

### SHANGHAI JIAO TONG UNIVERSITY



### THESIS OF BACHELOR



## 论文题目: Characterization and Masking Layer Effect on Sn segregation in GeSn

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### 锗锡材料的热稳定性及覆盖层效应的研究

#### 摘要

新型合金材料锗锡材料有着优良的性能,如直接带隙材料、高载流子迁移率等。在高性能半导体材料需求快速增长的今天,受到广泛关注,有望成为下一代主流半导体材料。然而,在高温下锡(Sn)的偏析和锗锡(Ge-Sn)在层间的互扩散都会破坏器件性能,这给这类材料的应用带来了挑战,因为高温热处理在制造中不可避免。因此本文着重探究了外延生长的锗锡材料(Ge<sub>0.92</sub>Sn<sub>0.08</sub>/Ge/p-Si)的热稳定性。在本文中,我们研究了不同热处理条件对Ge-Sn互扩散的影响,以及退火时间条件对Sn 的偏析的影响,并创新性地提出了以氮化硅或氧化硅为覆盖层来抑制Sn的偏析。本文在研究了不同热处理条件下GeSn 样品的化学组分信息后,发现由于样品外延生长控制的技术缺陷,并不能利用表征手段呈现出互扩散现象的规律,而偏析现象相较于互扩散现象有更直观、可解释的表征结果。本文随后控制退火温度在450摄氏度,探究了不同退火时间对Sn 偏析的影响。通过分析表面化学组分信息、表面形貌特征,发现退火超过5分钟的条件下,样品表面能观察到明显的偏析现象,并且经过化学组分分析证实为GeSn 的分解和Sn 的偏析。而退火时间少于1分钟的条件下,不会出现Sn 的偏析。除此之外,在对比采用多种表征手段进行研究后我们也发现,拉曼光谱并不适用于厚度较大的材料分析,应采用穿透深度更大的X射线衍射来进行组分分析。

关键词: 锗锡薄膜, 热稳定性, 互扩散, 偏析



### CHARACTERIZATION AND MASKING LAYER EFFECT ON SN SEGREGATION IN GESN

#### ABSTRACT

As the need for high-performance semiconductor devices grows in our world today, Germanium-tin  $\text{Ge}_{1-x}\text{Sn}_x$  materials emerged due to their attractive properties, such as the direct bandgap and high carrier mobility. GeSn is also promising to be the next generation semiconductor materials. However, Sn segregation and Ge-Sn interdiffusion are harmful to device performances, reducing carrier mobilities. The high temperature is also unavoidable due to necessary heat treatment during fabrication process, thus posing challenges to manufacturing. In this thesis, we focused on the thermal stability of epitaxial Ge<sub>0.92</sub>Sn<sub>0.08</sub>/Ge/p-Si structure. We studied the effect of heat treatment conditions on Ge-Sn interdiffusion behaviors, and the impact of annealing time on Sn segregation. Building on such primal groundwork, we originally proposed that the capping of a silicon nitride  $(Si_x N_v)$  or silicon oxide  $(SiO_x)$  would reduce Sn segregation. By investigating the chemical composition of GeSn samples under different heat treatment conditions, we found that the characterization methods we employed were not able to present the interdiffusion phenomenon due to the technical limitations in controlling the epitaxial growth. Instead, it was more feasible to study the segregation behaviors due to successful presentations of various characterization methods. Later, we investigated the impact of annealing time on Sn segregation with the annealing temperature being controlled at 450  $^{o}C$ . By analyzing the surface chemical composition and surface topography, we examined obvious segregation on the GeSn specimen surfaces when annealed over 5 minutes. The chemical composition analysis further confirmed the decomposition of GeSn and Sn segregation. Furthermore, there was no observable Sn segregation when annealed less than 1 minute. In addition to the above conclusion of Sn segregation, we also found XRD a better characterization method to analyze elemental fraction in such layered structures rather than Raman spectra due to a larger penetration depth of X-rays.

Key words: GeSn, Thermal Staibility, Interdiffusion, Segregation



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### **Chapter 1** Introduction

#### 1.1 Significance of Group IV Semiconductor Systems and GeSn

We are welcoming a new era of the Information Age, thanks to the rapid development of semiconductors in 20<sup>th</sup> century. The explosion of various invented applications of semiconductor devices became building blocks of electronic devices which revolutionized our lives<sup>[1]</sup>. There were great inventions developed in the mid of 20th century, transistor, integrated circuit, the metal-oxidesemiconductor field-effect transistor, to name a few. Group IV elements in the periodic table played a significant role in forming a wide range of commonly used semiconductors.

There are elemental semiconductors such as silicon (Si), germanium (Ge), where Si is the dominant elemental semiconductor. Si-based products count for nearly 90% occupation of the semiconductor market nowadays<sup>[2]</sup>. Si semiconductors were popular in the industry due to the mature technique in producing high-purity Si and the rich source of Si element in the nature.

There are also alloying semiconductors, including SiGe, SiGeC, GeSn, SiGeSn, etc. The advantages of substituting Si semiconductors into these alloying semiconductors include a better carrier mobility and flexibility in tuning band gap<sup>[3]</sup>. SiGe alloys were widely studied and became the most important materials in electronic devices in the past few decades. Ge had better performance than Si, being a more effective semiconductor material in the aspects of carrier mobility and photoelectric property<sup>[4]</sup>. Therefore, the SiGe alloy significantly enhanced the performance of standard semicon-ductor devices such as MOSFETs with its superior bulk mobility for electrons and holes compared to Si<sup>[5]</sup>.

However, the industry is calling for novel materials to keep pace of the growing need of better performance electronic device. There is a well-known Moore's Law in the semiconductor industry, indicating the exponentially growing number of transistors on a microchip. The need of device scaling posts new challenges to developing post-scaling technology of Si-based devices while improving performance<sup>[5]</sup>. As a result, researchers in the past years turned to study GeSn materials intensely due to the limitations of Si-based devices.

Germanium tin  $\text{Ge}_{1-x}\text{Sn}_x$  semiconductor materials emerge for their attractive properties<sup>[6]</sup>. Both Si and Ge are indirect bandgap materials, making it difficult to produce light emissions<sup>[7]</sup>. However, by increasing Sn content in the Ge lattice, the hole effective masses decrease, and the hole mobility increases. The energy band structures are thus tuned with the energy difference between valleys decreases<sup>[8]</sup>. The direct-transition semiconductors are achieved with a predicting Sn concentration in the approximate range of 6% - 10%<sup>[7, 9, 10]</sup>. For instance, Grant<sup>[11]</sup>demonstrated the feasibility of achieving direct-transition GeSn material by successfully fabricating a direct bandgap Ge<sub>0.86</sub>Sn<sub>0.14</sub> Quantum Well structure by using a strain relaxed Ge<sub>0.92</sub>Sn<sub>0.08</sub> buffer. Apart from the feasibility of bandgap engineering, GeSn materials also enjoy the advantages of achieving strainengineering for strained Ge, high carrier mobility, improving interface and defects properties, etc.



GeSn materials have diverse applications due to the outstanding properties. The feasibility of the energy band engineering makes GeSn alloys possible to realize high-performance electronic devices and optoelectronic devices<sup>[6]</sup>. They are attractive in fabricating direct bandgap optoelectronics and nanoelectronics<sup>[8]</sup>. Typical electronic device applications include MOSFETs<sup>[3]</sup>, Heterojunction bipolar transistors (HBTs). High-mobility channel MOSFETs are essential components in making high-performance and low-power consumption devices, such as integrated circuits (ICs), metal-oxide-semiconductor memory (MOS memory), complementary metal-oxide-semiconductor circuits (CMOS circuits), etc. It is widely acknowledged that MOSFETs lay the foundation of the modern electronic industry. GeSn alloys were also maufactured as optoelectronics, such as photovoltaic cells, infrared (IR) wave guides, near IR-photodetectors, IR light-emitting diodes (LEDs), and IR lasers, photodiodes, etc. Early in 2009, Mathews, J., et al. found that low Sn concentration GeSn photodiode detectors had better detector quantum efficiencies than pure-Ge devices<sup>[12]</sup>. Researchers also reported GeSn materials promising for solar cell applications, as Fang, et al.<sup>[13]</sup> reported their lattice-matched Si(100)/Ge/SiGeSn/InGaAs architectures on low-cost Si(100) substrates a feasible structure for fabricating high-efficiency and low-cost solar cells.

#### 1.2 The Necessity of Studying GeSn Interdiffusion and Segregation

Though there are various advantages of GeSn materials, many challenges are to overcome before the material can be applied for practical use. GeSn materials are difficult to maintain structural integrity during heat treatment<sup>[8]</sup>. According to the phase diagram of Ge-Sn system, the equilibrium bulk solubility of Sn in Ge is considerably low, being less than 1%. Therefore, Sn segregation and Ge-Sn interdiffusion are easily occurred at high temperatures<sup>[7]</sup>. The controlling of segregation and interdiffusion is challenging because high temperature is unavoidable in epitaxial growth and device processes. Steps with high temperature including oxidation, implant activation, contact formation, annealing, deposition, etc<sup>[2, 14]</sup>. Both interdiffusion and segregation are harmful to semiconductor properties.

The phenomenon of interdiffusion is a physical process of mixture. To minimize the free energy, microscopic particles (atoms, ions, electrons, holes, molecules, etc.) will automatically move to form a random and homogeneous solution<sup>[15]</sup>. The process of movement is defined as diffusion. For interdiffusion, it usually happens in a binary system, such as the GeSn alloy in our work. Figure 1–1 is helpful in interpreting the process of interdiffusion visually. Initially, there is a step in the concentration profile. After some time of heat treatment, both blue and orange atoms will diffuse to the other end across the interface. In the case of Ge-Sn interdiffusion at GeSn/Ge interfaces, both Sn atoms and Ge atoms will transport through the interface, resulting in the lattice composition changes. The mechanism of diffusion is due to the chemical potential gradients. Particles tend to move to a lower free energy state. Serious interdiffusion is problematic in degrading the electron mobility through reducing carrier confinement and increasing alloy scattering<sup>[3, 16]</sup>. It was demonstrated that implantation-enhanced Si-Ge inter diffusion degraded the electron mobility of strained-Si/relaxed-SiGe n-type MOSFETs<sup>[2]</sup>.





Figure 1-1 A schematic of interdiffusion phenomenon

There are three types of diffusion paths in thin films, including lattice diffusion mediated by point defects, short-circuit diffusion mediated by dislocations and grain boundary. Two types of point defects are common in dominating atomic diffusion, which are vacancies and interstitials. Atoms can directly move into a vacancy resulting in diffusion. An interstitial atom can replace an atom on the lattice cite and push another interstitial atom out, thus contributing to the movement of diffusion. There are also extended defects such as dislocations and grain boundaries impeding the diffusion behaviors. For semiconductor thin films, the most commonly encountered dislocations defects are threading dislocations (TDs) and misfit dislocations (MDs). Both threading dislocations should be reduced to enhance the properties of semiconductor devices.

Fick's law describes the diffusion process theoretically, which is expressed by the Equation 1–1:

$$J = -D\nabla C \tag{1-1}$$

where J is the diffusion flux, D represents the diffusion coefficient, and C is the concentration. From the above expression, we can also conclude that diffusion is driven by the concentration gradient. Furthermore, the diffusion coefficient is dependent on concentration in actual cases which is changing as the diffusion process goes on.

The concept of segregation is the enrichment of particles at a microscopic system. As described in Figure 1–2, particles tend to assemble into regions at the free surface, forming a second phase on top of the original phase. Sn segregation occurs due to its low solid solubility in the Ge-Sn binary system. The mechanism of Sn segregation tendency can be explained by the low surface energy and large covalent radius of the Sn atom. When the temperature reaches around 200  $^{o}C$ , Sn will tend to precipitate. Just as the interdiffusion behaviors, the Sn segregation also degrades the electrical properties of semiconductor devices<sup>[17]</sup>. Sn precipitation from GeSn alloys is one of the serious problems during GeSn growth and post-processing, occurring both during the epitaxial growth of GeSiSn ternary alloys and during the oxidation of GeSn layers<sup>[6]</sup>.





Figure 1–2 A schematic of segregation phenomenon

According to the assessed Germanium-tin (Ge-Sn) system equilibrium phase diagram, Sn had a rather small solubility in the solid solution of Sn in Ge. The maximum solubility is about 1.1 atomic percent Sn at 400  $^{o}C$ . The solubility at the eutectic point at 231.1  $^{o}C$  is even lower than 1 at.%. The equilibrium phase diagram demonstrated that Sn is easily segregated out in the solid solution of Sn in Ge due to a low eutectic temperature at aroung 200  $^{o}C$  as well as the extremely low solubility of Sn less than 1 at.%.



Figure 1–3 The assessed equilibrium phase diagram of Germanium-tin (GeSn) binary system<sup>[18]</sup>

### **1.3 Research Background of Ge-Sn Interdiffusion and Sn Segrega**tion in GeSn

Over the few decades, researchers have investigated the thermal stability of group IV semiconductor materials intensely. The interdiffusion behaviors and segregation behaviors were studied



from various aspects, including empirical experiments, modeling, and mechanisms. For interdiffusion studies, the impacts of annealing temperature, strain status were investigated in previous researches.

The annealing temperature is demonstrated to have significant influence on interdiffusion performances. Wei Wang et al<sup>[16]</sup> examined the thermal stability of strained  $\text{Ge}_{0.9}\text{Sn}_{0.1}$ /Ge multiplequantum-well (MQW) samples within a range of temperature from 300 °C to 600 °C. They found that there was no observable interdiffusion when annealed lower than 300 °C, while the interdiffusion occured for annealing temperatures above 380 °C. Furthermore, the Ge-Sn interdiffusion was so severe that there was obvious Sn segregation when annealed above 450 °C. Dian Lei et al<sup>[17]</sup> later in 2017 carried out another experiment in studying thermal stability using a different GeSn structure of Ge<sub>0.96</sub>Sn<sub>0.04</sub> fin structures. It was demonstrated to have severe segregation when annealed above 500 °C.

Strain status is another significant influencing factor on interdiffusion. Evidences<sup>[19]</sup> suggested that strain impact on the interdiffusion in semiconductor heterostructures, compressive biaxial strain that enhanced interdiffusion significantly. It was studied by Xia, G., et al.<sup>[3]</sup> that with the increase of compressive strain, the interdiffusivity will also increase. They had demonstrated this phenomenon in the case of SiGe materials, that the Si-Ge interdiffusivity increases by 4.4 times for every 0.42% in the magnitude of biaxial compressive strain. This change of strain status was able to be presented by Raman characterization due to the strain dependence of Raman frequency shift, which was demonstrated in Ge<sub>0.917</sub>Sn<sub>0.083</sub> epilayer structure<sup>[20]</sup>.

A model for the other group IV elemental interdiffusivity, that is Si-Ge interdiffusivity, in strained Si/relaxed  $Si_{1-x}Ge_x$  heterostructures was constructed by Xia, G., et al.<sup>[3]</sup>. As known, the coefficient of diffusion is dependent on the concentration, Xia' s work took it into consideration and gave out a universally applicable model which successfully predicts experimental interdiffusion coefficients in various SiGe heterostructures. The model incorporated experimental results of Si-Ge interdiffusivity after statistical analysis. They measured the diffused Ge profiles by SIMS and used the data as basis to extract the interdiffusivity using Boltzmann-Matano analysis.

Other than interdiffusion behaviors concerning annealing temperature and strain status, the studies on Sn segregation were also popular topics in recent years.

The observation of segregation relied on appropriate characterization tools. Wang, W. et al.<sup>[21]</sup> found that Sn segregation was only observable with surface enrichment of Sn by X-ray photoelectron spectroscopy (XPS), but without discernible results using X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM). Also, there were obsevable Sn segregation when annealed above 300  $^{o}C$ . Various characterization methods were also employed in many of studies focused on Sn segregation in GeSn. XRD and the contour plot of reciprocal space maps helped in determining GeSn bulk lattice constant<sup>[22]</sup>. XTEM was useful in determining threading dislocations and lattice mis-fit<sup>[9]</sup>. The roughness and the surface morphology were studied using AFM or SEM<sup>[16]</sup>. Rutherford backscattering spectrometer was also an alternative tool to study the elemental fraction.

The segregation performance of different structures were also investigated. As discussed in previous paragraphs, both the thermal stability of GeSn/Ge multiple-quantum-well (MQW) structure and GeSn fin structure were investigated and compared with bulk GeSn structure<sup>[16, 17]</sup>. Both of the structures showed an obvious presentation of segregation when annealed above 500  $^{o}C$ , indicating



the unstability of Sn at high temperatures.

Furthermore, Heiko Groiss, et al.<sup>[10]</sup> proposed a mechanism for Sn precipitation in metastable GeSn epilayers for the first time. The study carried out in-situ annealing experiments in a scanning electron microscope investigating phase separation, which gave us a view of the dynamics of Sn precipitaiton. During the phase separation process, liquid Sn droplets played a crucial role by facilitating the phase separation of metastable GeSn layers. The Sn precipitates move in preferential crystallographic directions to take up Sn and Ge from the GeSn layer. As the Sn composition reduces, single-crystalline Ge will re-deposit on the surface creating a second phase comparing to Sn phase.

#### **1.4** Scope of the Thesis

The thesis was innovative to study the thermal stability of GeSn by considering interdiffusion and segregation at the same time using multiple characterization methods. Previous studies in the field lacked a systematic study on temperature and time domains by examining both interdiffusion and segregation behaviors. For instance, Driesch, et al.<sup>[8]</sup> merely studied Sn diffusion regime in strained GeSn binary alloys by XRD and SIMS at a low temperature (<650 °*C*) without further investigation in distinguishing the temperature range where activates interdiffusion and segregation. Not come singly but in pairs, many studies widely investigated Sn segregation behaviors for different structures (multiple quantum well structure<sup>[16]</sup> and fin structure<sup>[17]</sup>), temperature and time domains for GeSn<sup>[21]</sup>, but these studies did not mention the potential interdiffusion behavior. Thus, this thesis was first to examine both interdiffusion and segregation behaviors to investigate the thermal stability, hoping to provide an empirical thermal budget in determining the order of two phenomenon and to better avoid interdiffusion and segregation.

Furthermore, this thesis put forward a promising structure to prevent Sn segregation which haven't been studied before. Many researches observed and reported the phenomenon of Sn segregation, but no study focus on the prevention of the segregation. Our study was the first to add a capping layer on the structure to study whether the silicon nitride  $(Si_xN_y)$  or the silicon oxide  $(SiO_x)$  will reduce the segregation. The structure we proposed might be a promising solution to the segregation.

	Interdiffusion study		Segregation Study		
	Study 1.1	Study 1.2	Study 2.1	Study 2.2	Study 2.3
Topic (Method)	SIMS	Raman and XRD	Raman	XRD, SEM, & OM	Capping layer effect of PECVD Si <sub>x</sub> N <sub>y</sub>
Thesis Session	Chapter 2.2	Chapter 2.3	Chapter 3.1	Chapter 3.2	Chapter 3.3
Conclusion	Need more precise growth control of Sn composition (not available)	Design comparable experiments to study the impact of annealing conditions	Unable to identify Sn segregation due to the limitations in probing depth	GeSn decomposed into Sn and precipitated out during annealing	Experiments were scheduled, but not performed due to the pandemic.

Figure 1-4 A Summary table of the thesis structure



Chapter 2 will focus on the study of Ge-Sn interdiffusion behaviors, where we performed SIMS, Raman, and XRD to characterize. Our initial goal was to investigate the GeSn interdiffusion phenomenon, as such, we did some trials through the usage of the SIMS method and the Raman method. However, we were not able to obtain the desired epitaxial structures and got sufficiently accurate SIMS due to some technical limitations in the study of interdiffusion. We then used XRD method to characterize, but there were no comparable results. Therefore, we were not able to succeed in our first two attempts. In the following reports, I will discuss the experiments performed and improvements needed to complete these studies in Chapter 2 in detail. Related introductions to the theoretical fundamentals and experimental methods will also be presented in Chapter 2.

In Chapter 3, the impact of thermal annealing on Sn segregation will be investigated. After the interdiffusion study, we changed our research direction to study Sn segregation. Segregation study was more feasible due to successful presentations through various characterization methods. Firstly, we did more annealing trials to have comparable experiment results. We aimed to study whether there was Sn segregation in GeSn epitaxial layers after annealing and how the annealing time impacts the segregation behavior. Characterization methods were employed to investigate the presentation of segregation, including Raman spectroscopy, XRD, SEM, etc. Lastly, to find a solution to reduce Sn segregation, we proposed that capping layer might be effective in prohibiting segregation. The detailed experiments and results analysis will be discussed in Chapter 3, as well as the proposed solution to reduce segregation.

Methodology	Information	Function
SIMS	Concentration vs depth profiles	Probing interdiffusion behaviors
Domon	Different types of bonding	Probing interidiffusion and
Kalilali	and bond numbers	segregation behaviors
XRD	Lattice constants of a phase	Probing interdiffusion,
		detecting Sn as a second phase
Ontigalimaging	Surface images	Examining segregation,
Optical imaging	Surface images	surface morphology
SEM imaging	Surface images with higher contrast	Examining segregation,
	and resolution	surface topography
EDC : CEM	Regional elemental concentration	Probing segregation,
		determining the composition of each region

 Table 1–1 An overview of the methodology employed in the thesis with corresponding information and function for each method

The following Table 1–1 provided an overview of the methodology we are going to employ in the thesis. Secondary-ion mass spectrometer (SIMS) can probe the interdiffusion behaviors by extracting the concentration profiles as a function of the depth. Both Raman spectroscopy and X-ray diffraction (XRD) were used to probe the interdiffusion and segregation behaviors. Raman spectra provide information of different types of bonding and bond numbers on the sample surface while XRD measures the lattice constants of a phase. In this thesis, a second phase of Sn will be detected



using XRD, which is helpful in studying Sn segregation. Furthermore, optical imaging and SEM imaging show visual presentations of the surface with information about the morphology. Sn segregation will be observed in these images. Last but not least, EDS in SEM measures the regional elemental concentration, which determines the composition of each region. It is employed to probe the segregation behavior.

To summarize, this thesis provides a systematic study on the thermal stability of GeSn and found the thermal budget for interdiffusion and segregation behavior. The findings of the thesis were very helpful in selecting an appropriate thermal budget for GeSn related device fabrication.

### Chapter 2 Ge-Sn Interdiffusion Study

### 2.1 Epitaxial Structure of GeSn/Ge and the Growth of Epitaxial GeSn/Ge

The epitaxial structure of GeSn/Ge used in our studies were provided by Graduate Institute of Electronics Engineering, National Taiwan University (NTU). 200-mm p-type Si (001) films were prepared as the substrates of the epitaxial structure. Firstly, Si substrates were dipped into the diluted HF (1:50) solution before growing Ge and GeSn layers and waited 60 seconds for reaction. To remove native oxide on the Si substrates, they were baked in-situ at 1100 °C in the hydrogen atmosphere. Afterwards, to grow Ge buffer layer on top of the Si substrate, Ge<sub>2</sub>H<sub>6</sub> and SnCl<sub>4</sub> were used as the precursors, followed by the deposition of a 500-nm Ge layer. The Ge buffer layer was annealed in-situ at 800°C to relax the strain of the Ge layer, which was a necessary step. Later, they employed reduced pressure chemical vapor deposition (RPCVD) technique to grow the GeSn epitaxial films on Si substrates, precursors Ge<sub>2</sub>H<sub>6</sub> and SnCl<sub>4</sub> were employed again. To avoid the Sn segregation, the growth temperature was controlled at a low level ( $\leq 350$  °C) of both GeSn layers and a Ge cap layer on top of all films.



B570

Figure 2–1 The schematic of B570 sample

All of the sample structures had a Ge/GeSn/Ge buffer/p-Si heterostructure. A 500-nm Ge buffer layer was grown on 200-mm p-type Si (001) substrate to separate Si substrate and GeSn films due to the large lattice misfit. There are three types of epitaxial structures with different strain state and Sn concentration, presenting descriptions and sample number in Table 2–1. Epitaxial films were then deposited on Ge buffer layer. To avoid Sn segregation, a Ge layer was capped on the top of the structure. For the first structure, an 80-nm  $Ge_{0.96}Sn_{0.04}$  epitaxial film was deposited on Ge buffer layer, creating a strained undoped epitaxial structure with 4% Sn composition. This sample was





Figure 2–2 The original wafer piece

capped with 200 nm Ge layer on the top and labeled No. B569. The relaxed strained structure was fabricated with  $Ge_{0.96}Sn_{0.04}$  growing to 400 nm thick on Ge buffer layer. The capping Ge layer on the top grew to 300 nm. The relaxed undoped strained  $Ge_{0.96}Sn_{0.04}$  structure was marked B574. For the third structure B570, the composition of Sn increased to 8% and the layer structure was the same as B574 sample with 400-nm  $Ge_{0.92}Sn_{0.08}$  and 300-nm Ge capping layer. Figure x showed the schematic of three structures. All testing samples employed in the thesis were cut from the 1/4 of 8" piece of the above sample structures, showing in Figure 2–2.

Sample No.	Strain Status	Sn concentration (%)
B569	strained	4
B570	relaxed	8
B574	relaxed	4

Table 2-1 Samples provided by NTU and descriptions

### 2.2 Previous Summary on Ge-Sn Interdiffusion Study by Secondary-Ion Mass Spectroscopy (SIMS) and Data Analysis

The topic of studying the Ge-Sn interdiffusion performance was previously performed by a postdoc in our group, Taga Kazuhiro. My work continued his unfinished work in analyzing the Secondary-Ion Mass Spectroscopy (SIMS) data and drew a conclusion. In this section, I will give a brief summary on his previous work and present my analysis based on his data.





Figure 2–3 The schematic of temperature profiles of annealing process in this thesis

#### 2.2.1 Annealed Samples by Taga Kazuhiro

To find out how annealing temperature, annealing time, and ramp speed affect the performance of interdiffusion, Taga gave 3 trials in using different annealing conditions, preparing three new samples B570B, B570C, and B570D. All specimens were cut from B570 sample, whose size were approximately 1mm x 1mm. The first sample labeled B570A was originally grown without further heat treatment, using as a reference. Another three samples were annealed under different conditions. B570B and B570C were annealed at 450 °C while B570D was heated at 400 °C. The ramp speed for B570B was controlled to be 100 °C  $\cdot$  min<sup>-1</sup> and increased to 200 °C  $\cdot$  min<sup>-1</sup> for B570C and B570D. The annealing time was different case by case, which was 30 minutes for B570B, 5 minutes for B570C, and 20 minutes for B570D. The annealing conditions were summarized in Table 2–2, with temperature, time, and ramp speed listed.

Table 2-2 The annealed samples prepared by Taga with temperatures, annealing time, andramp speed noted

Sample No.	Temperature $(^{o}C)$	Time (min)	Ramp ${}^{o}C \cdot min_{-1}$
B570A	As grown	-	-
B570B	450	30	100
B570C	450	5	200
B570D	400	20	200



Samples were annealed using a furnace with the annealing conditions discussed in the above paragraphs applied. The samples were placed in the center of the heating stage, which was electrically heated. Before heating up, the furnace was filled with nitrogen, creating an ambient heating environment. Tubes were connected to the furnace, filling with circulating water to stabilize the heating temperature and keep the stage body cool. The temperature profile was shown in Figure x, explaining the temperature change during the annealing process. In this work, the temperature rampup speed and ramp-down speed were at the same level, which was  $100 \, {}^{o}C \cdot min^{-1}$  or  $200 \, {}^{o}C \cdot min^{-1}$ , to be specific. After ramping up, there was a steady stage when temperature held unchanged at 450  ${}^{o}C$  or  $400 \, {}^{o}C$ . The duration of the steady stage corresponded to the annealing time in the Table 2–2.

After annealing, the as grown sample as well as three annealed samples were analyzed by SIMS to obtain the Sn fraction profile, hoping to learn about the Ge-Sn interdiffusion performance under different annealing conditions. In this study, 4 samples were sent to the Evans Analytical Group (EAG) for SIMS measurements with accurate element concentrations and layer structure identifications, which is a leading industrial company in providing high quality SIMS analysis. 2 KeV Cs<sup>+</sup> primary ion beam sputtered on our samples with secondary ions emission analyzed with a quadrupole mass analyzer. The profiling depth was set to be 1200 nm with first 5-10 nm unreliable region from the surface removed for profiling. The profiling data density in our study was controlled to be less than 0.3 nm per data point.

#### 2.2.2 SIMS Results and Analysis

There were many interdiffusion research approaches studied by various groups, including SIMS<sup>[3]</sup>, X-Ray Diffraction (XRD)<sup>[16]</sup>, and self-diffusivity approach [Dong et al 94]. Secondary-ion mass spectrometry (SIMS) was a satisfying approach in studying interdiffusivity due to its accuracy and easily implementable format. SIMS is a popular analytical technique because the method can accurately measure elemental concentration in the depth dimension. Previous research efforts such as Cowern et al.<sup>[23]</sup>, Xia et al.<sup>[3, 19]</sup>, employed SIMS to measure diffused Ge profiles to study the interdiffusion behavior of Si-Ge.

SIMS approach employs a focused primary ion beam to strike the surface of a sample. Atoms on the surface will be ejected from the surface, producing monatomic and polyatomic particles which are secondary ions. These ions will be collected and measured by a mass spectrometer, creating a mass spectrum based on the mass/charge ratios of these ions. The mass spectrum can provide information on the elemental composition of solid surfaces and thin films<sup>[24]</sup>. However, we will need depth profiles for diffusion studies. As a result, SIMS analysts will use a profilometer to obtain the sputter crater depth as well as measuring the secondary ion count rates as a function of time<sup>[25]</sup>.

Based on the elemental composition profiles as a function of depth from SIMS, the interdiffusivity can be extracted using Boltzmann-Matano method. In 2006 and 2007, the Boltzmann-Matano analysis was first introduced by Xia, G., et al<sup>[3, 19]</sup> in studying Si-Ge interdiffusivity. The method is able to extract the interdiffusivity in accordance to the elemental concentration profiles in binary metal alloys<sup>[2, 3]</sup>. Because the interdiffusivity is usually concentration dependent, thus it is hard to theoretically predict the level of interdiffusivity. However, Boltzmann-Matano analysis is a graphical method, extracting concentration-dependent interdiffusivity from the experimental curves. The



interdiffusivity expression using Boltzmann-Matano analysis was presented in Equation 2-1.

$$D(C_0) = -\frac{1}{2t} \left(\frac{dz}{dC}\right)|_{C_0} \int_{C_L}^{C_0} (z - z_m) dC$$
(2-1)

where  $D(C_0)$  is the interdiffusivity where Sn concentration equals  $C_0$ , t is the annealing time, z is the depth from the sample surface, C(z) is the Sn concentration as a function of depth, and Matano plane locates at the position of  $z_m$  with regard to the reference plane.

However, the interdiffusivity is not only sensitive to the alloy concentration, but also is dependent on strain state. Boltzmann-Matano analysis only takes concentration into consideration, which is not applicable to all actual cases. The strain dependence can be expressed as a linear function of elemental concentration in coherent epitaxial films, as Xia, G., et al<sup>[2]</sup> forwarded. Therefore, the interdiffusivity can simply be expressed as a function of Sn fraction at a given temperature, while also taking strain impact into consideration. Xia, G., et al.' s<sup>[3]</sup> work revealed that elemental fraction and biaxial compressive strain were exponentially relevant with the interdiffusivity.

In this study, Sn profiles were first obtained through SIMS analysis. Later, Boltzmann-Matano analysis would be applied to extract Ge-Sn interdiffusivity. Practically, to apply Boltzmann-Matano analysis, it is required to have an initially abrupt step concentration profile and a steep post-processing profile with stable platforms on the left and right sides. Therefore, we carried out simulations using Matlab before we analyze the actual data from SIMS analysis.

The profiles presented in Figure 2–4 and Figure 2–5 simulated the impact of annealing time and annealing temperature on the Sn fraction profiles. The initial profile was designed to have a step at the depth of 100 nm, showing an abrupt increase normal to the x-axis. The interdiffusivity follows the expression in Equation 2–2, which is temperature and time dependent.



Figure 2–4 Simulation of Sn fraction profile when annealed at 400 °C



The concentration dependent diffusivity is simulated using finite difference technique, which calculates the diffusivity from position to position. The initial diffusivity was set to be  $D_0 = 2.9e^{-7}$  and the activation energy was  $E_a = 1.21eV$ . The initial input data was a step-shape Sn fraction



profile with the plateau Sn concentration controlled to be  $3.41e^{21}$ . The concentration was determined by calculating from atomic density of Sn in GeSn lattice and the lattice constant 5.725  $e^{-8}cm$  cited from the literature. Atomic density of GeSn is calculated by 8 atomic percent of Sn divided by (lattice constant)<sup>3</sup>. The diffused Sn fraction profiles were plotted after 6 minutes, 30 minutes, and 60 minutes annealing, showing greater tangent slopes as annealing time increasing. Also, when the annealing time was set to be higher, the tangent slope of the Sn profiles also increased when annealed for the same time. Furthermore, there were all platforms on both sides after diffusion in all cases.

However, these were only ideal shapes of the profiles. There were errors of measurement noises, fabrication limitations, etc. It was necessary to compare the simulation with real measured data. When we observed actual data and simulation at the same time, we discovered a huge difference between theoretical data and our measurement. Figure 2–6 presented the profiles of the as grown sample, putting simulation and real data together. There were slight slopes in the step regions due to the interdiffusion in fabrication processing. The platform also had intense waves instead of being straight. Even the concentration level did not fit with the theoretical calculation.



Figure 2–6 The plotting of simulation result and practical Sn profile measure by SIMS of the as grown sample B570A

Accordingly, it was of great significance to use the measured as grown data as the initial input for simulations of the elemental concentration profiles after annealing. However, with that being said, the SIMS profile for now was too rough to be simulated. Smoothing was necessary before further analysis and simulation. As a result, I smoothed the curves using a Matlab function "smooth" and the results were presented in Figure 2–7. The curve in red color was the result after plateau smoothing of the as-grown B570 sample. However, the pleateau after smoothing was still wavy and not qualified for applying Boltzmann-Matano method to extract Ge-Sn interdiffusivity.

To conclude what I had discussed above, SIMS technique and Boltzmann-Matano method were not applicable to analyze our GeSn samples and to obtain Ge-Sn interdiffusivity because of the unsmooth plateau of Sn fraction profiles. To successfully perform SIMS analysis, we will need more precise growth control of Sn composition. Nevertheless, our samples were provided by NTU but not fabricated by ourselves, making it not available to improve the growth control of epitaxial films.





Figure 2–7 The plotting of Sn profile after smoothing plateau of the as grown sample B570A, with irregular waves on the plateau

Therefore, we found alternative characterization methods to study the interdiffusion performance, which was discussed in the following section.

# 2.3 Ge-Sn Interidiffusion Study by Raman Spectroscopy and X-Ray Diffraction (XRD)

Raman and XRD are common characterization choices in the industrial and research fields to study important parameters of group IV semiconductor material heterostructures, such as the type and magnitude of strain in epitaxial layer, elemental fraction, etc<sup>[26]</sup>. Sn concentration and strain are two crucial factors in studying interdiffusion performance, which could be measured simultaneously by both Raman spectroscopy and XRD. Accordingly, we employed these two characterization methods in this study to continue analyzing the Sn fraction of these annealed samples. which was discussed in the following section.

#### 2.3.1 Introduction to Raman Spectroscopy and X-Ray Diffraction (XRD)

Before getting down to details of experimental design, I would like to give a brief introduction to both Raman and XRD principles.

Raman spectroscopy is widely employed to investigate the properties of semiconductor structures, by obtaining the elemental fraction and type and magnitude of the strain at the interface simultaneously. Early in 1996, Jain, S. C., et al<sup>[27]</sup> proposed empirical equations describing the position of the characteristic Raman peaks as a function of both Ge fraction and strain status. Recently, Dian Lei et al<sup>[17]</sup> used Raman spectroscopy to investigate the thermal stability of GeSn films by comparing samples that were annealed at temperatures ranging from 300 oC to 500 oC. The differences in Raman spectra of Ge bulk, GeSn, and germanium-tin-on-insulator (GeSnOI) samples indicated the change of positions of characteristic peaks for each composition. The Raman spectra also presented the peak shift and the material quality after thermal annealing, which were also supplementary



characterization to study the critical thermal treatment for interdiffusion behaviors. Besides, strain relaxation of GeSn was also studied using Raman spectroscopy by Kang, Y. Y., et al<sup>[28]</sup>. The observation that Raman peak shifts towards the lower wavenumbers as the GeSn fins decreasing the width, indicating the relaxation of the compressive strain in the fins. The strain status thus can be expressed by peak shifts. Apart from the convenience of obtaining elemental fraction and strain status by a single trial of characterization, Raman characterization method enjoyed an advantage that the detection was lossless without destructing original structures and changing the composition, comparing to SIMS. Furthermore, the penetration depth of Raman was relatively small, thus it was ideal for characterizing thin films near the sample surface. Also, the scan time for a single investigation was short, from several seconds to a few minutes, which was far more efficient comparing to other characterization methods such as XRD.

Raman scattering was first discovered by an Indian scientist C. V. Raman in 1928. Scattering can be categorized into Rayleigh scattering (elastic scattering) and Raman scattering (inelastic scattering), according to the energy of phonons. Typically, Raman scattering was generated when a certain molecular was stroked by the incident phonons, and emitted scattering phonons whose frequency would be changed. Therefore, there was conversion of energy when having the Raman scattering.

Raman spectroscopy relies on the Raman scattering which was discussed above. As the scattering is inelastic with frequency change, the difference of the scattering frequency and the incident frequency was Raman shift, plotting as the x-axis of Raman spectra. Each chemical bond has its featured phonon vibration modes, which help us identify molecules by matching the characteristic Raman shifts. The working principles of Raman spectroscopy are simple. A selected laser beam illuminates the target sample, whose wavelengths are usually in the visible, near infrared, or near ultraviolet range. Emission of the scattered radiation is first filtered and collected by a detector. Signals are later converted to readable results on computer, with Raman shift as the x-axis and intensity as the y-axis.

Apart from Raman spectroscopy, X-Ray Diffraction is also widely used in semiconductor structure characterization. It could be used for determining lattice parameters and analyzing phases. XRD can be performed on various types of materials to study the basic physical properties. Materials in the form of powder can be detected directly, such as composites. Some solid materials can also be measured after grinding. XRD is also a popular characterization technique to investigate semiconductor materials due to the flat surface of specimens. As a result, semiconductor materials can be directly measured by XRD method.

Several researches already employed XRD to explore the Sn segregation phenomenon and Ge-Sn interdiffusion properties. The annealed GeSn bulk in-plane lattice constants were obtained by XRD with the assistance of contour plot of reciprocal space maps. By comparing the lattice constants with different annealing temperature, Sn composition was thus calculated according to the lattice constant since the lattice constant was composition dependent for GeSn alloys<sup>[22]</sup>. Other researches carried out High Resolution X-Ray Diffraction (HRXRD) analysis to learn about how the GeSn/Ge periodic satellite peaks shift in accordance with the thermal treatment, analyzing the epilayer structure and Sn composition<sup>[6, 16]</sup>. As Raman spectroscopy measured the surface of thin films, XRD had a larger penetration depth, investigating the embedded layers with material information in



a more complicated structure.

Wilhelm Röntgen first discovered X-ray in 1895. It was later confirmed by a scientist Max von Laue that X-ray had waves of electromagnetic radiation in 1912, which was a form of light. It was defined that the X-ray wavelength was in the range from 1 angstrom –100 angstroms. The wavelengths of X-ray were at the same level as the spacing d between lattice planes in a crystal. Therefore, the incident of X-ray was able to produce diffraction with the lattice spacing with a same order of magnitude with the wavelength. William Henry Bragg and his son Lawrence Bragg won the 1915 Nobel Prize in Physics due to their contribution in proposing a way to analyze the crystal structure by X-ray. Since then, X-ray diffraction was widely used to characterize the crystal structure in the field of material science and was a fundamental technique to obtain crystallographic information in present days.

Atoms are regularly arranged in crystals, with a lattice spacing between planes. Electrons of these atoms will be scattered when X-ray waves strike these electrons, producing secondary spherical waves. These spherical waves interact with each other, with some having destructive interference and others having an add up in phase, leading to reflections to a specific direction. The interference happens only when the difference of optical path equals to an integral multiple of X-ray wavelength. The Bragg law perfectly summarized the rule and gave out the condition in Equation 2–3.

$$2d\sin\theta = n\lambda \tag{2-3}$$

Where *d* is the spacing between lattice planes,  $\theta$  is angle between the incident beam and the diffracting planes, *n* is a random integer, and  $\lambda$  is the wavelength of the incident X-ray beam. A schematic of the route for diffracted X-ray beam was presented in Figure 2–8.



Figure 2–8 Schematic of X-ray diffraction, where the array represents lattice, d is the spacing of lattice plane, and  $\theta$  is the angle between lattice plane and the incident beam.<sup>[29]</sup>

Usually, XRD instruments employ a vacuum hot-cathode X-ray tube to produce X-rays. Hot electrons are emitted by Tungsten filament and accelerated with controlled high voltage, then hitting the metallic target material. X-rays are thus generated with various wavelengths. Each metallic target material has its own continuous spectrum and characteristic spectrum. The characteristic spectrum has peaks with extremely large intensity, including K, L, M radiations. A corresponding filter will be selected to filter out the disturbing peaks such as  $K_{\beta}$ . To ensure the incident X-rays are monochromatic, a monochromator is usually equipped. When performing XRD characterization,



samples are placed in the center, with radiation and counter rotating at a regular scanning velocity in the range of set angles. The diffracted beam intensity of signals collected by the counter are recorded and later plotted on the software. A peak intensity occurs when there are reflections where the incident angle satisfies the Bragg law. There might be tens of peaks indicating the signs of many compositions. The XRD spectrum provides information about chemical information, which can be compared and analyzed with a public database containing XRD patterns for all compositions. By measuring the diffraction angle, we can obtain the corresponding lattice constants, so as to speculate the crystal structure to find out the elemental composition in the sample.

#### 2.3.2 Design and Experiments

The as grown sample B570A and 3 previously annealed samples, B570B, B570C, and B570D, prepared by Taga were selected to perform Raman and XRD characterizations. The as grown sample B570A was used as a reference to other annealed samples. We aimed to study the elemental fraction in a complicated structure with multiple layers, Sn fraction in particular.

Raman measurements were performed on these four samples using a Horiba Scientific Raman spectroscopy system LabRam HR. He-Cd laser was chosen to emit a laser beam with a visible 442-nm wavelength. The system allows high-resolution Raman measurements with a 50X objective lens to focus the beam light. The signals will be collected by CCD (Charge Coupled Device) detector and transformed to visual signals on PC. We used Labspec to adjust the acquirement parameters and carried out simple analysis such as peak finding. Before testing our samples, p-type Si sample was measured to do the spectral axis calibration. After zero-calibration, the Si signal was calibrated to locate at 520.5  $cm^{-1}$ . We detected the Raman shift in the range from 200  $cm^{-1}$  to 350  $cm^{-1}$  and set the filter to be  $D_{0.3}$ , and the accumulation to be twice. The exposure time was same for these four samples, that was 160 seconds. To ensure accuracy of the results, we measured three times in different regions and chose the most stable result among all trials for each sample.

These four samples were also sent to perform XRD measurements. Rigaku MultiFlex XRD of the Electron Microscopy Laboratory of the UBC Materials Engineering Department was employed to do XRD characterization. A monochromator and a target material Cu were equipped. After sticking the sample by conductive adhesive, I manually adjusted the height of the objective stage to ensure the sample surface align with the diffractometer axis. The XRD measurements in this study were performed in the range from  $63^{\circ}$  to  $72^{\circ}$ , with a scanning speed of  $0.5^{\circ}$  per minute.

#### 2.3.3 Results and Discussion

The Raman spectra for the as grown (B570A) and 3 annealed samples (B570B, B570C, B570D) were presented in Figure 2–9. The x-axis measured Raman shift and the y-axis was scaled intensity. As we can observe from the plot, the red curve indicated the Raman signal of B570C sample with a peak at 297.2  $cm^{-1}$ , which also had the largest intensity. The Raman spectrum of the as grown sample B570A was plotted in dark blue, with the peak locating at 297.4  $cm^{-1}$ . The curve with green color was the Raman characterization result of B570B sample and the light blue one was the plot of the B570D sample. These two curves shared a same peak position at 297.6  $cm^{-1}$ . To summarize the results above, there were no significant difference in Raman shift peak positions, surrounding



297.4  $cm^{-1}$ , which was characterized as Ge-Ge peak. Moreover, there was no sign of Ge-Sn peak or Si-Si peak. There was a difference in the Ge-Ge peak intensity. The Raman signal intensity of B570C was the largest while that of B570D was the smallest.

To conclude the results from Raman characterization, there were no effective results due to little difference in Raman shifts and the disappearance of Ge-Sn peak and Si-Si peak. Though there were intensity difference between samples, the practical results did not correspond to the theoretical assumptions. It was assumed that the Raman signal peak intensity would decrease when Sn segregate out. This mismatch could be explained from two perspectives. On the one hand, the instrument errors influenced the peak intensity and could not be corrected without reference Si peak. Also, these measurements were performed separately, especially for sample B570C which was tested on the other day, so any environmental condition difference would affect the accuracy of the results.



Figure 2–9 The Raman spectra of the as grown sample B570A and 3 annealed samples B570B, B570C, B570D

Figure 2–10 presented the results of XRD measurements for samples B570A, B570B, B570C, and B570D, with annealing conditions labeled on each plot. We adjusted the plots on the scale of angle according to the position of Si characteristic peak. The valley between two characteristic Si peaks were used as the reference. The plots were also normalized with regard to their intensity to make these results comparable. Upon annealing, Si characteristic peaks remained unchanged of having 2 splitting peaks due to the separate radiation of  $K_{\alpha 1}$  and  $K_{\alpha 2}$  when  $2\theta$  get larger. The XRD measurement of the as grown sample B570A was plotted as a reference. Three identifiable regions of peak can be characterized as GeSn, Ge, Si, from left to right respectively. The green plot of B570C sample and the purple plot of B570D sample also presented three peaks at the same region as to the as grown sample XRD plot. Though there were observable decreases in the intensity when the annealing temperature increased. However, when the sample was annealed for 30 mintues at 450  $^{\circ}C$ , the GeSn peak disappeared on the XRD spectra with Ge peak got broader.

To discuss the results of the XRD measurements above, we can conclude that GeSn decomposed during annealing. Especially when the annealing time reached 30 minutes at 450  $^{o}C$ , there were no detectable GeSn composite within the detectable region of XRD method.





Figure 2–10 The XRD spectra of the as grown sample B570A and 3 annealed samples B570B, B570C, B570D

The decomposition of GeSn reminded us that, in all probability, there might be Sn precipitation during annealing instead of simply the interdiffusion of Ge and Sn at a rather high annealing temperature. However, we could not draw further conclusion based on the experimental design. There were at least two annealing condition variables between trials, thus these measurements were not comparable. We need to further carry out trials with one variable left, either two conditions among annealing temperature, annealing time, and ramp speed, should be controlled.

### Chapter 3 Sn Segregation Study in GeSn

#### 3.1 Sn Segregation Study by Raman Spectroscopy

#### 3.1.1 Design and Experiments

It is necessary to have thermal annealing in the modern manufacturing of semiconductor devices, such as metal oxide semiconductor field effect transistors (MOSFETs), one typical application of GeSn devices. There are also different types of thermal anneals in the semiconductor device manufacturing, some of the examples being furnace annealing, rapid thermal anneals (RTA), etc<sup>[25]</sup>. Therefore, the thermal conditions during thermal annealing processing will lead to interlayer interdiffusion or even segregation. Such conditions are also affected the performance of segregation, leading to different levels of precipitation, thus affecting the properties of devices. Various factors concerning thermal conditions affect the performance of Sn precipitation in GeSn, such as temperature, annealing time, ramping speed, Sn concentration, etc.

In this study, we chose the B570 sample, a strain relaxed sample that has 8 % Sn concentration, to anneal for different period of time at the same annealing temperature and the same ramping speed. This primary aim of our study is to investigate the impact of the length of annealing time on Sn segregation. By controlling other annealing conditions while only changing the annealing time, we are able to compare the characterization results and learn about how time affects segregation both qualitatively and quantitatively.

Firstly, the annealing condition of B570B sample from Taga's work was chosen as the standard, that was 450  $^{o}C$  for the annealing temperature and 100  $^{o}C \cdot min^{-1}$  for the ramping speed. Six new samples were prepared in this study to carry out annealing with controlled time. We kept the annealing temperature and the ramping speed unchanged for the heat treatment. We designed annealing time to be less than 30 minutes and set in a step wise. As listed in Table 3–1, the 6 samples were annealed for 20 minutes, 10 minutes, 5 minutes, 20 seconds, 40 seconds, 1 minute, which were labeled in sequence, B570B1, B570B2, B570B3, B570B4, B570B5, B570B6, respectively. The as grown sample without annealing was marked B570A, functioning as a controlled trial for comparison with other samples in this study group. Furthermore, we employed furnace annealing to carry out the heat treatment.

To prepare samples for the annealing experiment,  $\text{Ge}_{1-x}\text{Sn}_x$  samples were first cut from relaxed undoped GeSn/Sn wafer pieces. The sample size was controlled to be approximately 1mm ×1mm, in order to fit in the heating stage. The cutting process was performed at room temperature on a flat desk in our lab.

Then these samples were annealed using furnace annealing at 450  $^{o}C$  with the same ramp speed 100  $^{o}C \cdot min^{-1}$  for different period of time, 30 min, 20 min, 10 min, 5 min, 1 min, 40 s, 20 s, respectively. The annealing was carried out by the furnace discussed in Section 2.2.1. The furnace was electrically heated, with sample placing in the middle of the heating stage. There was also an ambient environment filling with nitrogen and a cooling system functioned by circulating water in connected tubes. In this work, the temperature ramp-up speed and ramp-down speed were at the



Sample No.	Temperature $(^{o}C)$	Time	Ramp ${}^{o}C \cdot min^{-1}$
B570A	As grown	-	-
B570B	450	30 min	100
B570B1	450	20 min	100
B570B2	450	10 min	100
B570B3	450	5 min	100
B570B4	450	20 s	100
B570B5	450	40 s	100
B570B6	450	1 min	100

Table 3-1 Newly annealed GeSn/Sn sample pieces and the annealing conditions of
corresponding samples

same level, which was 100  ${}^{o}C \cdot min^{-1}$ , to be specific. After ramping up, there was a steady stage when temperature held unchanged at 450  ${}^{o}C$ . The duration of the steady stage differed from each sample, ranging from 20 seconds to 30 minutes in our study, to investigate the effect of annealing time on Sn segregation.

To investigate the segregation properties, we employed Raman methods to do characterization. As discussed in Section 2.3.1, Raman was an ideal tool to obtain the information of element fraction and strain state in the top layers of samples. Therefore, we employed Raman spectroscopy to obtain learn about how GeSn characteristic peaks change with annealing conditions, that is also to say the Sn element composition change in GeSn. Because Raman is able to collect the phonon vibration modes which help us identify elements and composition. We first did Raman characterization on B570A, B570B1, B570B2, and B570B3, to compare whether there will be Raman shift after annealing. However, when we discovered no difference in peak positions, we tried to reduce the heating time and tested three new samples, B570B4, B570B5, B570B6, by Raman method. And compare the three Raman spectra results with the as grown sample Raman spectrum B570A.

The Raman measurements in this study were performed by a high resolution Raman microscopy system LabRam HR by Horiba Scientific. The system applied an excitation wavelength of 442 nm (visible) from He-Cd laser. The Raman signals were collected through a 50X objective lens at room temperature, later transmitting to a thermo-electric cooled CCD (Charge Coupled Device) detector, and finally displaying results on computer. A software Labspec was used for controlling parameters in collection and first-hand analysis (peak search, signal pattern overview). Before collecting Raman results of samples, we first did calibration using Si sample and took Si peak as the standard, adjusting Si signal to the position of 520.5  $cm^{-1}$ . We also carried out trails to find the best measurement parameters for our samples. A twice accumulation and a  $D_{0.3}$  filter was set for collecting a Raman signal during a time period of 120 seconds, for all existing GeSn/Ge samples. GeSn/Ge samples were placed on one piece of glass slide in sequence and were tested one by one. We performed the Raman spectra collection with optimum parameters, allowing the most stable signals and the most distinguishable peaks.

#### 3.1.2 Results and Discussion

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The Raman spectra for the as grown and 4 annealed samples over 5 minutes were shown in Figure 3–1. The x-axis indicated the Raman shift while the y-axis displayed an approximate intensity. For all signal patterns, as-grown and annealed samples, shared one but single peak at around 297  $cm^{-1}$ , which indicated the existence of Ge-Ge bond. However, there were no evident differences between peaks. Moreover, there was no sign of Ge-Sn peak or Si-Si peak, which was expected to show at around 260  $cm^{-1}$  and 500  $cm^{-1[20]}$ . With the Ge-Sn peak, we can observe whether there will be segregation of Sn element. Because the segregation of Sn element will change the composition of GeSn, leading to a shift of the peak in Raman spectra. Si-Si peak can be taken as a standardized characteristic peak, contributing to the calibration.





Figure 3–1 Raman spectra of B570 samples annealed over a period of time in the range from 5 minutes to 30 minutes. The spectra of the as grown sample B570A was plotted as a reference

Figure 3–2 Raman spectra of B570 samples annealed over a period of time in the range from 20 seconds to 60 seconds. The spectra of the as grown sample B570A was plotted as a reference

Since we can conclude from Figure 3–1 that there was no evidence of comparable signals, we assumed that it may be the result of overheating. Typically, the annealing time was shorter than several minutes if annealed at a high temperature over 300 °C, such as 6-min annealing at 300 ~  $600^{\circ}C$  and 40-second annealing over 440 °C. If the annealing time was up to 20 minutes, the annealing temperatures were also milder, less than 300 °C. If the annealing temperature and time are high over the boundary segregation condition, it is possible that nearly all tin composition within composite GeSn segregates out, thus showing a Raman spectrum without Ge-Sn peak. As a result, I carried out another group of studies with shorter annealing time less than 1 minute, that were 20 seconds, 40 seconds, and 60 seconds, respectively. We changed the signal collection range to 100  $cm^{-1} \sim 320 \ cm^{-1}$ , hoping to find Sn-Sn peak near 110  $cm^{-1}$ . The filter and accumulation setting remained unchanged for collection.

Figure 3–2 showed the Raman spectra for 3 annealed samples less than 1 minute and the asgrown sample. For samples, B570A, B570B4, B570B5, and B570B6, all had a significant peak at around 270  $cm^{-1}$ . As we can see from the marked red line, four peaks align each other and locate at the same position as to the x-axis. Also, there were no signs of the characteristic peaks of Sn-Sn.



To conclude, we cannot detect any Ge-Sn peak or Sn-Sn peak with Raman spectroscopy. One possible explanation is the limited probing depth. The probing depth of this wavelength without filters is around several nanometers<sup>[25]</sup>. The corresponding probing depth is even smaller with filters on.

However, the first layer of our sample is a 300 nm-thick Ge layer. GeSn layer is underneath the Ge layer. Thus, the excitation light cannot reach the GeSn layer, having no sign of Ge-Sn peak or Sn-Sn peak in turn. Based on the condition of our experimental equipment, we can only investigate the composition information from the surface but cannot obtain useful information to analyze the performance of segregation which occurs in the second layer.

To conclude the research above, only Ge-Ge characteristic peak existed in Raman spectra of all annealed samples as well as the as grown sample without signs of Ge-Sn peak and Si-Si peak due to the shallow probing depth of Raman spectroscopy technique. Furthermore, there were no significant Raman shifts between Ge-Ge peaks for different annealed samples, indicating that Raman spectroscopy was not available to identify Sn segregation. We needed to apply alternative characterization methods to study Sn segregation behaviors.

#### 3.2 Sn Segregation Study by XRD, OM and SEM

There are various alternative characterization methods employed by previous researchers to study elemental composition in group IV semiconductor materials, such as XPS, XRD, SEM, XTEM. Here we employed XRD that we had trials in previous interdiffusion study as well as optical microscope and scanning electron microscope to investigate the surface morphology of specimens.

# 3.2.1 Introduction to Optical Microscope (OM) and Scanning Electron Microscope (SEM)

The introduction of XRD was discussed previously in Chapter two, here I will introduce principles of optical microscope and scanning electron microscope before presenting results and analysis.

Optical microscope was the most popular surface characterization method due to its low cost and convenience. It employed visible light to illuminate the sample and lens to magnify the region to observe details that cannot be discovered by naked eyes. Typical applications include biological materials, electronic devices, metals, etc. However, the resolution and the magnification of OM were both limited, being unable to provide enough details in analyzing surface morphology. Thus, OM was usually used as a supplementary method to first have an overview of the surface.

To reveal the specimen topography, Scanning Electron Microscope (SEM) image is a suitable characterization with much higher resolution than the optical microscope, achieving resolution better than 1 nanometer.

SEM generates a focused beam of electrons to scan the surface of the specimens to produce SEM images. There are various signals generated by interacting with the electron beam, including secondary electrons (SE), backscattered electrons (BSE), X-rays, transmitted electrons, absorbed electrons, and cathodoluminescence (CL). To detect these signals, corresponding detectors are needed for SEM equipment, where secondary electron detectors are standard equipment. These signals are detected with information on specimen topography and composition included, being re-modulated



into images. Typically, the number of secondary electrons is detected for common SEM cases. Here we also used BSE mode to image the surface morphology.

According to the principles of SEM characterization, the wavelength and intensity of signals received by the detectors change according to the surface morphology and the chemical composition of the detected substance. Take secondary electrons mode as an example, there will be a stronger signal at regions with sharp morphology, showing a brighter region on the image. As for the case of backscatters electrons mode, the signal intensity is strongly related to the atomic number, with brighter imaging results in larger-atomic-number regions. Therefore, SEM images allow for visual observation of the specimen, revealing the detailed surface morphology and chemical composition.

There is another powerful analytical tool equipped in several SEM equipment, called Energy Dispersive X-Ray Spectroscopy (EDS). EDS is able to obtain the elemental information about the regions of interest or chemical characterization of a specimen. The electron beam in SEM is functioned as the excitation source to generate X-ray signals. The X-ray detector will collect the X-rays and convert the energy into voltage signals. Not only the types of element can be analyzed, detailed composition is also available with mass percentage or atomic ratio presenting. As a result, the elemental content in the epilayer microstructure was investigated using EDS in this study.

#### 3.2.2 Design and Experiments

Aside from Raman Spectroscopy, X-Ray Diffractometer (XRD) is an another frequently used equipment in characterizing thin-film structures. Raman spectra present information about surface while XRD spectra provide more information of the whole structure including embedded layers, because the penetration depth of XRD is larger than that of Raman Spectroscopy. XRD method can provide information about phase composition and lattice constant, while Scanning Electron Microscope (SEM) and Optical Microscope (OM) can help examine the surface morphology of samples after annealing.

Accordingly, in this study, various characterization techniques (XRD, SEM, OM) were employed to study the phase composition and surface morphology. 5 samples were selected to carry out XRD characterization, that was B570B1, B570B2, B570B3, B570B6, B570A, respectively. Samples with longer annealing time than 20 minutes that is 30-minute annealing and shorter annealing time than 1 minute were not selected, because we believed the selected samples were already representative to examine whether there was segregation. Optical images of all samples including samples B570B, B570B4, B570B5, were taken for observation. Two magnifications of the lens were selected to observe the samples, 10x and 50x, respectively. It was originally designed to take SEM images of all samples and to provide supplemental and more detailed surface information as to OM images. However, due to the shut-down of labs, I took SEM images of B570B sample and the corresponding EDS analysis on selected regions.

In this thesis, I carried out XRD measurements using Rigaku MultiFlex XRD with a 2kW x-ray generator at room temperature. We employed monochromator in XRD measurements and chose copper (Cu) as the target material. The sample was placed in the center of the diffractometer circle, sticking to the holder by conductive adhesive. Due to the small size of the sample, it cannot physically coincide with the diffractometer axis. Thus, I did manual adjustment to the height to



ensure that the sample surface was at the same height of the diffractometer axis, so that the XRD signals would be more accurate. According to Wang, W., et al.<sup>[16]</sup>, Li, H., et al.<sup>[22]</sup>, the characteristic peaks of Si, Ge, GeSn are around 70°, 67°, 65°, respectively. Thus, we performed the XRD tests in the range of angle  $2\theta$  from 63° to 72°, with a scanning speed of 0.5 degree per minute.

The optical microscope images were taken using the attached microscope in the Horiba Scientific Raman microscopy system, with 10X and 50X objective lens. Images were processed by the software Labspec and were saved using screenshot. Later I adjusted the size of these images by Adobe Photoshop.

The SEM images were shot by a conventional Tungsten hairpin filament source SEM-Hitachi S3000N VP-SEM with EDX. The system was also available for EDS analysis with an X-ray detector inside and backscatter mode images with a backscatter detector equipped. Firstly, the B570B sample was attached to the specimen holder by conductive adhesive and placed within the vacuum chamber. After inserting the vacuum chamber, the SEM was vacuumed by a pump to avoid disturbing on electron beams. The electron beam was generated by an electron source and later was directing to the specimen by magnets and lens. Resolution and imaging regions were adjusted to find the image with the best quality. The images were later scanned and captured as photograph. EDS scan was carried out by capturing a selected region. To avoid noises, we selected the elements for analysis, Ge, Sn, Si, in our study. We also carried out 5 trials of EDS scans, choosing the whole region for average composition, and two segregation spots, two smooth spots for specific analysis.

#### 3.2.3 Results and Discussion

The results of XRD measurements were presented in Figure 3–3. Si characteristic peak in each measurement was used as reference to adjust the error in  $2\theta$  between trials. The levels of intensity were also normalized according to the intensity of Si peak. The peak position of Si remained unchanged upon annealing, showing 2 splitting peaks around 71°. There were also 2 splitted Ge peaks around 67.5° for all samples. Ge peaks were broader but also remained unchanged after annealing, as indicated by the red line. However, a third peak was identified in the XRD spectra for samples that had been annealed over 5 minutes. GeSn characteristic peak showed around 66.5°. But when the annealing time exceeds 5 minutes, the GeSn peak disappeared. We can also observe a decrease in the GeSn peak intensity of B570B6 sample comparing with that of the as-grown sample. The peak position of GeSn also remained unchanged.

The phenomenon of having splitting peaks can be explained by the theory of XRD. When  $2\theta$  reaches a high level, the converged Cu  $K_{\alpha_{1,2}}$  radiation will split into two peaks,  $K_{\alpha_1}$  and  $K_{\alpha_2}$ , respectively<sup>[30]</sup>.

The decrease and the disappearance of GeSn characteristic peaks may be related to Sn segregation and interdiffusion during annealing. The appearance of a third peak that converged with Ge peaks may be due to the Sn segregation and Ge diffusion in GeSn layer. As a consequence, we assumed that longer annealing time leads to more Sn segregation and precipitation. The relaxed undoped Ge<sub>0.92</sub> Sn<sub>0.08</sub> would have observable Sn segregation when annealed over 5 minutes at 450  ${}^{o}C$ .





Figure 3–3 The XRD spectra of the as grown sample B570A and 4 annealed samples B570B1, B570B2, B570B3, B570B6



Figure 3–4 The optical images of the as grown sample B570A and 5 annealed samples B570B, B570B1, B570B2, B570B3, B570B6



To confirm our hypothesis that longer annealing time leads to more Sn segregation and precipitation, we followed up by observing the samples through optical microscope. Figure x presented the optical images of as grown and 4 annealed samples. The images were shot by the optical microscope attached to the Horiba Scientific Raman microscopy system, using 50X lens. According to Figure 3–4 e) and f), there were no observable segregation on the surface for the as-grown and 1-minannealed samples. When the annealing time exceeds 5 minutes, the optical images showed dispersed white spots on the surface, as Figure 3–4 a), b), c), d) presented. These white spots indicated Sn segregation, which matched our hypothesis in predicting segregation over 5-min-annealing.



# Figure 3–5 The SEM image of B570B sample Figure 3–6 The SEM image of B570B sample in SE mode in BSE mode

The XRD measurements and optical images provided basic information about the surface. To further acquire information of the surface and the Sn composition, we employed SEM to carry out qualitative and quantitative analysis.

We conducted SEM analysis by Hitachi S3000N VP-SEM with EDX, displaying observable Sn segregation in SEM images. The images were taken using the magnification of 3000x, the voltage of 15kV, and WD of 9.5 mm. Figure 3–5 performed a Secondary Electron mode (SE2) with red arrows pointing to Sn segregation area and GeSn area, respectively. There were light-colored lump areas dispersed in the selected area. Black dots were impurities, surrounded by the large area of uniform dark grey surface. Lighter areas were bumps that extruded out, while darker areas were smooth, according to the interaction principles of secondary electrons and the detection areas. We proposed that these lighter-colored areas were Sn segregation and the uniform areas were composed of GeSn. The observation corresponded to the results of optical images, confirming our hypothesis. Figure 3–6 employed Backscatter Electron (BE) mode. With higher contrast, we were able to observe a clearer difference between areas. White bumps that shaped polygon were segregated Sn. Similar to the presentation in SE mode, GeSn areas were located at surrounded dark area. Since parts will be brighter when the atomic number gets larger under the BSE mode, we can draw the conclusion that the chemical elements in bright areas have larger atomic numbers than the elements in dark areas.





Figure 3-7 The selected region of B570B sample for EDS analysis, with spots and area marked

Table 3–2 The EDS results of B570B sample where presents the atomic percentage of Silicon
(Si), Germanium (Ge), and Tin (Sn)

Spectrum	Silicon (atom%)	Germanium (atom%)	Tin(atom%)
Overall area	23.52	56.02	20.47
Spot 570B2	43.00	8.21	48.79
Spot B570B3	41.68	12.76	4 5.56
Spot B570B4	29.14	64.92	5.95
Spot B570B5	28.83	65.65	5.51

In order to confirm the assumption of composition of elements, we carried out EDS (Energy Dispersive Spectrometer) analysis using the same Hitachi SEM equipment. The selected areas for EDS analysis were labeled and showed in Figure 3–7. Correspondingly, the data of atomic composition of Silicon, Germanium, and Tin were listed in Table 3–2. The rectangle-shape Area 1 include the whole visible area. The results of the atomic percentage were an average outcome after scanning the whole area. As marked in Figure 3–7, spot 570B2 and 570B3 were located at light-colored areas, while spot 570B4 and 570B5 stood inside the uniform darker area.

According to Table 3–2, there were over 50 % of Ge in the whole area on average, while both of the concentration of Si and Sn were approximately 20%. However, a great decrease in percentage of Ge composition was observed in the results of spot 570B2 and 570B3, dropping to around 10%. On the other hand, both the atomic percentage of Si and Sn significantly increased to a level over 40%. As for spot 570B4 and spot 570B5, the composition of Ge was higher than the average percentage, which was nearly 65%. The atomic percentage of Sn for spot 570B4 and 570B5 was neglectable of being 6%.

To conclude, the EDS measurement of element atomic percentage help us confirm that lightcolored areas were highly concentrated Sn, which were likely to be Sn precipitation. The uniform darker areas were composed of GeSn. The concentration ratio of the experimental measurements was



close to the ratio of the as-grown sample, which demonstrated that the darker areas were  $Ge_{0.92}Sn_{0.08}$ . As stated in the following Equation, the experimental ratio was slightly smaller than the as grown ratio. The fact further confirmed the segregation of Sn. The EDS analysis confirmed our hypothesis on compositions of different areas.

Experimental ratio (Ge/Sn) = 
$$\frac{65\%}{6\%}$$
 = 10.8 < 11.5 =  $\frac{92\%}{8\%}$  = As-grown ratio (Ge/Sn) (3-1)

To briefly conclude the section, I summarized the characterization and corresponding observations into a table, listed in Table 3–3. XRD signals presented footprints of decomposition of GeSn, which related to observable segregation in optical images. SEM images as well as the EDS analysis further confirmed the hypothesis that the segregation was composed of Sn.

Sample No.	Annealing time	XRD	ОМ	SEM
B570A	As grown	GeSn, Ge, Si signals	No observable segregation	-
B570B	30 min	Ge, Si signals	Observable segregation	Sn segregation
B570B1	20 min	Ge, Si signals	Observable segregation	-
B570B2	10 min	Ge, Si signals	Observable segregation	-
B570B3	5 min	Ge, Si signals	Observable segregation	-
B570B4	20 s	-	No observable segregation	-
B570B5	40 s	-	No observable segregation	-
B570B6	1 min	GeSn, Ge, Si signals	No observable segregation	-

Table 3–3 Sample pieces and the corresponding characterization results summary

#### 3.3 Capping Layer Impact on Se Segregation : Experiment Design

To solve the problem of Sn segregation during high temperature annealing, we proposed that a capping layer might help reduce Sn segregation. Because previous researches had demonstrated the passivation effect on multi-Si solar cells based on PECVD silicon nitride<sup>[31]</sup>.

The epilayer material of  $Si_x N_y$  and  $SiO_x$  were chosen as our major components of the capping layers. The silicon nitride and oxide can be deposited using the furnace system over 835 degree C, which can be both low stress and stoichiometric. However, the temperature was too high for GeSn materials due to potential serious segregation of  $Sn^{[32]}$ . As a result, we decided to employ the plasma-enhanced chemical vapor deposition (PECVD) system to deposit silicon nitride. The PECVD had the advantages of low temperature (<75  $^{o}C$ ) as well as accommodation with small substrates.

We planned to have 200 nm oxide on one sample and 200 nm nitride on the other sample to compare which capping layer would have better impact in reducing segregation. We had already contacted 4D labs located at Simon Fraser University for assistance in PECVD deposition. However, due to the unexpected shut down of all labs during pandemic, we were not able to carry out our experiments but left it for future study.



### **Chapter 4** Conclusion

#### 4.1 Summary

GeSn materials emerged for their attractive properties such as having direct bandgap and high carrier mobility. Therefore, GeSn is a popular high mobility channel material with wide applications such as MOSFETs, optoelectronics etc. However, it is unavoidable to have Ge-Sn interdiffusion and Sn segregation during thermal annealing, which degrades the electrical properties. Previous researches studied interdiffusion phenomenon and segregation behavior separately, and did not investigate the prevention of Sn segregation. This thesis was original in providing a comprehensive view of thermal stability of  $Ge_{0.92}Sn_{0.08}/Ge$  structure by examining interdiffusion and segregation behaviors simultaneously. We also provided a guideline of thermal budget for segregation, which might be helpful in avoiding segregation in future stages of manufacturing. Furthermore, the proposal to study capping layer effect on reducing segregation was also promising in solving the problem of property degradation after heat treatment.

In this thesis, we performed studies to investigate the impact of annealing conditions on Ge-Sn interdiffusion behaviors and Sn segregation. Various characterization methods were employed, including SIMS, Raman spectroscopy, XRD, SEM, EDS, OM, etc.

To extract Ge-Sn interdiffusivity by applying Boltzmann-Matano analysis, Sn profiles were obtained by SIMS analysis. We plotted the theoretical step-shape Sn fraction profile along with the smoothed practical SIMS profile, finding a wavy plateau which did not meet the requirement of Boltzmann-Matano analysis. The solution to the problem was to fabricate new wafer pieces with more precise growth control of Sn composition to avoid the unsmooth plateau. However, it was not available for our lab to improve the growing of epitaxial films because all our samples were provided by NTU. Therefore, alternative characterization methods were needed to study the Ge-Sn interdiffusion performance.

As a result, Raman spectroscopy and XRD were employed as alternative characterization methods to study the Sn concentration respectively. By comparing the Raman spectra of the as grown sample and annealed samples, it was observed that there was little difference in Raman shifts of Ge-Ge peak and the intensity sequence was not consistent with the assumption that the intensity decreases with increasing the annealing time or annealing temperature. The instrument errors and environmental disturbance may contribute to the inaccurate results. The XRD measurements presented reasonable results, with the intensity of GeSn peak and Ge peak decreased after annealing. Also, the GeSn peak disappeared on the XRD spectrum of B570B sample which was annealed at  $450 \, ^{o}C$  for 30 minutes. The disappearance of GeSn peak can be seen as an evidence to demonstrate the decomposition of GeSn during annealing. Accordingly, it might be the occurrence of Sn precipitation instead of wholly Ge-Sn interdiffusion behaviors when GeSn samples were annealed at high temperatures. Nevertheless, due to the limitations of experimental design without comparable groups, further trials were needed to study the influencing factors of GeSn decomposition and whether there was Sn segregation.



After finding footprints of Sn segregation in previous studies, we designed further studies to investigate the impact of annealing time on Sn segregation at the same annealing temperature. We performed thermal annealing at 450  $^{o}C$  for a wide annealing time range from 30 minutes to 20 seconds, producing 6 newly annealed samples. These samples were investigated using various characterization methods, including Raman spectroscopy, XRD, SEM, EDS, OM, etc.

Raman spectra of the previous B570B sample and 6 annealed samples were obtained and plotted firstly, along with the as grown sample Raman spectra as a reference. We expected to observe Ge-Sn peaks to analyze the Sn composition change in accordance to Raman shift change of Ge-Sn peak. Nonetheless, there was only Ge-Ge characteristic peak instead of Ge-Sn peak or even Si-Si peak due to the limitation of Raman spectroscopy. The probing depth of Raman spectroscopy was small so that the embedded GeSn layers as well as Si substrate were not detectable. In addition, the Ge-Ge peaks of different annealed samples aligned each other without significant position difference. Hence, Raman spectroscopy was not available to identify Sn segregation.

In an attempt to successfully characterize Sn segregation, we explored alternative methods other than Raman spectroscopy. XRD measurements were thus carried out to study the elemental composition of embedded epitaxial layers due to large penetration depth of X-ray. Three characteristic peaks were observed in the XRD spectra for the as grown sample as well as the annealed sample less than 1 minute, indicating existence of GeSn, Ge, and Si. However, the GeSn characteristic peak disappeared and converged with the Ge peak as the annealing time increased over 5 minutes. The disappearance of GeSn peak demonstrated the decomposition of GeSn after annealing at  $450 \, ^{o}C$  for over 5 minutes, which was also a sign of Sn segregation.

The specimen topography was examined by optical images and SEM images. Optical images revealed that there were increasingly distributed bright regions when annealed for over 5 minutes where used to be a uniform surface before thermal annealing. These bright regions, in other words, were segregated out during annealing, which were likely to be composed of Sn. The SEM images of B570B sample further confirmed the observation from optical images with greater contrast and better resolution in both SE mode and BSE mode. There were irregular shaped precipitation regions dispersed on the uniformly grown surface. The compositions of different regions were then studied by EDS analysis, in an attempt to confirm the segregation. Consequently, the results of high atomic percentage in the bright regions demonstrated the precipitation was mainly composed of Sn. The fact confirmed the assumption that GeSn decomposed into Sn and precipitated out during annealing.

To summarize major contributions in this thesis, I listed bullet points as follows:

1. The thermal stability of the relaxed undoped  $\text{Ge}_{0.92}\text{Sn}_{0.08}$ /Ge structure was studied by examining Ge-Sn interdiffusion behaviors and Sn segregation. Due to technical limitations in controlling the epitaxial growth, interdiffusion behaviors were not able to be presented with SIMS profiles while Sn segregation had feasible presentations by various characterization methods.

2. The phenomenon of Sn segregation during annealing was observed. The XRD spectra as well as the imaging demonstrated the decomposition of GeSn and segregation of Sn on the specimen surface. Therefore, the thermal budget of the relaxed undoped  $\text{Ge}_{0.92}\text{Sn}_{0.08}/\text{Ge}$  structure can be concluded from the study. There was observable segregation when GeSn/Ge samples were annealed at 450  $^{o}C$  for more than 5 minutes. There might be Ge-Sn interdiffusion but no observable Sn segregation for this epilayer structure if annealed less than 1 minute.



3. This thesis originally put forward a structure to prevent Sn segregation, which is promising to realize the prevention by the capping of silicon nitride  $(Si_xN_y)$  or silicon oxide  $(SiO_x)$  layer.

4. In the thesis, we employed various kinds of characterization techniques to study the Sn segregation. We found XRD and SEM most useful due to the high probing depth for XRD and high resolution for SEM as well as the quantitative composition analysis by SEM equipped EDS. Raman was not ideal due to its small penetration depth but was powerful to study the elemental fraction and strain status for thin-films or surfaces.

#### 4.2 Prospect

In this thesis, we found the thermal budget for Sn segregation behavior during annealing and proposed that a capping layer might reduce the segregation after treating with the same thermal annealing. Therefore, the capping layer study can be continued to find out whether a  $Si_xN_y$  or  $SiO_x$  would prohibit the amount of segregation.

However, there were several limitations in our studies.

1. Due to the unexpected lab shut down during pandemic, we only did SEM analysis on one sample B570B. The study would be more complete with SEM images and EDS analysis performed on all annealed samples as well as the as grown sample. Comparisons of SEM images and EDS results were needed to analyze the segregation density change and Sn concentration difference.

2. Because of the limited laboratory conditions, our samples were sent to characterization without cleaning. Ultrasonic cleaning before characterizations will improve the quality of results and reduce the impact of impurities on the surface.

3. This thesis was more of an empirical study without studying capping layer impacts practically, which lacked meaningful findings to contribute to the field. Nevertheless, the comparable segregation studies between capped epilayer structure and original structure would probably give out a creative solution to reduce Sn segregation in GeSn materials.



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### Acknowledgements

First of all, I would like to express my gratitude to my supervisor, Dr. Guangrui Xia, for giving me this opportunity to do my graduation project abroad in UBC. I am grateful for the guidance in research training as well as patience and support in a brand new environment.

I would also like to acknowledge Dr. Chun Chao Chen, my supervisor in SJTU, who was so supportive being my backup for these years. The assistance through out the whole process of graduation project, the support when I was experiencing pandemic overseas, and also the encouragement during my transition journey gave me much energy to go through all the way long.

Many thanks go to my colleagues back in UBC. Thanks Taga Kazuhiro for the previous progress in this thesis study. And much appreciation to Yunlong Zhao, Zeyu Wan, Liming Wang, Teren Liu for providing me hands-on training and insightful discussions. Lastly, I was so grateful to have a "lunchroom gang" with Yuting Zhou and Liming Wang, being the closest friends overseas. Thank you all for much care and many precious memories.

Last but not least, I deeply appreciate my parents, who were always my backup and gave me so much support in doing everything I like. Also my dearest friends, Yun Zhang and his fiancé Yuying Zhang, Gabriella Zhao, Jane Zheng, and Lily Zhu, thank you all for supporting me through this journey.