, or simply diffuses as a bound pair (known as the interstitialcy mechanism) to diffuse along the bond direction, as illustrated in Figure 2-2 (a) and (b). In most literature, both the kick-out and interstitialcy processes are simply referred to as interstitial-assisted diffusion [79].

Figure 2-1 Schematic of vacancy-assisted diffusion mechanism.

Figure 2-2 Schematic of interstitial assisted kick-out diffusion (a) and interstitialcy-assisted diffusion mechanism (b).
2.1.2 Doping Introduced Fermi-level Effect

Point defects in semiconductors can be neutral or exist in various electronic states. This is because point defects introduce energy levels into the band gap of a semiconductor [80]. Whether a defect is neutral or ionized depends on the position of the Fermi level. Consider the case with high n-type doping level, as illustrated schematically in Figure 2-3 [79]. In this situation, $E_F$ is above the $V^-$ level. Thus, this level will be populated by an electron; i.e., the vacancy will be acting as an acceptor and will be charged negatively. It is therefore that the dominant vacancy charge state will be $V^-$ and not the neutral vacancy.

Let us consider a point defect $X, X \epsilon (V,I)$. Suppose that both V$s and I$s exist in various charged states. The total concentration of the defect X at thermal equilibrium can be written as [80]:

$$C_X^{eq} = C_{X0}^{eq} + C_{X^-}^{eq} + C_{X=}^{eq} + C_{X^+}^{eq} + C_{X^{++}}^{eq},$$

(2.1)

where the concentration of uncharged defects, $C_{X0}^{eq}$, depends only on the temperature and pressure. The concentrations of charged defects can be presented as [80]:

---

Figure 2-3 Approximate location of charged vacancy energy levels in the silicon bandgap. $E_i$ is the intrinsic (without doping) Fermi level. $E_F$ is the Fermi level in N-type material. [79]
\[ C_{X^-}^{eq} = C_{X^0}^{eq} \exp\left( \frac{E_F - E_{X^-}}{kT} \right) \]  
(2.2)

\[ C_{X^=}^{eq} = C_{X^0}^{eq} \exp\left( \frac{2E_F - E_{X^-} - E_{X^=}}{kT} \right) \]  
(2.3)

\[ C_{X^+}^{eq} = C_{X^0}^{eq} \exp\left( \frac{E_{X^+} - E_F}{kT} \right) \]  
(2.4)

\[ C_{X^{++}}^{eq} = C_{X^0}^{eq} \exp\left( \frac{E_{X^{++}} + E_{X^=} - 2E_F}{kT} \right), \]  
(2.5)

where \( E_F \) is the Fermi level, which is a function of the doping concentration and the temperature:

\[ \frac{n}{n_i} = \exp\left( \frac{E_F - E_i}{kT} \right), \]  
(2.6)

where \( n \) is the electron concentration, and for high n-type doping level, \( n \approx \) dopant concentration; \( n_i \) is the intrinsic electron concentration. Combine Equations (2.1) – (2.6), the total concentration of defects is given by:

\[ C_X^{eq} = C_{X^0}^{eq} + C_{iX^-}^{eq} \left( \frac{n}{n_i} \right) + C_{iX^=}^{eq} \left( \frac{n}{n_i} \right)^2 + C_{iX^+}^{eq} \left( \frac{n}{n_i} \right)^{-1} + C_{iX^{++}}^{eq} \left( \frac{n}{n_i} \right)^{-2}, \]  
(2.7)

where \( C_{iX^{j\pm}}^{eq} \) denotes the equilibrium concentration under intrinsic condition (\( n = n_i \)) for defect \( X \) with charge state \( j \pm \). Since defects in various charge states act as diffusion-vehicles, diffusion in semiconductors is affected by the doping level. Similar to Equation (2.7), the diffusivity dependence on dopant in n-type doped semiconductor can be expressed as [79]:

\[ D = D_0 + D_- \left( \frac{n}{n_i} \right) + D_0 \left( \frac{n}{n_i} \right)^2 + D_+ \left( \frac{n}{n_i} \right)^{-1} + D_{++} \left( \frac{n}{n_i} \right)^{-2}, \]  
(2.8)

where parameter \( D_0, D_- \) and so forth, are chosen because on an atomic level, these different terms are thought to occur because of interactions with neutral and charged point defects. Experimentally, for n-type doped case, if the total interdiffusivity, \( D \), is linearly dependent on the ratio \( \frac{n}{n_i} D_- \left( \frac{n}{n_i} \right) \) term is dominant, and the interdiffusion is mostly mediated by \( V^1^\pm \) point defects.
If the total interdiffusivity, $D$, is quadratically dependent on the ratio $\frac{n}{n_i}$, $D = \left(\frac{n}{n_i}\right)^2$ term is dominant, and the interdiffusion is mostly mediated by $V^2$ point defects.

The diffusivity under intrinsic conditions, i.e. the doping level is less than $n_i$, is given by:

$$D_A^* = D_0 + D_+ + D_\pm + D_{++}, \quad (2.9)$$

For atoms like P and As, diffusion is mainly through neutral and negative charged point defects. The fourth term $D_+$, and the fifth term $D_{++}$ are neglected in literature [50]. With this simplification, for those that diffuse via neutral and negative charged point defects, the diffusion coefficient measure under extrinsic condition ($n > n_i$) can be elegantly described as [79]:

$$D_A^{\text{eff}} = D_A^* \left( \frac{1+\beta\frac{n}{n_i}+\gamma\left(\frac{n}{n_i}\right)^2}{1+\beta+\gamma} \right)^{1/2}, \quad (2.10)$$

where $\beta = D_-/D_0$ and $\gamma = D_\pm/D_0$. Expressed in this manner, the factor $\beta$ represents the linear variation in the diffusion coefficient in a doped material, which is related to $V'$ point defects, and $\gamma$ represents a square law variation in the diffusion coefficient in a doped material, which is related to $V^*$ point defects [79].

2.1.3 Line Defects: Dislocations

It is well established that dislocations and grain boundaries act as rapid diffusion short circuits in metals and also in non-metals such as ionic materials and semiconductors [77]. In general, short-circuit diffusion proceeds with lower activation energy than lattice diffusion.

In the devices based on SiGe thin films, the two most common types of line defects are misfit dislocations (MDs) and threading dislocations (TDs). Since the lattice constant of SiGe is larger than Si, in the early stages of SiGe epitaxial growth, the in-plane lattice constant of SiGe is
constrained by the Si substrate, resulting in the distortion of the cubic unit cell to a tetragonal cell. When an epitaxial layer is greater than the critical thickness, it is energetically favorable to generate dislocations to relieve the strain in the epitaxial layer [81]–[83]. As is shown in Figure 2-4, these dislocations exist as dislocation half-loops in the epitaxial layer [84]. Each dislocation half-loop is combined with one misfit dislocation which lies in the planes parallel to the interface, and two TDs arms lie in the closely packed (111) planes which is inclined at 60° with respect to the interface.

MDs play a key role in strain relaxation in multilayered thin films while TDs can act as high diffusivity paths (pipe effect) for diffusions in thin films [85]. As discussed in Section 1.3.3, the impact of TDs is dependent on Ge fraction and their density. In the thesis, TDs density is an important parameter to evaluate the dislocations-related diffusion.

![Figure 2-4 A schematic structure of a SiGe epitaxial thin film with a MD and TD in it [84].](image)
2.2 Material Characterization Techniques in Si-Ge Interdiffusion

As it is mentioned in Chapter 1, four aspects will impact the Si-Ge interdiffusion, i.e. Ge concentration, strain status, TDs density, and n-type dopants. The first three aspects have been well studied. The impact of n-type dopant, P, on Si-Ge interdiffusion is the topic of this study. Accordingly, in this work, different techniques were applied to characterize these aspects.

2.2.1 Secondary Ion Mass Spectrometry (SIMS)

The interdiffusion studied here is on the atomic scale, which requires high accuracy in characterizing concentration profiles. Secondary ion mass spectrometry (SIMS) is the most appropriate analytical technique for this study, because it has the highest detection sensitivity ($>10^{17} \text{ cm}^{-3}$) for measuring elemental concentrations, and can profile in the depth dimension with high precision [79].

![Figure 2-5 Schematic of SIMS process.](image-url)
The principle of SIMS technique is illustrated in Figure 2-5. The typical SIMS test area on a sample surface is around 200 × 200 µm [79]. This area is physically sputtered by an incident ion beam, and the sputtered atoms are then collected from a smaller, central probe area. Among the sputtered atoms, those that happen to be ionized atoms can be accelerated by an electric field, mass analyzed, and counted. By sputtering away the surface of the sample at a constant rate, a depth profile of the chemical species can be obtained.

SIMS is an excellent technique for profiling dopants in the SiGe system. However, a couple of effects in the SIMS analysis can influence the accuracy of the depth profile. First, in ultra-shallow depth profiling, a steady-state sputter rate may not be reached close to the surface, and the SIMS profile may be unreliable in this region [79]. Second, there is a knock-on effect caused by the ion beam that physically strikes and recoils the near surface target atoms into deeper layers, thus degrading the depth resolution for the target atoms [86], [87]. Third, profiling through a multilayer structure is difficult because the different materials have inherently different ion yields for the target atoms, leading to a “matrix effect” [79], which degrades the reliability of the measurement especially at the interfaces.

To achieve accurate depth profiles with the lowest knock-on and mixing effect, a general solution is to combine low ion beam energy with roughness suppression techniques [79]. In this thesis, samples in Chapter 3 and 4 were all performed SIMS measurements by Evans Analytical Group, which is the industry leader for commercial SIMS analysis. The samples were sputtered with a 1 keV Cesium (Cs) ion beam which is obliquely incident on the samples at 60° off the sample surface normal. The sputter rate was calibrated by a stylus profilometer that measures the sputtered carter depth. With the known sputter rate variation with SiGe composition, the sputter
rate was corrected on a point-by-point basis. The measurement uncertainty in Ge atomic fraction is ± 1%. The depth/thickness uncertainty is about 5%.

2.2.2 High Resolution X-ray Diffraction (HRXRD)

As strain impacts diffusion greatly, it is important to monitor the strain status of samples. HRXRD has been used for decades to investigate semiconductor structures. It is a powerful tool for non-destructive ex-situ investigation of epitaxial layers. From HRXRD, information about the composition and strain can be obtained [78], [88].

The principle of X-ray diffraction is illustrated in the figure below. The interaction of an X-ray beam with matter results in scattering by the electrons of atomic constituents. The scattering process is most easily understood by considering the diffraction of the X-ray beam from a plane
of atoms. From X-ray diffraction, the information about lattice constant could be obtained, which is determined by Bragg’s law:

\[ 2dsin\theta = n\lambda, \]

where \( d \) is the spacing between diffraction planes, \( \theta \) is the incident angle and \( \lambda \) is the wavelength of incident X-ray beam [89]. For a specified XRD equipment, \( \lambda \) is fixed. Strong diffraction occurs when incident angle \( \theta \) satisfies Equation (2.11). Therefore, the measurement of the incident angle of the X-ray beam is essential for the accuracy of results. For modern HRXRD, angular precision of tens of arc-seconds is achieved[79].

The measurements of samples in Chapter 3 were performed using a PANalytical X’Pert PRO MRD with a triple axis configuration available in the Semiconductor Defect Spectroscopy Laboratory at Simon Fraser University. Samples in Chapter 4 were performed in Advanced Materials and Process Engineering Laboratory (AMPEL) at UBC using a PANalytical X’Pert PRO MRD with a triple axis configuration. The X-ray tubes were all operated at 45 kV and 40 mA in the line focus mode. The \( Cu-K\alpha \) wavelength (\( \lambda = 1.5406 \text{ Å} \)) was selected by a monochromator, giving a collimated monochromatic beam.

According to Equation (2.11), XRD measurements can obtain the lattice constant that is perpendicular to the characterized plane. However, the value is determined by both strain and chemical composition of the sample. In this work, the information of chemical composition was obtained from SIMS analysis. The calculation of strain in epitaxial layer was then processed by PANalytical Epitaxy software to match the XRD peak separation between the peak from epitaxial layer and the peak from the substrate. Details of the calculation using the software were attached in the Appendix.
2.2.3 Measurement Techniques for Threading Dislocation Density

Conventionally, two methods are used to determine the dislocation density in semiconductor materials: transmission electron microscopy (TEM) and etch-pit-density (EPD) observation. TEM observation is the most reliable method. However, since this method requires large magnification, the detection limit of the dislocation density is high, which is only suitable to detect samples with high TDD (>10^8 cm^{-2}) [90].

On the other hand, EPD observation is suitable to detect samples with low TDD (<10^6 cm^{-2}). The process of EPD observation is usually done by etching and subsequent counting the etch pits in an optical microscope. When an etch solution is applied on the surface of a piece of material, the etch rate at threading dislocations is faster than other regions due to the lower energy barrier, which resulting in pits on the surface. However, sufficient etching depth is required to form large pits that can be easily observed under a microscope. Therefore, when the etch pits are large, the value of TDD will be underestimated because multiple dislocations may overlap in one etch pit [91].

Overall, EPD observation is suitable when TDD is less than 10^6 cm^{-2}, and TEM observation is suitable when the TDD is higher than 10^8 cm^{-2} [91], [92].

In Chapter 3, samples with Ge-on-Si epitaxial structures were characterized by EPD measurement. The Ge layer were etched with iodine (I_2) solution for 200 nm depth. The I_2 solution is a mixture of CH_3COOH (100 ml), HNO_3 (40ml), HF (10 ml), I_2 (30mg) [93]. The etch rate is approximately 200 nm/min. After etching for 20 seconds, 4 – 6 different positions with a size of 180 um × 180 um on the surface were imaged by an optical microscope with bright/dark field
modes, and the images were captured via a CCD camera. In Chapter 4, TEM samples were prepared and imaged in Advanced Nanofabrication, Imaging and Characterization Core Lab at King Abdullah University of Science and Technology (KAUST) using a Titan3 80-300 TEM. The thickness of the TEM-specimens was estimated to be around 100 nm by using low-loss EELS analysis. The TDs are estimated directly from these TEM images of the cross section of the samples. To obtain the TDD from cross-sectional TEM images, the number of TDs in a horizontal line were counted first. The dislocation density per unit length is the number of dislocations divided by the length in the TEM image. Finally, the TDD is the square of the dislocation density per unit length [94].

2.3 Interdiffusivity Extraction Method

In this work, the Si-Ge interdiffusivities were routinely extracted from the diffused Ge profiles of samples in Chapter 3 and 4 by Boltzmann-Matano analysis. Details of this method are discussed below.

2.3.1 Boltzmann-Matano Analysis

It is known that the equations governing common diffusion process in solid materials are Fick’s laws: the first law and the second law:

\[ J = -D \nabla C, \]

\[ \frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C), \]

where \( J \) is the diffusion flux, \( D \) is the diffusivity, \( t \) is the time, and \( C \) is the concentration.
When the interdiffusivity is concentration dependent, such as Si-Ge interdiffusivity, the shape of the diffused profile contains the information about the local diffusivity. The interdiffusivity can be extracted by the Boltzmann-Matano analysis as a function of the concentration [95], [96]. Based on Fick’s laws, the Boltzmann-Matano analysis is a graphical method to extract diffusivity from the shapes of diffused profiles. It has been widely used to extract interdiffusivity in binary metal alloys and Si [97]–[100]. The analytical expression for interdiffusivity extraction by the Boltzmann-Matano analysis is given by:

\[
D(C') = -\frac{1}{2t} \left( \frac{dz}{dC} \right)_{C=C'} \int_{C_L}^{C'} (z - z_M) dC,
\]

(2.14)

where \(D(C')\) is the interdiffusivity at Ge concentration \(C'\), \(t\) is the annealing time, \(z\) is the depth, \(z_M\) is the position of the Matano plane. The definition for Matano plane \(z_M\) should satisfy the following condition:

\[
\int_{C_L}^{C_R} (z - z_M) dC = 0,
\]

(2.15)
where \( C_R \) and \( C_L \) are two constant concentrations (R and L denoted for right and left), as shown in Figure 2-7. In addition, for the analysis to be valid, it is required that the interdiffusivity be expressed as a function of only the local Ge fraction \( x_{Ge} \). Besides, the diffusion profile should satisfy the initial and boundary conditions:

\[
C(\eta = \infty) = C_R, \quad (2.16)
\]
\[
C(\eta = -\infty) = C_L, \quad (2.17)
\]

and \( \eta \) is defined as:

\[
\eta = \frac{z}{\sqrt{t}} \quad (2.18)
\]

### 2.3.2 Time-Averaged Diffusivity –Boltzmann-Matano Analysis

In Xia’s analysis [60], when a SiGe epitaxial layer is grown on Si substrate with a low dislocation density \((<10^5 \text{ cm}^{-2})\), the Si-Ge interdiffusivity will be a function of Ge fraction only,
which satisfied the condition of Boltzmann-Matano analysis. However, for samples in Chapter 4 in this work, the condition that Si-Ge interdiffusivity is a function of Ge fraction only could not be fully satisfied. Firstly, the TDD in our samples is high ($\approx 10^8 \text{ cm}^{-2}$). The distribution of TDs and its impact on Si-Ge interdiffusivity are not dependent on Ge fraction only. Secondly, the concentration of P in our samples may also influence the Si-Ge interdiffusivity. Moreover, during the annealing process, the local dislocation densities and P concentration may change as a function of time, which makes the interdiffusivity time dependent.

Nevertheless, we can still extract an equivalent time-averaged diffusivity from a sample by Boltzmann-Matano analysis.

$$D(C') = -\frac{1}{2t_0} \left( \frac{dz}{dc} \right)_{C = C'} \int_{C_L}^{C'} (z - z_M) dC \quad (Temperature \ T = T_0), $$  \hspace{1cm} (2.19)

In this case, the physical meaning of the time-averaged diffusivity is: after annealing for time $t_0$ at temperature $T_0$, the diffusion profile of the sample can be reproduced with the time-averaged diffusivity, which is constant during the diffusion time.

In this work, before the analytical expression of the Si-Ge interdiffusivity is obtained, the time-averaged diffusivity was utilized as a reference, so that we could quantitatively compare the diffusivities of different samples with the same thermal budget.

2.4 Data Fitting and Numerical Simulations

In this work, the data fitting and numerical simulations were performed with software MATLAB provided by Mathworks. MATLAB is a powerful tool for numerical computation and visualization. It allows matrix manipulations, plotting of functions and data, implementation of algorithms, etc.
In Chapter 4, we implemented our Si-Ge extrinsic interdiffusivity model with MATLAB to simulate the Si-Ge interdiffusion. The process of the interdiffusion was simulated by finite difference time domain (FDTD) method, which is a classical method for diffusion simulation [79]. Details of this method and the Matlab code is attached in the section Appendix A.
Chapter 3: Enhanced Si-Ge Interdiffusion in High Phosphorus-doped Germanium on Silicon

As introduced previously in Section 1.3.4, n-type dopants such as As and P can accelerate Si-Ge interdiffusion. However, for impact of P on Si-Ge interdiffusion, only SiGe materials with low Ge fraction was reported. Device structures like Ge-on-Si lasers, the impact of P on Si-Ge interdiffusivity at high Ge end is in great need. Besides, previous reports are mainly phenomenological observation. The mechanism behind the impact is still unknown. In this chapter, to study the Si-Ge interdiffusion at high Ge concentration with the effects of P doping, samples with different P doping configuration were designed. This subject is of technical significance for the structure, doping and process design of Ge-on-Si lasers and Ge-based MOSFETs.

3.1 Experiments: Structure Design, Growth and Defect Annealing

Four Ge-on-Si structures were designed with different doping configurations, which are shown in Figure 3-1. Sample UGUS, UGPS, PGUS and PGPS stand for undoped Ge/undoped Si, undoped Ge/P-doped Si, P-doped Ge/undoped Si, and P-doped Ge/P-doped Si, respectively.

All the structures were grown in a reduced pressure chemical vapor deposition (RPCVD) system, ASM Epsilon 2000 model. A three-step Ge growth method was used, and the targeted Ge thickness was 1 μm. Step one was the low temperature (LT) growth at 400 °C to obtain a rather flat and continuous Ge seeding layer of about 100 nm thickness. Step two was low to high temperature (LT–HT) ramp at a rate of 6.5 °C per minute for temperature ranging from 400 °C to 600 °C. Step three was the HT growth at 600 °C to reduce the overall deposition time. Thermal
cycling was introduced immediately after the HT growth to enhance the surface mobility of the Ge atoms and also to reduce the threading dislocation density and confine the misfit dislocations at the Ge/Si interface. Post-deposition thermal cycling was performed by repeating (8×) a hydrogen annealing cycle between low annealing (T$_L$) and high annealing temperature (T$_H$) ranging from 680 °C to 725 °C, which was higher than the growth temperature of 600 °C at HT growth. Each annealing step at T$_H$ was 8 min, at T$_L$ was 1 min, and the annealing was performed in an H$_2$ environment to improve the quality of the Ge epitaxial film. This temperature is within the range of a typical defect annealing, or a drive-in annealing to diffuse P from delta-doped layers [101]. For samples with P doping, P was in-situ doped during the growth of samples.

Figure 3-1 Schematic diagrams of the structures in this work.
3.2 Results and Discussions

3.2.1 Concentration Profiles

Figure 3-2 and 3-3 show the Ge and P SIMS profiles, respectively. It is worth to mention that the profiles from different samples are shifted laterally. The reasons why doing that are the following: 1) during the epitaxial growth, a +/-3% cross-wafer thickness non-uniformity is typical, which shifts the Ge profile laterally and 2) the SIMS depth measurement uncertainty is about \( \pm 50\text{nm} \), which is close to the interdiffusion length (10~60 nm) of samples in this study. Therefore, one cannot use the absolute depth of the SIMS profiles due to the thickness/depth errors discussed above, even if the two samples are taken from the same wafer side by side. To compare the amount of interdiffusion, the slope of the Ge profiles is used as evaluation criteria. Steeper Ge profiles mean less interdiffusion and vice versa.

Before annealing, all samples have the same sharp Ge profiles at Ge/Si interfaces. From Figure 3-2, we can see that sample UGUS has the least interdiffusion while sample PGPS and PGUS have the largest. The interdiffusion profiles show a large Ge fraction dependence, where much more diffusion happens in high Ge regions than in low Ge regions. The interdiffusion regions for PGPS and PGUS are 225 nm thick if we define the interdiffusion region is from \( 0.02 < \chi_{\text{Ge}} < 0.98 \). It is 159 nm thick if we define the interdiffusion region as \( 0.05 < \chi_{\text{Ge}} < 0.95 \). The time-averaged interdiffusivity was extracted by the Boltzmann-Matano analysis and discussed in section 3.3.4.
Figure 3-2 Ge profiles measured by SIMS. The Ge profiles are shifted laterally for easy comparison. Dash line is the Ge profile of sample PGPS before annealing.

Figure 3-3 Phosphorus profiles measured by SIMS in sample PGPS, PGUS and UGPS after HT/LT annealing.
Figure 3-3 shows the P profiles of UGPS, PGUS and PGPS. The decreasing P profiles near surface show the surface transport and P evaporation. P peaks as high as $2 \times 10^{20}$ cm$^{-3}$ were measured in sample PGPS and PGUS at the Ge/Si interfaces. This highlights the P segregation behavior, as P tends to segregate towards Si and regions with high defect densities. In UGPS, where P was doped in the Si substrate, there is a P peak up to $3 \times 10^{19}$ cm$^{-3}$ at the Ge/Si interface as well.

Figure 3-4 shows the P and Ge SIMS profiles of sample PGPS without the HT/LT defect annealing. A high P peak of over $1 \times 10^{20}$ cm$^{-3}$ is seen. Similarly, a high P peak in the range of $10^{19} \sim 10^{20}$ cm$^{-3}$ at the Ge/Si interface was observed after P-doped Ge layer growing at 600 °C without any annealing in Ref. [102]. Therefore, the high P peak was formed during the Ge layer growth.
growth when P transported and segregated to the highly defected Ge seedling layer. It was not due to the HT/LT defect annealing afterwards.

3.2.2 XRD

The (004) symmetric XRD scans in Figure 3-5 show sharp Ge peaks, which means that the Ge films have a high crystal quality. In addition, the Ge peaks are asymmetric, and they are broadened on the side towards higher incidence angle. This broadening can be attributed to Si–Ge interdiffusion as seen from the SIMS data. The PGPS and PGUS samples have similar trends and more broadening than UGPS and UGUS, showing more interdiffusion, which is consistent with the SIMS profiles. The Ge peaks are shifted to the right compared to that of the Ge bulk substrate as a result of tensile strain. This tensile strain is thermally induced in the Ge epilayer during cooling after HT growth as Ge and Si have different coefficients of thermal expansion. The

![Figure 3-5 (004) symmetric XRD scans of the four structures. The angle is relative to the angle of the Si substrate peak.](image)

Figure 3-5 (004) symmetric XRD scans of the four structures. The angle is relative to the angle of the Si substrate peak.
tensile strain in the Ge layer was extracted by simulations with the PANalytical Epitaxy software package, which is 0.20%. Details of the simulation method was included in the Appendix.

3.2.3 EPD

Table 3-1 lists the average TDD values in the Ge films of the four samples measured by EPD. Details of the experiment are included in section 2.2.3. For the four samples characterized after thermal cycling, the TDD values were estimated to be in the range of \((2.0–5.3) \times 10^7 \text{ cm}^{-2}\). Within the error bar of the EPD technique, phosphorus doping does not appear to influence the TDD of the samples greatly. The TDD values for PGUS and PGPS samples with faster interdiffusion are less. Therefore, it is concluded that the Si–Ge interdiffusion differences in them samples are not due to TDD.

<table>
<thead>
<tr>
<th>Samples</th>
<th>UGUS</th>
<th>UGPS</th>
<th>PGUS</th>
<th>PGPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPD after HT/LT</td>
<td>((5.3 \pm 2.0) \times 10^7)</td>
<td>((4.8 \pm 2.0) \times 10^7)</td>
<td>((2.8 \pm 2.0) \times 10^7)</td>
<td>((2.0 \pm 2.0) \times 10^7)</td>
</tr>
</tbody>
</table>

3.2.4 Effective Interdiffusivity Extraction

Boltzmann–Matano analysis was used to extract the time-averaged effective interdiffusivity from the concentration profiles in Figure 3-2. It is worth comparing the extracted interdiffusivity of UGUS in this work with two relevant studies. Gavelle et al. [68] studied the interdiffusivity of highly defected Ge layer on Si substrate with a dislocation density of about \(10^{10}\)
cm$^{-2}$. Dong et al. [61] established thermodynamic model for Si–Ge interdiffusion with low defect density (about $10^5$ cm$^{-2}$) and no doping. The major thermal budget in this work was the HT anneals at 725 °C, which is different from the temperatures used in their work. To make the results comparable, interdiffusivities were calculated at 725 °C using models from Gavelle et al. and Dong et al.’s papers, as shown in Figure 3-6.

From Figure 3-6 we can see that, at the Si end, the time-averaged effective interdiffusivity extracted from UGUS is $2 \times 10^{-16}$ cm$^2$ s$^{-1}$, which is six orders of magnitude higher than the low-defect case and two orders of magnitude higher than the Gavelle et al.’s samples. At the Ge end,
the difference between the three interdiffusivities curves is within a factor of two. Also, the
interdiffusivity of UGUS is less dependent on the Ge concentration, showing almost constant
diffusivity for the $x_{Ge}$ range up to 80%.

From the SIMS data in Figure 3-2, we can see that in sample UGUS, the interdiffusion
happens mainly in the 100 nm thick Ge seeding layer. According to [103], TDD in Ge seeding layer
is larger than $10^{11} \text{ cm}^{-2}$. In addition, there is a high density of point defects in the seeding layer
[104]. As interdiffusion can be mediated both by threading dislocations and by point defects in
the lattice as seen in equation (3.1), the large effective interdiffusivity in UGUS can be attributed
to the highly defected Ge seeding layer. In [68], the dislocations-mediated term $\bar{D}_{\text{dislocation}}$ was
modeled to have a weaker Ge dependence than the point-defects-mediated term $\bar{D}_{\text{lattice}}$. In our
case, dislocation density in the seeding layer is even larger. $\bar{D}_{\text{dislocation}}$ dominates in the $x_{Ge} <
0.8$ region and is estimated to be $2 \times 10^{-16} \text{ cm}^{2} \text{s}^{-1}$. At the Ge end, according to Darken’s law,
$\bar{D}_{\text{lattice}} = D_{\text{Si,in,Ge}}$. Our extracted interdiffusivity $\bar{D}$ total at the Ge end (97% Ge) is $1 \times 10^{-15} \text{ cm}^{2} \text{s}^{-1}$. After excluding $\bar{D}_{\text{dislocation}}$ ($2 \times 10^{-16} \text{ cm}^{2} \text{s}^{-1}$), $\bar{D}_{\text{lattice}}$ is $8 \times 10^{-16} \text{ cm}^{2} \text{s}^{-1}$, which agrees the
reported Si diffusivity $8 \times 10^{-16} \text{ cm}^{2} \text{s}^{-1}$ in crystalline Ge in [55].

$$\bar{D}_{\text{total}} = \bar{D}_{\text{lattice}} + \bar{D}_{\text{dislocation}}$$  \hspace{1cm} (3.1)

Although the annealing in [61] and [68] was performed in an inert ambient, and our
samples were annealed in a hydrogen environment, no significance difference in Si–Ge
interdiffusion was reported for the anneals with two different gases.

Figure 3-7 compares the extracted time-averaged effective interdiffusivity from the four
structures, which were annealed using the same tool with the same recipe. PGPS and PGUS have
the highest interdiffusivity. Especially in $x_{Ge} > 0.7$ region, the interdiffusivity is 10–20 times of
that of UGUS and UGPS. For sample UGPS, the interdiffusivity is slightly higher than UGUS, about 2–3 times for $x_{Ge} > 0.7$ region. From our observation, as long as high P doping exists in the Ge side, the Si–Ge interdiffusivity will be greatly enhanced. Possible explanations are discussed in Section 3.3.

![Graph showing interdiffusivity comparison between UGUS, UGPS, PGUS, and PGPS](image)

**Figure 3-7** The time-averaged interdiffusivity from UGUS, UGPS, PGUS, and PGPS. The major thermal budget is the HT anneals at 725 °C.

### 3.2.5 P Segregation at Ge/Si Interface

As discussed above, P peaks were formed during the Ge layer growth before the HT/LT annealing. Figure 3-8 shows the P and Ge profiles of sample UGPS, PGUS, and PGPS. The Ge and P profiles of PGUS and UGPS are shifted for clarity. The relative positions of Ge and P profiles
from one sample are kept unchanged to help understand the Ge profiles in Figure 3-2 and the interdiffusivity extracted in Figure 3-7.

PGPS and PGUS have similar Ge profiles after HT/LT annealing, although PGUS has an undoped Si side before annealing. The P profiles of PGPS and PGUS are very similar as well. If we define the Ge/Si interface to be at $x_{Ge} = 0.5$ after diffusion, we can see that the P main peaks on the Si sides, and on the left of it, P concentration shoulders slightly inside Ge which is trapped by

![Ge and P Profiles](image)

*Figure 3-8 Ge and P profiles showing the P segregation at the Ge/Si interface. The Ge and P profiles of PGUS and UGPS are shifted laterally for clarity. The vertical solid lines indicate the Ge/Si interfaces defined as the $x_{Ge} = 0.5$.\*
defects in Ge seeding layers. For UGPS, only one P peak is observed on the Si side and is much lower than the counterparts in PGPS and PGUS.

This difference is a result of much faster P diffusion in Ge compared to that in Si during the growth of the samples. At 725 °C, intrinsic P diffusivity in Ge is $4 \times 10^{-14}$ cm$^2$ s$^{-1}$, four orders of magnitude higher than that of P in Si at $2 \times 10^{-18}$ cm$^2$ s$^{-1}$ [79], [102], [105]. This suggests for the PGUS and PGPS sample, the P atoms that forms the P peak at the Ge/Si interface was mainly from Ge side. The P segregation is essentially a diffusion process at the atomic scale. As P diffusivity in Ge is much faster than that in Si, the piling up process from the Si side towards the Ge seeding layer is much slower resulting in a much smaller P peak in UGPS. Together with the P profiles in Figure 3-8, it is concluded that P prefers to accumulate in the Si side.

### 3.3 Mechanisms of Enhanced Diffusion

From the experimental results above, we can see that as long as high P doping exists on the Ge side, the Si–Ge interdiffusivity will increase drastically. To interpret this phenomenon, a few possible mechanisms are discussed:

(1) **Defect density.** The possibility that this enhancement is due to a defect density difference is quite unlikely as the EPD levels of all samples are close.

(2) **Strain.** From our XRD results, Ge layers of all samples are under 0.2% tensile strain from thermal expansion coefficient mismatch. From the growth point of view, the Ge layers are much thicker than the critical thickness. There were no sources to introduce significant strain difference. Therefore, the enhanced interdiffusion cannot be a result of strain difference.
(3) Fermi-level effect. It is known that when a dopant concentration is close to or higher than the intrinsic carrier concentration $n_i$, the Fermi-level effect can change the charged defect concentrations and thus the diffusivity [79]. Figure 3-9 shows the ratio of $n/n_i$ at the diffusion temperature of 725 °C. The ratio depends on the local Ge fraction. The calculation of $n_i$ is based on equation (3.2) [106]:

$$n_i(x_{Ge}) = n_{i,Si} \exp\left(-\Delta E_g(x_{Ge})/2kT\right)$$

(3.2)

where $n_{i,Si}$ is the intrinsic carrier concentration of Si [79] and $-\Delta E_g(x_{Ge})$ is the bandgap difference between Si and relaxed SiGe [107]. The solid solubility limit of SiGe is linearly interpolated between Si and Ge. The P profiles are all below the solid solubility limit at

![Figure 3-9 Ratio of $n/n_i$ at 725 °C of sample PGPS, PGUS and UGPS in the interdiffusion regions. The curves are shifted laterally for clarity. The dotted lines indicate the ratio of P solubility over $n_i$.](image_url)
this temperature [108], [109]. We can see that for PGPS, PGUS and UGPS, the majority of
the Si–Ge interdiffusion regions has P concentration above $n_i$, which indicates that the
Fermi-level effect existed during the annealing. The regions with highest $n/n_i$ up to 130
are places with the P peaks, which correspond to 0%–80% Ge. Compared to PGPS and
PGUS, ratio $n/n_i$ for UGPS is much less, which is consistent with the observation of faster
interdiffusion with higher P peak.

It has been reported in the literature that Si diffusion in Ge and Ge diffusion in Si are both
mediated mostly by vacancies [55], [110]. Therefore, our results suggest that Si–Ge interdiffusion
with P doping is mediated by negative point defects. Future study is necessary to identify the
contributing defect type.

The mass transport processes active in the samples included P diffusion, P segregation
and Si–Ge interdiffusion happening simultaneously and are difficult to model at this point. The
difficulties exist in the following aspects:

(1) P distribution is hard to model as it requires accurate knowledge of P diffusivity and
segregation coefficient in $Si_{1-x}Ge_x$ for $1 \geq x_{Ge} \geq 0$ range and with high defect density
as in the Ge seeding layer, which are unavailable.

(2) The Fermi-level effect is hard to model in $Si_{1-x}Ge_x$ for $1 \geq x_{Ge} \geq 0$ range as it should
depend on $x_{Ge}$, and the knowledge of this dependence is still lacking.
3.4 Chapter Summary

To summarize, the Si–Ge interdiffusion is studied with different P doping configurations. Significant interdiffusion happened when the Ge layers are doped with P in high \(10^{18}\) cm\(^{-3}\) range, which resulted in a SiGe alloy region thicker than 150 nm after the HT/LT defect annealing. With high P-doped Ge, Si–Ge interdiffusivity is enhanced by 10–20 times in the \(x_{Ge} > 0.7\) region compared with the control sample without P doping. This phenomenon is attributed to the much faster P transport towards the Ge seeding layers from the Ge side during the Ge layer growth, which increases the negatively charged vacancy concentrations and thus the interdiffusivity due to the Fermi-level effect in Si–Ge interdiffusion.
Chapter 4: Quantitative Modeling of Si-Ge Interdiffusion with High Phosphorus Doping

In Chapter 3, it is concluded that high P doping concentration can accelerate Si-Ge interdiffusion greatly due to the Fermi-level effect. This effect is commonly seen in diffusion (e.g. P, B), which occurs mainly via charged point defects. However, up to now, no quantitative model has been built for extrinsic Si-Ge interdiffusion.

The difficulty in studying Si-Ge interdiffusion with P doping using Ge-on-Si structures comes from the fact that P has a very high segregation peak at Ge/Si interfaces. This peak is very hard to measure accurately by SIMS because it is narrow and at Si/Ge interfaces. SIMS accuracy is greatly degraded due to the knock-on effect at interfaces and the mixing effect of narrow concentration peaks [79], [86], [87]. Another difficulty is the existence of Ge seeding layers that is required for the subsequent Ge layer growth, where high concentrations of defects play an important role in the mass transport of P, Si, and Ge, which add another layer of complexity in the modeling of Fermi-level effect. To circumvent this problem, new structures were designed and measured. A quantitative model of this Fermi-level effect on Si-Ge interdiffusion was proposed to model the extrinsic interdiffusion behavior. According to our knowledge, it is the first time that quantitative modeling of Si-Ge extrinsic interdiffusion has been reported.

4.1 Experiments: Structure Design, Growth, and Annealing

According to reference [83] and [114], the diffusivity of P in SiGe material systems is a function of both the Ge fraction \( x_{Ge} \) and the concentration of P \( C_P \). In the meantime, the
interdiffusivity of Si-Ge is also strongly dependent on $x_{Ge}$ and $C_P$ [61], [112]. On top of that, P segregates to regions with lower Ge content [112]. That means P diffusion, segregation, and Si-Ge interdiffusion are coupled, and it is very hard to extract P diffusivity and Si-Ge interdiffusivity from experimental data if all three processes occur simultaneously. Therefore, in this study, new structures were designed to minimize the diffusion and segregation of P such that we can focus on Si-Ge interdiffusion.

As discussed in Chapter 3, P segregation is inevitable at Ge/Si interface due to large amounts of defects in Ge seeding layers and different chemical potentials of P on both sides. To avoid the complications from Ge seeding layers, a diffusion structure was designed to be far away from the Ge seeding layer/Si interface. In the meantime, the Ge fraction in the Si side was intentionally increased to lower the chemical potential difference between both sides. As is shown in Figure 4-1, a Ge/Si$_{1.0}$Ge$_{0.75}$/Ge multi-layer structure was grown on Si substrates with $x \approx 75\%$. The Si-Ge interdiffusion region of interest was then moved to the Ge/Si$_{1.0}$Ge$_{0.75}$ (denoted as the Interface I) and Si$_{0.75}$Ge$_{0.25}$/Ge (denoted as the Interface II) interfaces, which was 0.5 micron away from the Ge seeding layer/Si interfaces. Two P doping configurations were designed: Sample 7450 (S7450) with no P doping and Sample 7452 (S7452) with P doping at $5 \times 10^{18}$ cm$^{-3}$ in the Ge/Si$_{1.0}$Ge$_{0.75}$/Ge multi-layer structure.

Both samples were grown on (100) plane of 6 inches Czochrolski (CZ) Si wafers in an Applied Materials “Epi Centura” system. For S7450, a thin Ge seeding layer was grown at 365 °C. Next, a 500 nm Ge layer was deposited at 650 °C, and then a 300 nm of Si$_{0.25}$Ge$_{0.75}$ layer was grown at 525 °C. On top of the Si$_{0.25}$Ge$_{0.75}$ layer, another 250 nm Ge layer was grown at 365 °C under the seeding layer growth condition. Finally, a 5 nm thin silicon cap was grown on top at
625 °C to prevent Ge evaporation during annealing. For S7452, it was grown by the same procedure except that P was in-situ doped with $5 \times 10^{18}$ cm$^{-3}$ concentration level during the growth of the Ge/SiGe/Ge structure.

Before annealing, samples were capped with a SiO$_2$ layer at 80 °C by plasma-enhanced chemical vapor deposition (PECVD) to prevent Ge outdiffusion. Inert annealing was performed in nitrogen atmosphere using an enclosed Linkam TS1200 high-temperature heating stage. Two annealing conditions were designed for both samples: 1) 750 °C for 120 min; 2) 800 °C for 30 min. Trial annealing was performed and this final annealing conditions were chosen such that Si-Ge interdiffusion is not too little to be detected by SIMS or too large for diffusivity extraction using Boltzmann-Matano analysis.

![Figure 4-1 Schematic diagram of the samples used in this work. (a) Sample structure (b) Depth profile of sample 7450 with no P doping; (c) Depth profile of sample 7452 with P doping concentration at around $5 \times 10^{18}$ cm$^{-3}$.](image-url)
The temperature ramp up rate was set to be 100 °C/min, and the cooling was by water cooling, which was 200 °C/min. The amount of diffusion during the temperature ramp up and ramp down was negligible compared to the diffusion in the isothermal annealing step, which was later confirmed by simulations using the model established in this work (Appendix).

SIMS measurements were employed to obtain the as-grown and annealed Ge, P profiles of S7450 and S7452. HRXRD measurements were performed to get the strain status in both samples. TEM was used to check the material quality of the as-grown and annealed samples by our collaborator Dr. Dalaver Anjum at King Abdullah University of Science and Technology (KAUST).

4.2 Experiment Results and Discussions

4.2.1 Strain and Interdiffusion Characterizations by XRD

In order to study the strain status in the Ge and SiGe layer, HRXRD measurements were performed. Figure 4-2 shows the (004) symmetric XRD scans of as-grown and annealed samples of 7450 and 7452. For each sample, the strongest peak is from the Si substrate, and the peak on the left of it is from the SiGe layer. The second strongest peak is from the Ge layers. For S7450 and S7452, the peak positions are very close, which indicates the similar strain status for both samples. Compared to the as-grown samples, the Ge and SiGe peaks of annealed samples are asymmetric and broadened on the side towards each other. This broadening can be attributed to Si-Ge interdiffusion. For annealed S7452, the broadening is much more obvious than annealed S7450, indicating larger Si-Ge interdiffusion in S7452. With the Si substrate peak as a reference,
we can see that the peak from the SiGe layer shifted towards left after annealing. This result suggests that after annealing, the SiGe layer has a lower strain due to in-plane strain relaxation.

In addition, based on the peak positions from the (004) symmetric XRD scans and Ge fractions from the SIMS data in Section 4.2.2, the strain levels in the Ge and the SiGe layers were extracted using the PANalytical Epitaxy software package, which are summarized in Table 4-1. For S7450 and S7452, the strain status for corresponding layers is very close. The difference between strains is within 0.05%, which suggests P doping did not affect the strain status of samples. Besides, the Ge and SiGe layers are both in tensile strain. According to Xia et al.’s observation, the tensile strain does not affect Si-Ge interdiffusion [60]. Therefore, tensile strains were not included in the modeling.
Table 4-1 Strain statuses of the Ge and SiGe layers in sample 7450 and sample 7452 calculated from the XRD measurements. For annealed S7450 and S7452, the thermal budget was 750 °C 120 minutes.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Strain</th>
<th>S7450 As-grown</th>
<th>S7450 Annealed</th>
<th>S7452 As-grown</th>
<th>S7452 Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>Strain</td>
<td>0.10%</td>
<td>0.16%</td>
<td>0.13%</td>
<td>0.16%</td>
</tr>
<tr>
<td>SiGe</td>
<td>Strain</td>
<td>0.52%</td>
<td>0.38%</td>
<td>0.50%</td>
<td>0.33%</td>
</tr>
</tbody>
</table>

4.2.2 Concentration Profiling by SIMS

Figure 4-3 shows the Ge profiles obtained by SIMS from S7450 and S7452. To compare the amount of interdiffusion, the Ge profiles are shifted laterally, so the difference between two samples can be easily seen. We can see that S7450 and S7452 have similar as-grown profiles and they are very steep at the interfaces. For annealed S7450 (undoped), the interdiffusion of Si-Ge show a large Ge fraction dependence, where much more diffusion happens in higher Ge regions than in lower Ge regions. For annealed S7452 (P-doped), however, the difference is not as obvious. By comparison, in the higher Ge regions ($x_{Ge} > 0.9$), the amount of interdiffusion in S7452 is similar to that in S7450. However, in the lower Ge regions ($x_{Ge} < 0.9$), S7452 has much more interdiffusion.

Figure 4-4 shows the P profiles and the ratio of $n/n_i$ in S7452. As expected, from Figure 4.4 (a), P segregation is much more reduced compared to the cases of P at Ge seeding layer/Si interfaces. It is still observable as after annealing there are higher P concentration in the SiGe layer than in the surrounding Ge layers. In as-grown S7452, a P peak appears at the Interface I.
This P peak was formed during growth, and the P concentration in the top Ge layer is about two times of that in the bottom Ge layer, which is due to the growth temperature change. After annealing, P concentration decreased and the P peak at the Interface I also disappeared. According to Equation 2.10, \( n/n_i \) is an important parameter for the Fermi-level effect calculations, and higher \( n/n_i \) means stronger doping introduced diffusivity change. In Figure 4-4 (b), we can see the ratios of \( n/n_i \) are all larger than 1 before and after annealing, and the ratio in the lower Ge regions (\( x_{Ge} < 0.9 \)) is higher than 2. This is consistent with the observation that more Si-Ge interdiffusion happened in the lower Ge region of S7452. For higher Ge regions, however, the ratios of \( n/n_i \) are close to one (~1.5) which explains the much closer interdiffusion in the higher Ge regions (\( x_{Ge} > 0.9 \)) of S7452 and S7450.

Figure 4-3 Ge profiles measured by SIMS. (a) samples annealed at 750 °C, 120 minutes; (b) samples annealed at 800 °C, 30 minutes; The Ge profiles are shifted laterally for easy comparison.
4.2.3 TEM and Defect Density Characterization

Figure 4-5 shows the cross-sectional TEM images of S7450 and S7452 before and after annealing. We can see that for each sample, before annealing, there were clear boundaries at the interface I and interface II. However, after annealing, those boundaries became disruptive and wavy. Compared with annealed S7450, the boundaries of S7452 are more disruptive. Massive misfit dislocations were generated on the boundaries during annealing to relieve the tensile strain between layers, as shown in XRD results.

For multiple layer structures, the threading dislocation densities can be estimated from the TEM images. In Figure 4-5, TDs were pointed out by white arrows. Table 4-2 lists the average TDDs for S7450 and S7452 measured by TEM before and after annealing. Details of the experiment were include in Section 2.2.3. The TDDs are similar for upper and lower interface.
is found that under same conditions, the ratio between TDD of S7450 and S7452 is in the range of (0.5-2), which suggests P doping did not affect the TDD of the sample. Therefore, TDD of S7450 and S7452 can be considered to be at same order.

Figure 4-5 Cross-sectional (bright field) TEM of S7450 (no P) and S7452 (with P). (a) as-grown S7450; (b) annealed S7450; (c) as-grown S7452; (d) annealed S7452. Threading dislocations are pointed out by white arrows. For annealed samples, the thermal budget is at 800 °C for 30 minutes.
Table 4-2 Average TDD values of Ge/SiGe (upper) interface and SiGe/Ge (lower) interface of S7450 and S7452. The thermal budget for annealed samples is at 800°C for 30 minutes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ge/SiGe Interface</th>
<th>SiGe/Ge Interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>S7450 as-grown</td>
<td>4.3 × 10^8 cm^-2</td>
<td>1.2 × 10^9 cm^-2</td>
</tr>
<tr>
<td>S7452 as-grown</td>
<td>2.7 × 10^8 cm^-2</td>
<td>5.4 × 10^8 cm^-2</td>
</tr>
<tr>
<td>S7450-annealed</td>
<td>6.2 × 10^8 cm^-2</td>
<td>6.5 × 10^8 cm^-2</td>
</tr>
<tr>
<td>S7452-annealed</td>
<td>1.1 × 10^9 cm^-2</td>
<td>7.1 × 10^8 cm^-2</td>
</tr>
</tbody>
</table>

4.2.4 Intrinsic Interdiffusivity Extraction

According to Equation (2.10), to investigate the impact of the Fermi-level effect, intrinsic Si-Ge interdiffusivity is needed as the baseline. From the above discussion, S7450 and S7452 have same strain and defect conditions, and similar Ge profiles before annealing. Therefore, it is assumed that S7450 and S7452 have the same intrinsic Si-Ge interdiffusivity.

Based on the TEM measurements of TDD, the defect density of the top Ge layer, SiGe layer and the bottom Ge layer are close. Therefore, it is considered that for S7450, the Ge–Si interdiffusion only depends on the Ge content, which satisfies the condition of Boltzmann–Matano analysis. Interdiffusivity values were extracted from the Ge SIMS profiles of S7450 using Boltzmann–Matano analysis which gives Ge–Si interdiffusion coefficient as a function of the Ge concentration.

Figure 4-6 shows the extracted interdiffusivity at 750 °C and 800 °C respectively. Interdiffusivity data from two relevant studies were used for comparison. Gavelle et al. studied the interdiffusivity of highly defected Ge layer on Si substrate with a dislocation density of about 10^{10} cm^-2 [68]. Dong et al. established a reference line for Si–Ge interdiffusivity with low TDD.
(about $10^5 \text{ cm}^{-2}$) [61]. The TDD of this work is on the order of $10^8 \text{ cm}^{-2}$, which is in the middle. For the high Ge region ($x_{Ge} > 0.9$), the extracted interdiffusivities of S7450 are within a factor of two compared to the reference diffusivities. This range is commonly seen in the diffusion studies in semiconductors (as diffusivities in Figure 1-5). Samples from different groups are not fully comparable. The interdiffusivities difference is due to different materials quality (TDD levels), temperature calibration, or errors from characterization equipment, etc.

From Figure 4-6, at 800 °C, it can be seen that the interdiffusivity of S7450 is in good agreement with Dong et al.’s value. At 750 °C, however, in the low Ge regime the extracted interdiffusivity is close to Gavelle et al.’s value, which is about five times higher than Dong et al.’s value. It was found that the extrapolated values of our experimental value (black dash line) from high Ge ($0.95 < x_{Ge} < 0.98$) regime to $x_{Ge} = 0.78$, is in good agreement with Dong et al.’s value. This phenomenon is due to the high TDD at the interface I and II, which accelerate the interdiffusion. The acceleration effect of TDs is more obvious in the lower Ge region [60], [68].

![Figure 4-6 Ge–Si interdiffusion coefficients as a function of Ge content at 750 and 800 °C, which were extracted from S7450 using Boltzmann–Matano analyses in comparison with literature models at the same temperature. Dashed lines show the extrapolation of our experimental values of S7450 annealed at 750 °C.](image)
With this intrinsic interdiffusivity, in the next section, we will build a model to describe the impact of the Fermi-level effect on Si-Ge interdiffusivity.

4.3 Modeling of the Fermi-level Effect on Si-Ge Interdiffusion

It is known that when a dopant concentration is close to or higher than the intrinsic carrier concentration $n_i$, the Fermi-level effect can change charged defect concentrations and thus the diffusivity [79], [80]. From the experiment result of Chapter 3, Si-Ge interdiffusion is mediated by negative vacancies. In $\text{Si}_{1-x}\text{Ge}_x$, it has been shown that both Si and Ge diffusion is vacancy mediated when Ge fraction is larger than 0.3 [53], [56], [57]. In sample 7452, the Ge fraction is above 0.75. In addition, according to the observation of Gavelle et. al. [68], when Ge layer is p-type doped, the Si-Ge interdiffusion is retarded, which suggests that the contribution of positive vacancies is negligible for the interdiffusion. Therefore, only negatively charged vacancies were considered in this model.

For Si-Ge interdiffusion, the total interdiffusion coefficient is given by the sum of the individual contributions of $D_{\text{Si},\text{Ge}}^{V_{r-}}$, i.e.:

$$D_{\text{total}} = \sum_{r=0}^{2} D_{\text{Si},\text{Ge}}^{V_{r-}} = \frac{1}{C_0} \sum_{r=0}^{2} f_r C_{eq}^{V_{r-}} D_{V_{r-}}^r,$$

where $C_0$ is the atom density of $\text{Si}_{1-x}\text{Ge}_x$; $f_r$ is the diffusion correlation factor. For diffusion via vacancies in diamond structures like in $\text{Si}_{1-x}\text{Ge}_x$, $f_r$ is considered to be independent of the charge state and is set to be $f_r = f_V = 0.5$ [113]; $C_{eq}^{V_{r-}}$ is the thermal equilibrium concentration of $V_{r-}$ point defects, and $D_{V_{r-}}$ is the diffusion coefficient mediated by $V_{r-}$ with $r \in \{0,1,2\}$, respectively. Assume $D_{V_{1-}} = m_1 D_{V^0}$ and $D_{V_{2-}} = m_2 D_{V^0}$, where $m_1, m_2$ are fitting parameters. Therefore, Equation (4.1) can be transformed as:
\[ D_{\text{total}} = D_{V^0} \frac{c_{V^0}^{eq}}{c_0} f_r \left( 1 + m_1 \frac{c_{V^{-}}^{eq}}{c_{V^0}^{eq}} + m_2 \frac{c_{V^{-2}}^{eq}}{c_{V^0}^{eq}} \right), \] (4.2)

The electronic states of vacancies depend on the energy levels that are introduced by \( V^{-} \) into the band gap of a semiconductor. The occupation of these energy levels depends on the position of the Fermi level \( E_f \). Meanwhile, \( E_f \) is a function of the dopant concentration. If the charge carrier concentration introduced by dopants exceeds the intrinsic carrier concentration \( n_i \), the Fermi level \( E_f \) will deviate from its intrinsic position, \( E_i \). As a result, the ratio of the charged V concentration to the neutral V concentration is given by Equation (2.2) and (2.3). These two equations neglect the spin degeneracy and degeneracy of the valence band. Although this approximation slightly alters the calculation of the position of the energy levels and the concentration ratio, the main results on the level ordering and the contribution of \( V^{-} \) to diffusion remain unchanged.

Combining Equation (4.2) with Equation (2.2), (2.3) and (2.6), the total diffusion coefficient can be expressed as:

\[ D_{\text{total}}(n) = D_{V^0} \frac{c_{V^0}^{eq}}{c_0} f_r \left[ 1 + \sum_{r=1}^{2} \left( \frac{n}{n_i} \right)^r m_r \exp \left( \frac{rE_i - \sum_{n=1}^{r} E_{V^{-n}}}{kT} \right) \right] \] (4.3)

when \( n = n_i \), the total diffusion coefficient is equal to the intrinsic interdiffusivity, \( D(n_i) \).

Therefore, the ratio between extrinsic and intrinsic diffusion coefficient is:

\[ \frac{D(n)}{D(n_i)} = \frac{1 + \sum_{r=1}^{2} \left( \frac{n_i}{n_i} \right)^r m_r \exp \left( \frac{rE_i - \sum_{n=1}^{r} E_{V^{-n}}}{kT} \right)}{1 + \sum_{r=1}^{2} m_r \exp \left( \frac{rE_i - \sum_{n=1}^{r} E_{V^{-n}}}{kT} \right)}. \] (4.3)

For simplicity, we denote:

\[ \beta = m_1 \exp \left( \frac{E_i - E_{V^{-}}}{kT} \right), \] (4.4)

\[ \gamma = m_2 \exp \left( \frac{2E_i - E_{V^{-1}} - E_{V^{-2}}}{kT} \right), \] (4.5)
where $\beta$ is related to the interdiffusion process mediated by $V^-$ point defects and $\gamma$ is related to the interdiffusion process mediated by $V^+$ point defects. Therefore the interdiffusion coefficient as the function of electron concentration can be described as:

$$D(n) = D(n_i) \frac{1 + \beta \frac{n}{n_i} + \gamma \left( \frac{n}{n_i} \right)^2}{1 + \beta + \gamma} \equiv D(n_i) \times FF,$$

(4.6)

which has the same form as that in dopant diffusion shown in equation (2.10). The term

$$\frac{1 + \beta \frac{n}{n_i} + \gamma \left( \frac{n}{n_i} \right)^2}{1 + \beta + \gamma}$$

is referred as the Fermi-enhancement factor (FF) in the discussions below.

In this study, $D(n_i)$ is the extracted interdiffusivity of S7450. Considering the charge neutrality equation $n = p + C_P$ and $n_i^2 = np$, the electron concentration $n$ of the P-doped Si$_{1-x}$Ge$_x$ samples can be expressed as:

$$n(x_{Ge}) = \frac{C_p + \sqrt{C_p^2 + 4n_i^2(x_{Ge})}}{2},$$

(4.7)

where the calculation of $n_i(x_{Ge})$ is based on Equation (3.2).

For $\beta$ and $\gamma$ in Equation (4.4) and (4.5), the energy term $rE_i - \sum_{n=1}^{r} E_V^{n-} \ (r \in \{1, 2\})$ is a function of Ge fraction in Si$_x$Ge$_{1-x}$. However, due to limited literature resources of the energy levels of $V^-$ and $V^{2-}$ in SiGe, i.e. $E_V^{-}(x_{Ge})$, and $E_{V^{2-}}(x_{Ge})$, for Ge fraction ranges from 75% to 100%, this terms was linearly interpolated between the value in Si and Ge, i.e.:

$$A_{r, SiGe}(x_{Ge}) = A_{r, Si}(1 - x_{Ge}) + A_{r, Ge}x_{Ge}, \ (0.75 < x_{Ge} < 1),$$

(4.8)

where $A_{r, SiGe}$ refers to the energy term $rE_i - \sum_{n=1}^{r} E_V^{n-} \ (r \in \{1, 2\})$ in SiGe. For Si, $A_{1, Si} = 0.1383 \text{ eV}$ and $A_{2, Si} = -0.1835 \text{ eV}$ [79]. For Ge, $A_{1, Ge} = -0.1134 \text{ eV}$ and $A_{2, Ge} = 0.0866 \text{ eV}$ [114].
With these parameters, the exponential terms in Equation (4.4) and (4.5) can be calculated. For the Ge fraction ranges from 0.75-1, $\exp\left(-\frac{E_i-E_V}{kT}\right)$ in Equation (4.4) is in the range of 0.56-0.28, and $\exp\left(-\frac{2E_i-E_{V1}-E_{V2}}{kT}\right)$ in the range of 0.28-0.37. The only unknown parameters in this model are constants $m_1$ and $m_2$ in Equation (4.4) and (4.5).

![Graph](image)

**Figure 4-7** (a) Impact of $m_1$ to Fermi-enhance factor with $m_2 = 1$; (b) Impact of $m_2$ to Fermi-enhance factor with $m_1 = 1$. For both calculations, the temperature was fixed at 750 °C, $x_{Ge} = 0.85$ and $n/n_i = 5$.

The impacts of $m_1$ and $m_2$ to Fermi-enhancement-factor are shown in Figure 4-7. When other parameters remain unchanged, as $m_1$ increases, the value of FF gradually approaches the reference line of $n/n_i$, which suggests that the interdiffusivity is almost proportional to $n/n_i$ when $m_1 > 20$. According to Equation (2.8), this indicates that the interdiffusion is dominated by $V^-$ point defects. Similarly, as $m_2$ increases, the value of FF gradually approaches the reference line of $n^2/n_i^2$, which suggests that the interdiffusivity is almost proportional to $n^2/n_i^2$ when
According to Equation (2.8), this indicates that the interdiffusion is dominated by $V^{2-}$ point defects.

4.4 Simulation Results and Predictions

4.4.1 Simulations of Extrinsic Si-Ge Interdiffusion

According to Equation (4.6) and (4.7), the extrinsic interdiffusion coefficient increases with the concentration of P. However, as shown in Figure 4-4 (a) that during annealing, the concentration profile of P in S7452 changed due to P diffusion and segregation. Ideally, it is best to simulate P diffusion, P segregation and Si-Ge interdiffusion simultaneously. However, the diffusion and segregation of P involve many unknown coefficients such as the P segregation coefficients in high Ge regime, which are beyond the scope of this study.

Therefore, in this simulation study, an approximation method was used that treated P concentration profile as unchanged during the process of Si-Ge interdiffusion in the Ge valley regime of S7452. This approximation is supported by two considerations: 1) the change from the as-grown P profile to the annealed P profile is small, which is from $2 \times 10^{19}$ to $8 \times 10^{18}$ cm$^{-3}$ in most regions of interest, and 2) P diffuses much faster than Si-Ge interdiffusion, e.g., $D_P$ in SiGe is about 100 times larger than $\bar{D}_{SiGe}$ [61], [102], [115], it is assumed that most P transportation happened before Si-Ge interdiffusion. Therefore, we took the annealed P concentration profile and selected the middle value in Figure 4-4 (a), i.e. P concentration profile in S7452 annealed at 800 °C for 30 minutes, as our background P doping profile in our simulation and assumed this
profile was unchanged during the interdiffusion. Figure 4-8 shows the revised $n/n_i$ profiles at 750 °C and 800 °C before annealing.

![Figure 4-8 The $n/n_i$ profiles at 750 °C and 800 °C before annealing. Dash line is the Ge fraction profile of as-grown S7452.](image)

The simulation was done by Matlab to calculate $D(n)$ in Equation (4.6) and to simulate diffusion profiles using Fick’s second law:

$$\frac{\partial c_{Ge}}{\partial t} = \frac{\partial}{\partial z} \left( D(n) \frac{\partial c_{Ge}}{\partial z} \right).$$

(4.9)

To solve the diffusion equation numerically, finite difference time domain (FDTD) method was used. Details of this method are included in Appendix A. Numerically, we treated the sample as 1D material and divided up the samples into planes with different Ge concentration. The distance between each plane $\Delta x$ is 1nm. The total annealing time $t$ is divided into many small time period of $\Delta t$ (0.1 second). The experimental data of as-grown Ge profile of S7452 is used as the initial profile of the simulation. The boundaries are chosen to be away from the interdiffusion region according to experimental data, and at the boundaries, the Ge concentration was fixed. Two
simulations were carried out with different annealing conditions that are the same as in the experiments. One is at 750 °C for 120 min, and the other is at 800 °C for 30 min.

By using different values of $m_1$ and $m_2$, we obtained several simulated Ge profiles, as shown in Figure 4-9. As we can see in Figure 4-9, $m_1$ was fixed to 1 and $m_2$ ranged from 1 to 100. When $m_1 = 1$ and $m_2 = 1$, the simulated interdiffusion at both temperatures was slower than the experimental interdiffusion profiles. Since increase $m_1$ will lower the FF, according to Figure 4-7 (a), the value of $m_2$ was adjusted in our simulation. As $m_2$ increases, the simulated interdiffusion becomes larger and is very close to the experimental profiles. Moreover, the simulated results become insensitive of $m_2$ when $m_2 \geq 20$. This is consistent with Figure 4-7 (b), when $m_2 \geq 20$, FF increases very slowly with $m_2$ and is approaching $n^2/n_i^2$. Therefore, our simulation suggests that for Si$_{1-x}$Ge$_x$ with $0.75 < x_{Ge} < 1$, the quadratic term dominates, which means that the Si-Ge interdiffusion is dominated by $V^{2-}$ point defects.

With the best-fitting parameters ($m_1 = 1$, $m_2 > 20$), Figure 4-10 shows the value of FF in S7452. According to Equation (4.6), the impact of Fermi-level effect depends on the ratio of $n/n_i$ which is a function of P concentration. The FF profiles are noisy, which resulted from the noisy P profiles from SIMS results. The tendency of the variation of FF with depth is the same as $n/n_i$, which is shown in Figure 4-8. For low Ge fraction region (Ge valley in the Figure), the interdiffusion has been enhanced over 8 times at 750 °C, and about 6 times at 800 °C. At the Ge/SiGe interfaces, FF ranges from 2 to 6 at 750 °C, and 2 to 4 at 800 °C.
Figure 4-9 Comparison between SIMS data of S7452 and simulated results by using extrinsic Si-Ge interdiffusion model (a) At 750 °C for 120 minutes; (b) At 800 °C for 30 minutes. $m_1$ is fixed to 1 in each simulation and $m_2$ is 1, 5, 20, 40, 100 separately.
According to our fitting results, $m_1 = 1$ and $m_2 \geq 20$ fit the experimental diffusion profiles well. We chose to have $m_2 = 40$. Then we used the model in Equation (4.4-4.6) and the best fitting parameters to predict the impact factor of the Fermi-level effect as a function of $x_{Ge}$, n-type dopant concentration, and temperature. Figure 4-10 shows the dependence of Fermi-enhancement factor on different impact factors. In Figure 4-10 (a), the FF is almost proportional to $n^2/n_i^2$. According to our simulation, for light n-type doping with $n/n_i = 2$, $x_{Ge} = 0.85$ at 750 °C, the FF is close to 4, which indicates the extrinsic interdiffusion coefficient is almost four times higher than intrinsic value. Therefore, in the case of heavy n-type doping, the Fermi-level effect on Si-Ge interdiffusion should not be ignored. In Figure 4-10 (b), for a SiGe wafer doping with P at $10^{19}$ cm$^{-3}$, as temperature decreases in the range of this study, the impact of the Fermi-level effect becomes more obvious. From 800 to 750°C, the enhancement of the FF is about 36%. 

Figure 4-10 The values of Fermi-enhancement factor at different temperatures as a function of depth. Dash line is the Ge profile of as-grown S7452. $m_1 = 1$ and $m_2 = 40$ were used in the calculation.
In Figure 4-10 (c), for $n/n_i = 4$ at 750 °C, the FF increases with Ge fraction. However, our simulation shows this dependence is not sensitive. The difference of FF between $x_{Ge} = 0.75$ and $x_{Ge} = 1$ is within 4%. This indicates that for $x_{Ge}$ in the range of 0.75-1.00, the mechanism of Si-Ge interdiffusion is similar, i.e. $V^{2-}$ point defects are dominant for Si-Ge interdiffusion.

![Figure 4-11 Dependence of Fermi-enhance factor on different factors. (a) FF dependence on $n/n_i$ with Temperature at 750 °C and $x_{Ge} = 0.85$; (b) FF dependence on Temperature with P doping concentration at $10^{19}$ cm$^{-3}$ and $x_{Ge} = 0.85$; (c) FF dependence on Ge fraction with Temperature at 750 °C and $n/n_i = 4$.](image-url)
4.5 Chapter Summary

In summary, the impact of the Fermi-level effect on Si-Ge interdiffusion in Ge/Si$_{1-x}$Ge$_x$/Ge multi-layer structure was investigated by both experiments and theoretical analysis. Experiments on Si-Ge interdiffusion under high P doping level with Ge fraction range from 0.75 to 1 revealed an accelerated Si-Ge interdiffusion compared to intrinsic conditions. The doping dependence of the Si-Ge interdiffusion can be described by the following equation:

$$ D(n) = \frac{D(n_i)}{D(n_i)} \equiv FF = \frac{1 + \sum_{r=1}^{2} \frac{n}{n_i} r m_r \exp\left(\frac{rE_i - \sum_{n=1}^{r} Ev_{n^-}}{kT}\right)}{1 + \sum_{r=1}^{2} m_r \exp\left(\frac{rE_i - \sum_{n=1}^{r} Ev_{n^-}}{kT}\right)} (m_1 = 1, m_2 \geq 20) $$

The Fermi-enhancement factor was shown to have a dependence on the temperature and a weak dependence on the Ge fraction. The fitting results showed that for Si-Ge interdiffusion coefficient with Ge fraction $> 0.75$, the interdiffusivity is proportional to $n^2/n_i^2$, which indicates that the interdiffusion in high Ge fraction is dominated by $V^{2-}$ defects.
Chapter 5: Summary and Future Work

5.1 Thesis Summary

Ge, as the most Si-compatible semiconductor, plays an important role both in Si photonics and Ge-based MOSFET. The recent development of n-type doped Ge-on-Si laser devices has brought Ge under the spotlight. As stated in Chapter 1, Ge-on-Si laser device is a promising solution to increase the interconnect speed and lower the power consumption with continued scaling chips.

Recently, adding high n-type doping and small tensile strain (~0.2%) in Ge have made Ge lasers possible. The optimization of n-type doping technology requires the precise evaluation of the Ge concentration in the sample and the understanding of the Si-Ge interdiffusion mechanism under high n-type doping condition.

This work contributes to the area of Si-Ge interdiffusion under high n-type doping condition both by experiments and theoretical modeling:

1. To observe the impact of P on Si-Ge interdiffusion, we designed the Ge-on-Si structure with four different P doping configurations. By SIMS analysis, significant Si-Ge interdiffusion was observed when the Ge layers are doped with P in high $10^{18}$ cm$^{-3}$ range, which resulted in SiGe alloys regions thicker than 150 nm after the HT/LT defect annealing. Besides, it was observed that P tends to segregate at the Ge-Si interface due to different diffusion coefficient for P in Ge and Si and high density of P traps (defects) at the interface. With high P concentration doped Ge, the Si-Ge interdiffusivity is enhanced by $10^{-20}$ times in the $x_{Ge} > 0.7$ region compared with the interdiffusivity of the control sample without P doping.
Further characterization of XRD and EPD results showed samples strain and dislocation density condition. After ruling out the interference of strain and dislocations, we attributed this phenomenon to the much faster P transport towards the Ge seeding layers from the Ge side during the Ge layer growth, which increases the negatively charged vacancy concentrations and thus the interdiffusivity due to the Fermi-level effect in Si-Ge interdiffusion.

2. To further understand the impact of the Fermi-level effect on Si-Ge interdiffusion, we designed the Ge/Si$_{0.25}$Ge$_{0.75}$/Ge multilayered structure with different P doping configurations. We proposed the extrinsic n-doped Si-Ge interdiffusion model with the Fermi-enhance factor to describe the impact of the Fermi-level effect. The validity of the extrinsic model was proved by the comparisons between the simulations and the SIMS data from experiments with different anneal temperatures and Ge fraction range at $0.75 < x_{Ge} < 1$. It was demonstrated by our model when the Ge fraction range is at $0.75 < x_{Ge} < 1$, the acceleration of the Fermi-level effect to Si-Ge interdiffusion is close to the quadratic ratio of electron concentration to the intrinsic electron concentration, i.e. $n^2/n_i^2$. This result suggested that for high Ge fraction, Si-Ge interdiffusion is dominated by $V^{2-}$ point defects.

5.2 Technological Implication

The results of this thesis have some impact on the design of Ge-on-Si lasers. Given that high concentrations of P accelerate Si–Ge interdiffusion drastically, for a Fabry–Perot laser with
a Ge layer thickness of several hundreds of nanometers, an interdiffused region can change a significant portion of the active Ge layer back to SiGe alloys and thus greatly offset the effort in making Ge into a direct bandgap material. A possible solution would be to use a bonding and etch-back approach, to make a GOI structure where the interdiffusion region is polished off [116]. This method, however, is not ideal due to the heat dissipation problem with the buried oxide. Another approach is to use higher stress to lower the requirement on high n-type doping, which will reduce the free carrier absorption and the lasing threshold at the same time. Also, it is a much better solution to overcome the interdiffusion introduced problems.

5.3 Future Work

In this thesis, the Si-Ge interdiffusion under P highly doping condition has been successfully modeled. This model can be used to predict n-type doped extrinsic Si-Ge interdiffusion with high Ge fraction. However, due to the scope of this thesis, many aspects of extrinsic Si-Ge interdiffusion are not addressed in this work, and can be topics for future studies:

Topic 1: Simulate P diffusion and Si-Ge interdiffusion simultaneously. It is known the diffusivity of P in SiGe material systems is a function of both Ge fraction \( x_{Ge} \) and the concentration of itself \( C_P \). In the meantime, the interdiffusivity of Si-Ge is also strongly dependent on \( x_{Ge} \) and \( C_P \). On top of that, P segregates to regions with lower Ge content. That means P diffusion, segregation, and Si-Ge interdiffusion are coupled, and it is very hard to extract P diffusivity and Si-Ge interdiffusivity from experimental data if all three processes occur simultaneously. In this work, P diffusion in Chapter 4 was neglected to simplify the simulation. However, in reality, there are many cases that P diffusion are significant, such as Ge-on-Si laser
with asymmetric P doping concentration in Ge and Si side. For better prediction, it is highly recommended to build a multi-element (P, Si, and Ge) diffusion model to simulate the n-type doped Si-Ge system.

**Topic 2: Simulate extrinsic Si-Ge interdiffusion over the full Ge range.** Theoretically, this work has built the expression of this topic as shown in equation (4.11). However, due to the limited literature resources, the energy level of \( V^- \) for the full Ge range is not available. For narrow Ge ranges, these parameters can be obtained by linear interpolation. However, for full Ge range, such approximation may cause errors. Besides, another challenge for modeling is the huge P segregation peak on the Si/Ge interface. As shown in Chapter 3, during annealing, the P peak will be moving along with the direction of Ge diffusion. Such P peak will greatly enhance the Si-Ge interdiffusion. However, the segregation coefficients of P over the full Ge range are not available. Therefore, precise simulation of both P diffusion in SiGe and Ge-Si interdiffusion over the full Ge range are needed.

**Topic 3: Simulate Ge-Si interdiffusion for other dopants.** In this thesis, only P is used as the dopant in our samples. Although there are reports about the impacts of Arsenic (As) and Boron (B) doping on Si-Ge interdiffusion. No numerical simulation has been done with those dopants. For Ge-on-Si laser and Ge based MOSFET, As and B are also candidate dopants. Furthermore, even we have proven that Si-Ge interdiffusion is dominated by \( V^{2-} \) point defects in the high Ge range, only one type of dopant cannot consolidate this conclusion. It is better to confirm our conclusion with other dopants.
References


Appendices

Appendix A: Overview of the Simulation Implement in Matlab™

In this work, we used Matlab™ to simulate Si-Ge interdiffusion in SiGe heterostructure. To solve the diffusion equation numerically, finite difference time domain method was used. Numerically, we divided up the samples into planes $\Delta x$ apart, labeled 0, 1, 2 ..., and at each plane, the concentration of atoms is $C_0, C_1, C_2$ ... . For the annealing time, the total time $t$ was divided into $N$ periods with $\Delta t$ for each period. Therefore at plane $i$, the analytical equation of Fick’s second law can be written numerically as:

$$\frac{C_i^+ - C_i}{\Delta t} = D_i \frac{C_{i+1} - C_i + C_{i-1} - C_i}{\Delta x^2},$$  \hspace{1cm} (A1)

where $D_i$ is the diffusion (interdiffusion) coefficient in each plane and $C_i^+$ is the atom concentration at plane $i$ after time period $\Delta t$. Therefore, after each period $\Delta t$, the concentration of atoms in each plane can be expressed as:

$$C_i^+ = C_i + \frac{D_i \Delta t}{\Delta x^2} (C_{i+1} - 2C_i + C_{i-1}).$$  \hspace{1cm} (A2)

Given the initial concentrations at different places and boundary conditions, we can calculate the subsequent concentration after time $t$. However, parameters $\Delta t$ and $\Delta x$ should be chosen such that they are relevant to the problem we are attempting to solve. For example, $\Delta x$ should be such that the profile is uniformly divided up into a sufficient number of distance intervals that the profile can be fitted in a reasonable manner by these piecewise linear approximations. Similarly, $\Delta t$ should be chosen so that the time interval is divided into a sufficient number of time steps to resolve the diffusion process. In addition, parameters, $\Delta x$ and $\Delta t$, should satisfy $\frac{D_i \Delta t}{\Delta x^2} \leq \frac{1}{2}$ such that $C_i^+$ will always larger than 0.
The codes of the modeling in Matlab™ are shown as follows:

%written by Feiyang
%This program is used for modeling Si-Ge interdiffusion in S7452
%
clear variables;
%close all;

Temp = 800;
time=30*60; dt=0.1; %unit sec
dx=1e-7; depth=130e-7:dx:750e-7; % unit cm; depth range: 130nm~750nm (valley)

Xge_asgrown = fileRW(depth,'S7452_DepthvsXGe_asgrown.txt'); %initial profile
Xge_anneal = fileRW(depth,'S7452_DepthvsXGe_800C30min.txt');
Phos = fileRW(depth,'S7452_DepthvsPhos_800C30min.txt');

% Xge_asgrown = fileRW(depth,'S7452_DepthvsXGe_asgrown.txt');
% Xge_anneal = fileRW(depth,'S7452_DepthvsXGe_750C120min.txt');
% Phos = fileRW(depth,'S7452_DepthvsPhos_800C30min.txt');

Cge_anneal = (25-(5-Xge_anneal*1.16).^2)*1e22/2.32;
Cge_asgrown = (25-(5-Xge_asgrown*1.16).^2)*1e22/2.32;
Cge = Cge_asgrown;

const = dt/dx^2;

for i=0:dt:time
    for j=2:620
        Cge(j)=Cge(j)+fDiff_800(Cge(j-1),Temp,Phos(j))*const*(Cge(j-1)-Cge(j))+fDiff_800(Cge(j),Temp,Phos(j))*const*(Cge(j+1)-Cge(j)); % SIMULATION S7450 800C 30MIN
        %Cge(j)=Cge(j)+fDiff_750(Cge(j-1),Temp,Phos(j))*const*(Cge(j-1)-Cge(j))+fDiff_750(Cge(j),Temp,Phos(j))*const*(Cge(j+1)-Cge(j)); % SIMULATION S7450 750C 120MIN
    end
end;

depth=depth*1e7;

function D_final = fDiff_800(Cge,T,Phos)
    n_Xge =(5-(25-2.32*Cge/1e22).^0.5)/1.16;
    kT = 8.617e-5*(T+273.15);
    %niGe = 6.4701E18; niSi = 1.0913E18; %750C
    niGe = 8.6242E18; niSi = 1.6465E18; %800C
    a1 = -0.2516; b1 = 0.13825; m1 = 1;
    a2 = 0.0969; b2 = -0.1835; m2 = 100;

    D_final = niGe*niSi*exp(-n_Xge)*sqrt((n_Xge+niGe)/niSi)/(kT*sqrt(pi*2*m1*1e-19)) + niGe*niSi*exp(-n_Xge)*sqrt((n_Xge+niGe)/niSi)/(kT*sqrt(pi*2*m2*1e-19));
beta=m1*exp((a1*n_Xge+b1)/kT);
gamma=m2*exp((a2*n_Xge+b2)/kT);

ni = niGe*n_Xge+niSi*(1-n_Xge);
n = (Phos+(Phos.^2+4*ni.^2).^0.5)/2;
_n_ratio = n./ni;

f_factor = (1+beta.*n_ratio+gamma.*n_ratio.^2)./((1+beta+gamma);

D_BM = BMdiff_7450GeSiGe800C(Cge);
D_final = D_BM.*f_factor;

End

function D = BMdiff_7450GeSiGe800C(Cge)
Xge=(5-sqrt(25-2.32*Cge/1e22))/1.16;
A1 = 6.51737e-23;
t1=0.05556;
y0=2.89406e-16;

D = A1*exp(Xge/t1)+y0;
end

function D_final = fDiff_750(Cge,T,Phos)
n_Xge=(5-(25-2.32*Cge/1e22).*.5)/1.16;
kT = 8.617e-5*(T+273.15);
niGe = 6.4701E18; niSi = 1.0913E18; %750C
%niGe = 8.6242E18; niSi = 1.6465E18; %800C

a1 = -0.2516; b1 = 0.13825; m1 = 1;
a2 = 0.0969; b2 = -0.1835; m2 = 100;

beta=m1*exp((a1*n_Xge+b1)/kT);
gamma=m2*exp((a2*n_Xge+b2)/kT);

ni = niGe*n_Xge+niSi*(1-n_Xge);
n = (Phos+(Phos.^2+4*ni.^2).^0.5)/2;
_n_ratio = n./ni;

f_factor = (1+beta.*n_ratio+gamma.*n_ratio.^2)./((1+beta+gamma);

D_BM = BMdiff_7450GeSiGe750C(Cge);
D_final = D_BM.*f_factor;

end

function D = BMdiff_7450GeSiGe750C(Cge)
Xge=(5-sqrt(25-2.32*Cge/1e22))/1.16;
y0 = 1.02384e-16;
a1 = 4.42028e-28;
t1 = 0.03556;
a2 = 1.41838e-17;
t2 = 1.47792e77;

D = a1*exp(Xge/t1)+a2*exp(Xge/t2)+y0;

end
Appendix B: Strain Simulation with software PANalytical Epitaxy

PANalytical Epitaxy is a part of PANalytical’s software package, which provides functionality for plotting and analyzing high-resolution X-ray diffraction data of rocking curves, 2-axes scans, reciprocal space maps and wafer maps. Epitaxy offers a wealth of key information on thin heteroepitaxial layers, particularly single-crystal and highly textured thin-layer samples, such as lattice mismatch and relaxation, composition and layer thickness.

In PANalytical Epitaxy, the relaxation \( R \) is used to model the change in the unit cell distortion that occurs in the imperfect interfaces where misfit dislocations are present. This parameter is used to calculate the correct peak positions in simulated rocking curves. The expression of the percentage relaxation can be written as:

\[
Relaxation = \frac{(a_A^* - a_B^*)}{(a_A - a_B^*)} \times 100\%,
\]

where \( a_A^* \) and \( a_B^* \) are the in-plane lattice parameters of layer A and layer B with partial strain relaxation, and \( a_A \) is the in-plane lattice parameter of layer A with no strain. For the fully strained case, i.e. \( a_A^* = a_B^* \), the relaxation \( R \) is 0%; for the fully relaxed case, i.e. \( a_A^* = a_A \), the relaxation \( R \) is 100%.

Figure B1 A typical scenario of mismatch strain between two layers with a cubic crystalline structure. The lattice parameter of B is larger than that of A, \( a_B > a_A \).
The strain level in layer A can be expressed as:

$$\varepsilon_A = \frac{a_A^*}{a_A} \times 100\%,$$

(B2)

By combining equation B1 and B2, we can obtain the strain level in layer A as:

$$\varepsilon_A = \frac{R(a_A - a_B^*) + a_B^*}{a_A}$$

(B3)

where \(a_A\) and \(a_B^*\) can be found from literature or previous calculation.

In this work, PANalytical Epitaxy is employed to do the rocking curve analysis for samples in Chapter 3 and Chapter 4. The information of the strain relaxation in the epitaxial layers can be derived from the XRD peak positions. After achieving the relaxation R of the epitaxial layer, we can calculate the strain level of target epitaxial layer by using equation B3.

The simulation procedure is shown as follows. For the simulations in PANalytical Epitaxy, firstly, an identical multi-layered structure as the real sample is built, shown in Figure B2. The peak position of target layer in simulated XRD profile is determined by two parameters (R and Ge fraction). For the value of Ge fraction, we used the data that obtained from SIMS analysis. By changing the input value of relaxation R of Ge layer, the simulation peaks can be matched with the experimental peak positions (relative to the substrate peak), as shown in Figure B3. More instructions are described in the guide of the software PANalytical Epitaxy [117].
Figure B2 An identical multi-layered structure built in PANalytical Epitaxy simulation.

Figure B3 Peak matching in PANalytic Epitaxy for sample UGUS in Chapter 3 with R = 104% in simulation.