## Liquid-Phase Epitaxy Growth of SiGe Graded Buffers on Si (001)

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#### Abstract

This thesis discusses the quality of SiGe graded buffers or films grown on Si (001) by a customdesigned, liquid-phase epitaxy (LPE) system. First, Low-Ge-content SiGe graded buffers were grown on Si (001) with the same initial solution composition ( $\sim 2\%$ Ge). The growth started at 950 °C but ended at different final temperatures 940 °C, 850 °C, 750 °C, 650 °C, 550 °C, and 450 °C. The growth maintains two-dimensional film until the temperature drops to 650 °C. Further temperature decreasing results in film morphologies with more three-dimensional growth. A detailed analysis of the strain states of the graded buffer reveal that the initial film at the buffer/substrate interface is fully strained initially and during a longer growth process becomes fully relaxed. As the growth continues with further temperature reductions, the latter parts of the film have both more Ge content as well as strain. This is the first report about the growth morphology and strain states evolution of SiGe graded buffers during the LPE growth process. In addition to investigating long growths of SiGe from a 2%Ge solution, the properties of films from short growths (950-940 °C) with different solution compositions (2%Ge, 4%Ge, 5Ge%) are presented. The initial growth transitions from the characteristic crosshatch morphology into a more three-dimensional morphology with increasing Ge content in the solution. We found that the highest Ge film that maintains two-dimensional film growth is 3.1%Ge. The initial film changes from fully strained to 30% partially relaxed and back to fully strained as the composition increases from 1.4%Ge to 3.1%Ge. This is the first report about tracking the quality evolution of initial LPE

films with increasing Ge content.

The properties of SiGe graded buffers grown with different solution compositions (2%Ge, 4%Ge, 5%Ge) from 950-750 °C are studied as well. The initial film of each graded buffer close to the

buffer/substrate is fully relaxed at high temperature but experiences tensile strain after cooled to room temperature. The film of the graded buffer further from the interface experiences compressive strain and becomes more strained. Also, an etch pit density process was developed to study the threading dislocation density (TDD) of LPE SiGe films and graded buffers. The TDD of graded buffers (i.e. thicker films) grown with 4%Ge- and 5%Ge-content-solution is ~10<sup>6</sup> cm<sup>-2</sup>, one order of magnitude lower than their own initial films (the film grown in the first ~10 °C growth interval) while the TDD of the graded buffers grown with 2%Ge-content-solution is similar to its low initial film TDD, ~10<sup>6</sup> cm<sup>-2</sup>. This is for the first time to present the TDD reductions by LPE SiGe graded buffers.

Finally, SiGe films were grown on CVD-grown Si<sub>0.88</sub>Ge<sub>0.12</sub>/Si (001) substrates with different composition solutions from 950-940 °C. The existing threading dislocations on CVD substrates make the misfit dislocation nucleation easier than on bare Si, which helps the initial film relax more ( $\geq$ 86%) than those on bare Si (fully strained or ~30% relaxed).

### Sommaire

Cette thèse porte sur la qualité des couches tampons graduelles de SiGe ou des couches déposées sur Si (001) au moyen d'un système d'épitaxie en phase liquide (LPE pour Liquid-Phase Epitaxy) conçu sur mesure. Premièrement, des couches tampons graduelles de SiGe à faible composition en Ge ont été déposées sur Si (001) à l'aide d'une solution de même composition initiale (~2% en Ge). La croissance débute à 950 °C et se termine à différentes températures finales: 940 °C, 850 °C, 750 °C, 650 °C, 550 °C ou 450 °C. La croissance bidimensionnelle de la couche est maintenue jusqu'à une température minimale de 650 °C. Une diminution supplémentaire de la température engendre une croissance de morphologie plus tridimensionnelle. Une analyse détaillée des états de contraintes de la couche tampon graduelle révèle que la couche initiale à l'interface couche tampon/substrat est à l'origine totalement contrainte et qu'elle se relaxe complètement quand la croissance se prolonge. Tout au long de la croissance et de la diminution continuelle de la température, les dernières portions de la couche comportent à la fois plus de Ge et de contraintes. Il s'agit de la première description de la morphologie de croissance et de l'évolution des états de contraintes dans les couches tampons graduelles de SiGe durant une croissance LPE. En plus de l'étude des croissances longues de SiGe à partir d'une solution à 2% de Ge, les propriétés de couches issues de croissances courtes (950-940 °C) pour des solutions de compositions différentes (2%, 4% ou 5% de Ge) sont présentées. La croissance initiale présente une transition du motif caractéristique en hachures croisées à une morphologie plus tridimensionnelle provoquée par la proportion croissante de Ge dans la solution. Nous avons établi que la quantité maximale de Ge qui permet une croissance bidimensionnelle est de 3.1%. La couche initiale est d'abord totalement contrainte puis présente un état de relaxation partielle de 30% et devient de nouveau totalement

contrainte quand la composition augmente de 1.4% à 3.1% en Ge. C'est la première description de l'évolution de la qualité de couches LPE initiales de composition croissante en Ge.

Les propriétés des couches tampons graduelles de SiGe déposés à l'aide de solution de différentes composition (2%, 4% or 5% de Ge) à 950-750 °C sont également étudiées. Le film initial de chaque couche tampon graduelle, proche de l'interface couche tampon/substrat, est complètement relaxé à haute température mais présente une contrainte en tension après refroidissement à température ambiante. Plus loin de l'interface, la couche tampon graduelle présente des contraintes de compression et se retrouve de plus en plus contrainte. De plus, un procédé de gravure chimique des dislocations a été développé afin d'évaluer la densité de dislocations traversantes (TDD pour Threading Dislocation Density) des couches de SiGe et des couches tampons graduelles obtenues par LPE. La TDD des couches tampons graduelles (i.e. des couches épaisses) issues de solutions à 4% et 5% de Ge, est de ~10<sup>6</sup> cm<sup>-2</sup>, soit un ordre de grandeur inférieur à leur propre couche initiale (la couche déposée pendant le premier intervalle de ~10 °C). La TDD des couches tampons graduelles déposés à l'aide d'une solution de Ge à 2% est similaire à la TDD de leur couche initiale qui est de ~10<sup>6</sup> cm<sup>-2</sup>. C'est la première démonstration d'une réduction de la TDD au moyen d'une couche tampon graduelle de SiGe obtenue par LPE.

Enfin, des couches de SiGe ont été déposées, à partir de solutions de différentes compositions, sur des substrats de Si<sub>0.88</sub>Ge<sub>0.12</sub>/Si (001) obtenus par dépôt chimique en phase vapeur (CVD pour Chemical Vapor Deposition) à des températures de 950-940 °C. Les dislocations traversantes présentes sur ces substrats CVD provoque la nucléation de dislocations de désaccord de mailles plus efficacement qu'une gaufre de Si, ce qui engendre une relaxation de la couche initiale plus importante ( $\geq$  86%) que dans la couche déposée sur une gaufre de Si (complètement contrainte ou relaxée à ~30%).

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# List of Acronyms

AFM	Atomic Force Microscopy
BSE	Backscattered Electrons
СМР	Chemical-mechanical Polishing
CVD	Chemical Vapor Deposition
EDS	Energy-dispersive X-ray Spectroscopy
EPD	Etch Pit Density
FCC	Face-centered Cubic
FM	Frank-van der Merwe
LPE	Liquid-phase Epitaxy
Μ	Metal
MBE	Molecular Beam Epitaxy
MJ	Multijunction
PIPS	Precision Ion Polisher System
PV	Photovoltaic
RLP	Reciprocal Lattice Point
RMS	Root Mean Square
RSM	Reciprocal Space Map
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SK	Stranski-Krastanov
TD	Threading <b>D</b> islocation

- TDD Treading Dislocation Density
- TEM Transmission Electron Microscopy
- VW Volmer-Weber
- XRD X-ray Diffraction

## **Contributions of Authors**

This thesis was written by Jun Wang and reviewed by Nate Quitoriano. Part of the work presented in chapter 6, chapter 7, and chapter 8 will be published elsewhere.

The LPE furnace was designed and developed by Jerome LeBoeuf, Andrew O'Reilly, and Jun Wang.

Jun Wang performed all the LPE growth experiments, did all the SEM, AFM, TEM, and XRD characterizations, analyzed the results presented in this thesis. Jun Wang developed the etch pit density process. Yu-Jack Shen etched the samples and Jun Wang analyzed the etch results. Christopher Heidelberger from Massachusetts Institute of Technology provided the CVD-grown SiGe/Si wafers.

### **Statement of Originality**

This thesis provides key contributions to the field of using liquid-phase epitaxy (LPE) technique to grow SiGe graded buffers as virtual substrates for lattice-mismatched semiconductors application. The primary contributions are listed as following:

- The growth mode of LPE SiGe graded buffer during the cooling process was tracked for the first time. The surface ridges width and height, ridge density, surface roughness, and morphology were discussed.
- 2. The composition profile of LPE SiGe graded buffer during the cooling process were investigated. Ge content was plotted as a function of thickness by using the thicknesses and X-ray diffraction (XRD) maps of buffers grown with same initial composition solutions from the same initial temperature but ended at different final temperatures.
- 3. The strain states variation of LPE SiGe graded buffers during the growth process were indepth discussed by plotting the strain relaxation via thickness based on thicknesses and XRD maps. We reveal that a longer growth process helps the film close to buffer/substrate interface fully relaxed. The upper parts, however, have more strain with further growth.
- 4. Surface morphologies and strain states of initial SiGe films grown on Si (001) with different composition solutions were investigated. We found out the highest Ge content of the initial deposition that maintains two-dimensional film growth.
- 5. Strain states of SiGe graded buffers grown with different solution compositions from 950-750 °C were discussed. We found the film of the graded buffer close to the buffer/substrate experiences tensile strain after cooled to room temperature while the upper parts experience compressive strain and become more strained with increasing thickness.

- 6. An etch pit density process was developed to study the threading dislocation density (TDD) of LPE SiGe graded buffers (grown from 950-750 °C) as well as their initial films (grown from 950-940 °C). Thick growth from 1.1 μm to 9.4 μm helps TDD reduce one order of magnitude from 10<sup>7</sup> cm<sup>-2</sup> of the initial film to 10<sup>6</sup> cm<sup>-2</sup> while it remains similar when the initial film TDD is around 10<sup>6</sup> cm<sup>-2</sup>.
- Strain relaxations of initial LPE SiGe films grown on substrates with generous dislocation sources (~8×10<sup>6</sup> cm<sup>-2</sup>) were examined and we found that existing dislocations helps the initial LPE film relax more than on bare Si.
- 8. The initially deposited SiGe composition as a function of solution composition was discussed compared to the calculated results from Alonso and Trah with temperature fixed at 950°C. The experimental results are lower than the calculation results and the difference becomes larger varying from 0.8%Ge to 9.4 %Ge as the solution composition increases from 2%Ge to 23%Ge.

### Chapter 1

#### Introduction

#### 1.1 Background

Solar cells, also called photovoltaic (PV) cells, typically made from semiconductor pn junctions, are devices that convert light into electricity. "Photovoltaic" comes from the Greek "photo" means "light" and "voltaic" means "electricity". Since the first silicon solar cell was developed in 1954 at Bell Laboratories [1], research in solar cells has made tremendous progress because solar energy is one of these gigantic, environmental pollution free, and renewable energy sources [2, 3]. Over  $1.5 \times 10^{22}$  joules solar energy reaches Earth every day, 10,000 times more than our daily energy consumption approximately  $1.3 \times 10^{18}$  joules [4]. Unlike abundant solar energy, fossil fuels, our most energy supply, are finite and require up to 200 million years for ancient plants stored beneath Earth's surface to form [5]. Also, burning fossil fuels produces a billion tons of carbon dioxide each year [2], which causes the average surface temperature of the Earth have increased 0.6 °C over the past 100 years and will probably rise  $1.4 \,^\circ$ C-5.8 °C for the next 100 years [6]. Furthermore, it is predicted that the total world energy consumption will increase ~50% from 2012 to 2040 [7]. The depleting fossil fuels, the environmental pollution, and the increasing energy demand drive researchers' attention to develop renewable energy resources such as solar energy.





Figure 1.1 shows the progress of solar cells over the past 40 years summarized by National Renewable Energy Laboratory [8]. Solar cells are typically classified as in one of three generations based on the material and processing technology used for fabrication [5, 9]. The first generation of solar cells marked by blue lines in figure 1.1 is silicon wafer-based photovoltaic accounting for more than 85% of the current commercial market. The second generation of solar cells marked with green lines is based on thin films of semiconductor materials such as copper indium selenide, cadmium telluride, amorphous silicon, and nanocrystalline silicon. Second solar cells are less expensive than the silicon-based cells but the efficiency is also lower. The third generation of solar cells marked with purple and red lines include dye-sensitized nanocrystalline solar cells, organic polymer-based photovoltaics, multi-junction solar cells, hot carrier solar cells, and thermophotovoltaic solar cells. The efficiency of the third generation especially multijunction solar cells is higher than the others. As we can see from figure 1.1, the most efficient solar cells are multijunction (MJ) solar cells with efficiency as high as 45%. MJ solar cells have such high efficiency because they allow a broader absorption of the incident solar energy and allow a large portion of the incident energy to be converted compared to single-junction solar cells [10]. Semiconductor material absorbs photons with energies equal or greater than its bandgap since their energy promotes electrons into the conduction band. Photons with energies equal to the semiconductor's bandgap will be absorbed and all their energies will be converted; photons with energies greater than the bandgap will be absorbed as well but the excess energy will be dissipated as heat and thus wasted; photons with energies less than the bandgap will not absorbed at all and will be transmitted through the material; thus, their energies are not used. From these viewpoints, solar cells made by large bandgap semiconductor materials only absorb a small portion of sunlight as most of the photons have less energies than the semiconductor's bandgap and the cells only

convert a very small portion of the incident energy; thus, results in a low efficiency; solar cells made by small bandgap materials basically absorb all the light but waste a large portion of the incident energy since most of the photons have greater energies than the bandgap; so they have low efficiency as well. MJ solar cells consist of multiple single-junction cells, based on III-V semiconductor materials, stacked on top of each other. Each layer from the top to the bottom has a smaller bandgap than the previous one; for example, three-junction solar cell GaInP/GaAs/Ge cell and the corresponding bandgap is 1.70 eV/1.18 eV/0.67 eV. When sunlight strikes on the MJ solar cells, the top cell absorbs photons with energy equal to or greater than the band gap of its semiconductor material and converts a portion of solar energy. Photons with less energy pass through the top cell and come to the second solar cell. As the same, the second cell absorbs these photons with energies equal to or greater than the band gap of its semiconductor material and converts anther portion of solar energy. Such process keeps going on until the bottom cell. Therefore, the total converted energy of MJ solar cells is much more than single-junction solar cells, which results in a higher efficiency of MJ solar cells.

The primary figure of merit for solar cells is the cost per watt; to address this both the efficiency as well as the cost need to be optimized. MJ solar cells have the highest efficiency as well as the highest cost; the cost of MJ solar cells ranges from \$6/cm<sup>2</sup> - \$11/cm<sup>2</sup> which is hundreds times higher than that of Si cells ranging from \$0.02/cm<sup>2</sup> - \$0.04/cm<sup>2</sup> [11]; making their cost/watt figure of merit too high for most applications. A large part of the expense for MJ solar cells is the Ge substrate that most MJ solar cells are fabricated on. An often suggested approach to reduce the cost is to use a Si substrate instead [11, 12]. Si is the most used semiconductor in the world; about 95% of all semiconductor devices are fabricated on Si. Compared to Ge wafers, Si wafers have a lower cost, lower weight, better mechanical strength, higher thermal conductivity and larger

diameter in available [12]. It is also reported that the cell cost will reduce 60% if MJ solar cells are successfully transited from a Ge to Si substrate [11].

Successfully bringing MJ solar cells onto Si is not to simply, directly grow GaAs, Ge or other related III-V semiconductor alloys used in MJ cells on Si because the lattice mismatch between Si and the semiconductor materials (Ge or GaAs) of these used in MJ cells is very high resulting in a large number of unacceptable threading dislocations on the order of  $10^9$ - $10^{10}$  cm<sup>-2</sup> [13]. Threading dislocations, acting as recombination centers, capture minority carriers so as to reduce the diffusion length and lifetime of minority carriers; thus, degrade the solar cell's efficiency which is generally agreed to be controlled below  $10^6$  cm<sup>-2</sup> [14].

A promising way to reduce the TDD in order to bring MJ cells on Si substrate is using a strainrelaxed SiGe graded buffer by gradually increasing the Ge content from 0 to 100% [15, 16]. In the graded buffer, a series of lattice-mismatched interfaces are created. The lattice mismatch of each interface is low preventing widespread dislocation nucleation and enabling the use of existing dislocations to relax the layers [17]. Thus, the final layer has a lower threading dislocation density than directly depositing it on the Si substrate. A uniform Ge cap layer is then grown on top of the graded buffer and the Ge/graded SiGe/Si is used as a 'virtual substrate' to grow the semiconductor materials of MJ solar cell. Since the uniform Ge cap layer, grown on top of the strain relaxed graded buffer, has a composition equal to the final concentration in the graded buffer, the Ge cap layer is strain-free and has a significantly reduced TDD, which will minimize the dislocations that could be introduced into the semiconductor materials fabricated on.

#### **1.2 Motivation**

Previously, all SiGe graded buffers have been grown by either chemical vapor deposition (CVD) or molecular beam epitaxy (MBE). CVD is a technique to synthesize desired semiconductor from gaseous phase by a chemical reaction. The chemical reactions to deposit SiGe are:

$$SiH_4 \rightarrow Si + 2H_2$$
  
 $GeH_4 \rightarrow Ge + 2H_2$ 

MBE is a process to deposit desired semiconductor materials from molecular beams on a heated substrate under ultra-high vacuum conditions. By controlling the flux ratio, the composition of the layer can be controlled. By controlling the flow time, the thickness of the layer can be controlled. More information about CVD and MBE see reference [18]. CVD and MBE have benefits to fabricate epitaxial thin films because they both operate far from equilibrium which permit the growth of highly lattice-mismatched layers and their vapor phase growth mechanisms enable precise composition and thickness control. However, these two techniques are limited by their high capital costs, low growth rates, toxic precursors (CVD) and low uptimes (MBE) [19]. Liquid phase epitaxy (LPE), on the other hand, which deposits semiconductor materials from a liquid phase, offers a solution to the problems of CVD and MBE. A large advantage of LPE is that high-quality SiGe layers with low dislocation densities can be obtained because growth occurs near equilibrium. Also, LPE could potentially serve to grow compositionally SiGe graded buffers (from Si to Ge) in one step because the layer becomes more Ge-rich as layers are grown by cooling the liquid solution from high temperature to low temperature [20]. Therefore, the layer grown by LPE from high temperature to low temperature is actually a compositionally continuous graded buffer. The most attractive aspect is that LPE is an economic and nontoxic technology. If we can use LPE to successfully grow relaxed, high-quality SiGe graded buffer with Ge content reaching 100% Ge

and use it for MJ cell fabrication, the cost of MJ solar cell will be further reduced. This thesis discusses the first initial step towards achieving a SiGe graded buffer on Si using LPE.

#### 1.3 Objectives

Si (001) is the most common substrate used and dislocations in the growth of SiGe films on Si (001) are easier to be engineered than the growth on other orientated Si such as Si (110) and Si (111). Therefore, we decide to grow LPE SiGe buffers on Si (001) for this study. For LPE SiGe growth on Si (001), low-Ge-content films favor planar growth while high-Ge-content films prefer three-dimensional, pyramidal-island growth. For the application of SiGe graded buffers, the buffer should: have a planar morphology, have high-Ge contents, be fully relaxed, and have a threading dislocation density below 10<sup>6</sup> cm<sup>-2</sup>. Our project aims to use LPE to grow high-Ge-content, strainrelaxed SiGe graded buffers with low threading dislocation density in a one-step growth but based on the current state of knowledge much work is required to achieve this aim. Previous work reports the surface morphology, the surface composition, the threading dislocation density of the LPE SiGe films; however, there is no report about the strain states of the LPE SiGe films which is an important aspect to be studied. Also, there is no discussion on the solution composition used in most work; so there is no way to decide what an appropriate solution composition we should use and to expect what the corresponding solid composition should be. This thesis is trying to provide the initial results for further research about using LPE to grow high-Ge-content, strain relaxed SiGe graded buffers with low threading dislocation density. The surface morphology, composition profile, strain state, and threading dislocation density of all LPE SiGe films grown in this thesis will be studied. The objectives of this study are:

- 1) To develop the LPE system and to make sure to grow continuous SiGe film on Si (001).
- 2) To study the evolution process of SiGe graded buffer during the LPE growth process.

- 3) To find out the greatest Ge content of the initial deposition that maintains planar growth and to study the properties of initial films as well as the graded buffers.
- To understand the effects of a substrate with a generous number of dislocation sources on the properties of the initial LPE films.

#### 1.4 Thesis overview

This thesis is divided into nine chapters. The current chapter gives general background, motivation and objectives of this thesis. The following chapters are organized as the following:

Chapter 2 introduces the basic concepts of dislocation, the growth mechanisms of SiGe/Si (001) system as well as the mechanism of graded buffers reducing dislocation density.

Chapter 3 provides an overview of LPE, the basic concepts involved in LPE SiGe growth, and the growth challenges of LPE SiGe.

Chapter 4 describes the LPE system developed, growth process, and necessary techniques to grow continuous and non-entertained film.

Chapter 5 briefly introduces the characterization methods.

Chapter 6 discusses the evolution process of SiGe graded buffers during the LPE growth process. Several SiGe graded buffers were grown with the same initial solution composition and same initial growth temperature but different final temperature. The properties of the graded buffers such as surface morphology, composition profile, strain state, and dislocation density are characterized.

Chapter 7 concentrates on SiGe films grown with different composition solutions from a short temperature interval. The quality of these initial films are studied and the greatest Ge content of the initial deposition maintains planar film growth are found. Also, SiGe graded buffers are grown with different composition solutions to study the properties of the graded buffers and compare with their own initial film.

Chapter 8 examines how existing dislocations in the substrate affect the properties of the initial LPE deposition. SiGe films are grown on a CVD-grown  $Si_{0.9}Ge_{0.1}/Si$  (001) substrate with different composition solution. The properties of the CVD film before and after heating are studied as well as the LPE films.

Chapter 9 gives the overall conclusions and future work.

### Chapter 2

### **Strain Relaxation in SiGe/Si (001)**

This chapter includes three sections. The first section introduces the basic concepts of dislocations such as strain relaxation, dislocations types, dislocations glide and misfit dislocations nucleation methods. The second section focus on the growth modes and strain relaxation mechanisms. The third section explains the mechanism of graded buffers reducing threading dislocation density.

#### 2.1 Dislocations fundamental

#### 2.1.1 Silicon and Germanium

Si, SiGe, and Ge all have diamond cubic crystal structure, in which each atom has a covalent bond with four adjacent atoms. A simple diagram of diamond cubic structure unit cell is shown in figure 2.1. The diamond cubic structure is a variation of face-centered cubic (FCC) with atoms at both FCC lattice points (atoms marked in black) as well as  $\frac{1}{4}$ ,  $\frac{1}{4}$  away (atoms marked in white). In diamond crystal structure, the most densely packed planes are {111} planes and the close-packed directions are <110> directions, thus the primary slip system is the {111}<110>-slip system. As an example, the (111)[ $\overline{1}10$ ] slip system is marked in grey and orange in figure 2.1.

The lattice constant of Si is 5.431 Å [21] and Ge is 5.658 Å [21] which is 4.2% larger than Si. Si and Ge are completely miscible to form  $Si_{1-x}Ge_x$  alloy and has a lenticular phase diagram as shown in figure 2.2. The lattice constant of  $Si_{1-x}Ge_x$  is given by the well-known Vegard's law [22]:

$$a_{SiGe} = a_{si}(1-x) + a_{Ge}x$$
(2.1)

where  $a_{si}$  is the Si lattice constant;  $a_{Ge}$  is Ge the lattice constant;  $a_{SiGe}$  is the Si<sub>1-x</sub>Ge<sub>x</sub> alloy lattice constant, and x is the Ge mole fraction.



Figure 2.1 A simple diagram of diamond cubic unit cell.



Figure 2.2 SiGe phase diagram [23].

#### 2.1.2 Strain relaxation and dislocations

Since SiGe has a larger lattice constant than Si, the lattice misfit between them leads SiGe film is totally elastic strained, or partially or fully relaxed by misfit dislocations when SiGe film is grown on Si. The total misfit, f, is defined as [24]

$$f = \frac{a_s - a_e}{a_e} = \epsilon + \delta \tag{2.2}$$

where  $a_s$  is the substrate lattice constant,  $a_e$  is the epilayer lattice constant,  $\epsilon$  is the elastic misfit strain in the epilayer, and  $\delta$  is the plastic strain.

When epitaxially growth initially occurs between SiGe and Si, the in-plane lattice constants of SiGe are compressed in the two orthogonal in-plane directions in order to match the Si lattice while the perpendicular lattice constant of SiGe is expanded in an attempt to preserve the same unit cell volume. As a result, SiGe experiences a biaxial compressive strain in the in-plane directions and a tensile stress in the perpendicular direction as indicated by the blue and red arrows in figure 2.3a.
When the layer is fully strained the film is pseudomorphic. In this case, the elastic strain energy,  $E_h$ , in the layer is given by [25]

$$E_h \approx 2G \frac{1+\nu}{1-\nu} \epsilon^2 h \tag{2.3}$$

where *G* is the shear modulus, v is Poisson's ratio, and *h* is the thickness of the strained layer. Strain energy in a pseudomorphic film increased as the film thickness until a critical thickness is reached. At the critical thickness, the strain energy is equal to the energy to form a dislocation which, by breaking bounds at the film/substrate interface, partially relaxes the strain in the film, and thus the strain energy. In this case, the lattice constant of the SiGe films more closely approximates that of the bulk lattice constant. Rows with broken atomic bonds are called misfit dislocations (marked by the T in figure 2.3b) and this kind of relaxation is called plastic deformation. The layer could be partially relaxed or full relaxed depending on how many misfit dislocations are present.



Figure 2.3 Schematic diagrams of pseudomorphic and partially relaxed SiGe films on Si (001), where  $a_{\parallel}$  is the in-plane lattice constant of the film,  $a_{\perp}$  is the perpendicular lattice constant of the film, and  $\top$  indicates the misfit dislocation.

Misfit dislocations are line defects and they typically form at the most densely packed line direction. In SiGe/Si (001) system, misfit dislocations are aligned along two orthogonal <110> directions at the layer/substrate interface, thus; form a misfit network as schematically shown in figure 2.4a. Misfit dislocations are the part of the dislocation that reside or near the film/substrate interface. Dislocations, however, must end at a surface or upon itself and typically, the dislocations end at the ambient/film interface. The part of the dislocation that connects the misfit to the ambient is called a threading dislocation (TD) and normally each misfit dislocation (MD) has two threading dislocations as shown in figure 2.4b. The contribution to relaxation from threading dislocations is much smaller than that of the misfit dislocations.



Figure 2.4 Schematic diagrams of misfit dislocation network (a) and an entire dislocation (b).

# 2.1.3 Dislocations types

Different types of dislocations can be presented in semiconductors [26]. The primary dislocation types in SiGe/Si (001) system are 60° dislocations and 90° dislocations [27, 28], which are

differentiated by the angle,  $\alpha$ , between the dislocation line direction and the Burgers vector, b. Both types of dislocations have a a/2 < 110 >-type Burgers vector and a < 110 >-type line direction. Misfit dislocations only relieve the elastic strain in the direction perpendicular to the dislocation line. Since 90° dislocations have a Burgers vector, b, in the direction perpendicular to the dislocation line, which are pure edge dislocations, the entire Burges vector contributes to the strain relaxation, that is, the effective Burgers vector  $b_{eff} = b$ ; thus, 90° dislocations are the most effective dislocation to relieve strain. However, 90° dislocations are sessile, cannot glide, because they belong to the <110> {100}-slip system, which is not the primary slip system. 60° dislocations have a Burgers vector with 60° angle to the dislocation line, which has a mixed edge and screw components. Only the edge component of the Burgers vector contributes to the strain relaxation and the  $b_{eff} = b/2$  as shown in figure 2.5. As a result, 60° dislocations are less effective than 90° dislocations but they are glissile because they exist in the <110>{111}-slip system, which is the primary slip system. It has been observed that 60° dislocation are the dominant type dislocation in low-misfit system (f < 2) while 90° dislocation is the main type dislocation in high-misfit system (f > 2) [24, 26].



Figure 2.5 Schematic of 60° dislocations Burgers vector and effective Burgers vector.

#### 2.1.4 Dislocations glide

Dislocations glide refers to the movement of dislocations in their slip system with the influence of strain. As discussed above, so-called 60° dislocations are glissile in SiGe/Si (001) system and figure 2.6 schematically shows the gliding of 60° dislocations in the slip system,  $<110>{111}$ -slip system. When strain acts on dislocations, threading dislocations glide and they extend the length of misfit dislocations as shown in figure 2.6 from position I to position II, which allow them to relieve more strain. Dislocations glide plays an important role in graded buffers to reduce the threading dislocation density and to relieve strain, which will be given later (section 2.3). The glide velocity of dislocations is thermally active and is given by [29]

$$\nu_g = B\epsilon \exp(-\frac{E_g}{kT}) \tag{2.4}$$

where  $v_g$  is the glide velocity, *B* is a constant,  $E_g$  is the thermal activation barrier for glide, *k* is the Boltzmann constant, and *T* is the temperature.



Figure 2.6 Schematic of 60° dislocations glide.

#### 2.1.5 Misfit dislocations nucleation

Serval mechanisms have been proposed to explain the nucleation of misfit dislocations in low misfit heterostructures [30]. Two of them are introduced here: the first one is misfit dislocations nucleated by glide of pre-existing threading dislocations which is the easiest way, and the second one is the half-loop nucleation mechanism which is simplest mechanism that misfit dislocations nucleated by themselves.

# 2.1.5.1 Glide of pre-existing threading dislocations

Misfit dislocations nucleated by glide of pre-existing threading dislocations is the way that requires lowest energy since the misfit dislocations instead of the entire dislocations are the only new dislocation segments to be created. Figure 2.7 shows the schematic diagram of misfit dislocations are nucleated by glide of existing threading dislocations at the substrate surface, which was first modeled by Matthews and Blakeslee [31-33]. Two main forces,  $F_E$  the total lateral force acting to elongate the threading dislocation in the interface, and  $F_L$ , the line tension force resisting the elongation of a dislocation, are considered in this model, which are given by [33]

$$F_E = \frac{2G(1+\nu)}{1-\nu} \epsilon bh \cos\lambda \tag{2.5}$$

$$F_L = \frac{Gb^2(1 - v\cos^2\alpha)}{4\pi(1 - v)} \left[ \ln\left(\frac{h}{b}\right) + 1 \right]$$
(2.6)

where *b* is the Burgers vector,  $\lambda$  is the angle between the slip direction in the film plane which is perpendicular to the line of intersection of the slip plane and the interface, and *a* is the angle between the dislocation line and its Burgers vector.

Three stages are in involved in this process as shown in figure 2.7. At stage (I), where the epilayer thickness, h is less than the critical thickness,  $h_c$ , that is,  $h < h_c$ , and  $F_E < F_L$ , the epilyaer is totally elastic strained and threading dislocations thread straightly through the epilayer to the

surface; At stage (II), where  $h = h_c$  and  $F_E = F_L$ , threading dislocations are bowed with the influence of the elastic strain. At stage (III), where  $h > h_c$  and  $F_E > F_L$ , threading dislocations elongate along the interface and thus form misfit dislocations. By balancing the total lateral force,  $F_E$  and the line tension force,  $F_E$ , the critical thickness,  $h_c$ , is determined as

$$h_c = \frac{b}{8\pi\epsilon} \frac{(1 - \nu \cos^2 a)}{(1 + \nu) \cos \lambda} \left( \ln \frac{h_c}{b} + 1 \right)$$
(2.7)

In graded buffers, misfit dislocations nucleated by glide of pre-existing threading dislocations at the surface of previous layer is the essential way that graded buffers are able to reduce threading dislocation density, which will be given later (section 2.3).



Figure 2.7 Schematic of misfit dislocations nucleated by glide of pre-existing threading dislocations [34].

# 2.1.5.2 Half-loop mechanism

Si substrates have a very low threading dislocation density,  $\sim 10^3$  cm<sup>-2</sup>, and misfit dislocations nucleated by such low density dislocations cannot contribute significantly to the strain relaxation observed in the epitaxial growth on Si [28, 35]. This brings the field that misfit dislocations are actually nucleated by themselves. The simplest mechanism is the so-called half-loop mechanism

as shown in figure 2.8, which was first modeled by Matthews [33]. In this model, a critical halfloop of radius  $R^*$  is required to be formed first at the epilayer surface (stage I). The energy required to create this critical half-loop is termed as activation energy  $E^*$ . Once this critical half-loop is created, it will spontaneously grow larger towards the film/substrate interface (stage II). When it reaches the interface, a misfit dislocation and two threading dislocations are easily identified (stage III). Misfit dislocations generated by half-loops inserted from the surface has been directly observed in the SiGe /Si (001) system by Bolkhovityanov [36].



Figure 2.8 Schematic of misfit dislocation nucleated by half-loop [24].

The two mechanisms discussed above are appropriated for the nucleation of 60° dislocations since dislocations gliding are required in both mechanisms and 90° dislocations cannot glide. The formation of 90° dislocations is not well known but probably by interaction of two complementary 60° dislocations [37, 38] or by the coalescence of separated nucleated, large lattice mismatched islands [26, 39].

#### 2.2 Growth modes and strain relaxation mechanisms

Three different kinds of growth modes are observed in heteroepitaxial growth: (a) layer-by-layer or Frank-van der Merwe (FM) mode, (b) island or Volmer-Weber (VW) mode, and (c) layer-bylayer plus island or Stranski-Krastanov (SK) mode [40-42]. Schematics of these three growth modes are shown in figure 2.9. The equilibrium growth mode is dependent on the surface free energy and lattice misfit. The surface free energy depends on the surface free energy of the substrate  $\gamma_s$ , the surface free energy of the epilayer  $\gamma_e$ , and the interfacial free energy between the epilayer and the substrate  $\gamma_i$ . In a lattice-matched system (there is no strain energy), layer-by-layer, FM mode will occur if the sum of the surface free energies of the interface and the epilayer is smaller than the substrate surface free energy [40]:

$$\gamma_i + \gamma_e < \gamma_s \tag{2.8}$$

In this growth mode, the system favors film formation or wetting the substrate. On the contrary, island, VW mode is active, in which the system prefers clustering together instead of covering the substrate completely. As the islands keep growing, coalescences happen and a continuous film eventually forms. In a lattice-mismatched system, the strain energy,  $E_h$ , must be considered. Layer-by-layer, FM will occur if the sum of the strain energy and the surface energies of interface and epilayer is smaller than the surface free energy of substrate:

$$\gamma_i + \gamma_e + E_h < \gamma_s \tag{2.9}$$

However, during the growth, the strain energy increases with increasing thickness which could make equation 2.9 no longer hold and the growth mode transitions to islands, VM growth. This growth mode from layer-by-layer to island is the so-called SK mode and it prefers to occur in a system such as SiGe/Si with a small interface energy but when the lattice misfit is greater than >2% [40, 43]. The islands may coalesce similar to VW growth as well.



Figure 2.9 Heteroepitaxial growth modes: (a) layer-by-layer or Frank-van der Merwe (FM) mode, (b) island or Volmer-Weber (VW) mode, and (c) layer-by-layer plus island or Stranski-Krastanov (SK) mode [42].



Figure 2.10 Growth modes and strain relaxation mechanisms observed in uniform composition  $Si_{1-x}Ge_x$  grown on Si (001) with misfit < 2. Symbols represent experimental data from references [45-56] and the data marked with grey dots and circles are from Mooney review [45].

During SiGe growth, the preferred growth mode and strain relaxation mechanism is not only determined by the misfit but also other growth conditions such as growth temperature. Low temperatures reduce atomic surface diffusion and helps planar growth [44]. Figure 2.10 summarizes the growth modes and strain relaxation mechanisms of CVD- and MBE-grown uniform composition SiGe on Si (001) with misfit less than 2% compiled from various works [45-56].

In both regions I and II shown in figure 2.10, the growth proceeds via layer-by-layer, FM mode. In region I, strain relaxation occurs by the introduction of  $60^{\circ}$  dislocations [57]. Growth starts with a pseudomorphic film with smooth surface and  $60^{\circ}$  misfit dislocations are generated at the film/substrate interface lying along the two orthogonal <110> directions to relax the film. Growth rates at these areas where misfit dislocations are located are high resulting in ridges formed at these areas. Therefore, the surface of these films is characterized with crosshatch morphology, a set of ridges and troughs aligned along the two orthogonal <110> directions (figure 2.11).



Figure 2.11 Crosshatch morphology of SiGe films along <110> directions [50].

In region II, strain relaxation happens with surface roughness followed by  $60^{\circ}$  misfit dislocations generation. During the pseudomorphic growth, the film relaxes by surface ripples in the form of ridges and troughs aligned along <100> directions (figure 2.12a). In this way, the in-plane lattice constant of the film at the ridge areas is bended greater than that of the substrate; thus, strain is partially relaxed. However, the in-plane lattice constant at the trough areas is smaller than that of the substrate and therefore these areas are highly strained. Such high strain concentration leads  $60^{\circ}$  misfit dislocations nucleated at the troughs for further strain relaxation and will result in a network of ridges and troughs aligned along <110> directions. Figure 2.12b schematically shows the variation of lattice plane curvature of SiGe film due to surface ripples along <100> directions.



Figure 2.12 Surface ripples along <001> directions (a) [50] and schematic of cross-sectional view of the lattice plane curvature by surface ripples along <100> directions (b) [52].

In region III, with higher Ge fraction or misfit and higher temperature, growth typically follows the SK mode. Growth starts with layer-by-layer, FM for the first serval monolayers, a twodimensional (2D) wetting layer. Because of the increasing strain energy, the growth changes into islands, VW mode which elastically relieves part of the strain. The islands are dislocation-free and under compressive strain, and the wetting layer and substrate below the islands are under tensile strain while the layers away from the islands are under compressive strain (figure 2.13) [58]. When the islands reach a critical size, misfit dislocations are observed to be generated at the edge of the islands for strain relaxation eventually [59-61].



Figure 2.13 Schematic diagram of lattice plane curvature in SiGe/Si (001) system following the SK growth mode [58].

As figure 2.10 shown, at a given composition, there is a critical temperature transition from one growth mode to another. Similarly, there is a critical composition between two growth modes at a given temperature. While figure 2.10 is based on results of SiGe films grown by CVD and MBE, the critical temperature or the critical composition for LPE growth may be different to CVD and MBE growth because LPE is grown at close to equilibrium which is not the case for CVD and MBE that operates far from equilibrium. For example, it is much harder to grow planar, lattice-mismatched films in LPE than CVD and MBE. That being said, we can use this graph to understand the general trends, for example if we want to grow two-dimensional (2D) planar layer

at high temperatures, the Ge content of the layer should be very low since SiGe LPE normally starts at a temperature higher than 900 °C. Growth of SiGe by LPE will be discussed in chapter 3.

# **2.3 SiGe graded buffers reduce dislocation density**

Misfit dislocations are required for strain relaxation but not threading dislocations. The total density of misfit dislocations to fully relax a lattice-mismatched layer is determined by the lattice misfit [46]. If a lattice-mismatched layer is directly grown on a substrate, many discrete misfit dislocations maybe generated. As each misfit dislocation normally has two threading dislocations, the threading dislocation density will be very high if there are a large number of discrete misfit dislocations [62]. Directly growth of lattice-mismatched system greater than 1-1.5% results in numerously short misfit dislocations and a threading dislocation density typically  $10^7$ - $10^9$  cm<sup>-2</sup> [63, 64]. If we can instead generate a long misfit dislocation which has the same length as the many discrete misfit dislocations, this long misfit dislocation still can fully relax the lattice-mismatched layer but only results in two threading dislocations. Thus, threading dislocation density is reduced substantially. Graded buffers reduce the threading dislocation density in a similar way and it has been reported by many that graded buffer is an effective technique to grow relaxed, latticemismatched heteroepitaxial layers with low threading dislocation densities ( $\leq 10^6$  cm<sup>-2</sup>) [17, 65-71]. Instead of growing a high lattice-mismatched layer which results in a large number of discrete misfit dislocations and threading dislocations at once, the Ge content can be increased gradually. In this case, a series number of interfaces are created and each interface in the graded buffer has a low lattice misfit preventing rapid misfit dislocations nucleation [16, 17, 72, 73]. Also, the growth conditions are such that the dislocations glide quickly to relax each individual layer to be used as virtual substrate for the subsequent layer [16, 17, 72, 73]. This process continues until the Ge

content reaches the final desired content and then a strain-relaxed, uniform composition layer with the composition equals to the final concentration in graded buffer are grown on top.



Figure 2.14 Schematic diagram of dislocation glide in a step-graded buffer on Si (001) substrate (a) and cross-sectional TEM image of a relaxed SiGe layer on a step-graded SiGe buffers [73]. Note the top layer is dislocation-free.

Two requirements in graded buffer growth are: minimize the dislocation nucleation rates and maximize the dislocation glide velocity [73, 74]. By gradually increasing the Ge content (typically  $\leq 10\%$ Ge/µm) can low the dislocation nucleation rates. By growing at high temperature ( $\geq 750$  °C) can activate high dislocation glide velocity. If these two conditions are met, SiGe graded buffers will be relaxed by the glide of pre-existing threading dislocations once initial dislocations are nucleated at the buffer/substrate interface (figure 2.14a) and thus have low threading dislocation density. The strain-relaxed layers grown on the graded buffers will have significantly low threading dislocation density as well (figure 2.14b). In addition, another requirement during graded buffers growth is the decreased roughness. Surface roughness with the underlying misfit dislocations tend to block dislocation glide and lead to dislocation pile-up [75-77]. This could cause further misfit dislocation nucleation since the blocked dislocations can no longer contribute to strain relaxation and thus results in a high threading dislocation density. Using chemical-

mechanical polishing (CMP) to remove the rough surface during 100%Ge graded buffer growth can reduce dislocation pile-up and lower threading dislocation density an order of magnitude than that without using CMP [15].

# Chapter 3

# Silicon-Germanium Liquid-Phase

# Epitaxy

In this chapter, the growth principles, cooling techniques, and various growth systems of LPE are provided first. The second section introduces the solvents, ternary phase diagram, surface morphology, cooling rates, and growth challenges of LPE SiGe growth in order to determine the growth conditions for SiGe graded buffers.

# **3.1 Liquid Phase Epitaxy**

Liquid phase epitaxy (LPE) is a crystallization technique to grow semiconductor materials on a crystalline, oriented substrate from metallic solutions. It was invented by Nelson in 1963 for the growth of GaAs [78]. Since then, LPE has received extensively applications in the growth of III-V, II-VI, and IV-VI semiconductor materials. Many comprehensive reviews have already been written covering various aspects about LPE [79-83]. In this section, we introduce some basic concepts about LPE including its growth principles cooling techniques, and various growth systems.

# 3.1.1 LPE growth principle

As it was said above, LPE is a crystallization technique to grow semiconductor materials from metallic solutions. The metallic solutions contain a small quantity of solutes, which are the desired materials to be grown, and a large quantity of solvent. A driving force is required for the crystallization and the thermodynamic driving force for LPE is the Gibbs free energy difference between the liquid and crystalline phases  $\Delta G < 0$  [84]. This is generated by cooling a saturated solution, which is illustrated by a typical Si-metal binary phase diagram in figure 3.1. For example, the composition and temperature of a saturated solution are at position A. As the temperature is cooled by  $\Delta T$ , the system moves to position B, a liquid-solid, two-phase region. The liquid composition follows the liquidus line moving from positions A to C while the solid composition follows the solidus line moving from positions D to E.



Figure 3.1 Silicon-metal binary phase diagram [85].

The most outstanding feature that LPE distinguishes CVD and MBE is that it operates close to the thermodynamic equilibrium. Figure 3.2 shows the estimated driving force of different growth techniques. LPE has a driving forces less than 0.03 kcal mol<sup>-1</sup>, very close to the thermodynamic equilibrium, whereas CVD and MEB have a driving force orders of magnitude higher than LPE which take place far away from the equilibrium. Since LPE operates near the thermodynamic equilibrium, the biggest benefit of LPE compared to CVD and MBE is that it can yield high-quality crystalline layers with low dislocation densities. This advantage is also a shortcoming because misfit dislocations maybe hard to nucleate near equilibrium. In addition, some other main benefits of LPE are: the equipment cost of LPE (25-100 K) is much lower than that of CVD (300 K-1M) and MBE (300 K-1M) [86]; LPE can achieve growth rates up to 10  $\mu$ m min<sup>-1</sup> which is significantly faster than CVD (0.1-1.0  $\mu$ m min<sup>-1</sup>) and MBE (0.01-0.1  $\mu$ m min<sup>-1</sup>) [86]; and the raw materials and the waste products of LPE are definitely less toxic and not pyrophoric.



Figure 3.2 Gibbs free energy difference between the feeding and crystalline phases of different growth techniques [87].

# 3.1.2 LPE cooling techniques

LPE growth requires cooling a saturated solution in order to transport the solutes from the bulk solution towards the solution-solid interface and this can be achieved by one of three different cooling techniques shown in figure 3.3. The substrate and the solution are not in contact with each other initially and they are both heated to the same temperature, the saturation temperature, T<sub>S</sub>. The first cooling technique is step-cooling (figure 3.3a). The substrate is brought into contact with the solution at temperature  $T_A$  after an initial supersaturation of the solution by  $\Delta T = T_s - T_A$ , and the temperature maintains at T<sub>A</sub> until the growth ended by removing the substrate away from the solution. The layer grown by step-cooling has a constant composition as the growth temperature is fixed and the layer thickness is limited by the amount of initial supersaturation as the growth will stop once the liquid-solid system reaches thermodynamic equilibrium, that is, the difference in Gibbs free energy between the liquid and solid phases  $\Delta G = 0$  [84]. The second cooling technique is equilibrium-cooling (figure 3.3b). The substrate is brought into contact with the saturated solution at the saturation temperature, T<sub>S</sub>, and the solution is cooled immediately at a constant rate until the temperature reaches the desired final temperature, T<sub>F</sub>. The driving force is maintained constantly through the whole growth and the layer may have varied composition following the solidus line of the phase diagram. The third cooling technique is super-cooling (figure 3.3c), which is a combination of step-cooling and equilibrium-cooling. The substrate and the solution are brought into contact with each other at temperature TA after an initial supersaturation of the solution by  $\Delta T = T_s - T_A$  like step-cooling. Then, the solution is cooled at a constant rate throughout the growth like equilibrium-cooling until the desired final temperature T<sub>F</sub>. Super-cooling increases the driving force for crystal nucleation compared to the other two

cooling techniques [88]. The initial superstation  $\Delta T$  is typically few Kelvins ( $\leq 6 \,^{\circ}$ C) [39, 88, 89]; otherwise, bulk crystallization happens at the surface of solution or in the solution.



Figure 3.3 LPE cooling techniques. Step-cooling (a), equilibrium-cooling (b), and super-cooling (c).

In a simple binary system, the layer thickness is given by the following relationships when the

growth is diffusion-limited [88, 90]:

For the step-cooling technique,

$$d = 2\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \left(\frac{1}{C_s m}\right) \Delta T t^{\frac{1}{2}}$$
(3.1)

For the equilibrium-cooling technique,

$$d = \frac{4}{3} \left(\frac{D}{\pi}\right)^{\frac{1}{2}} \left(\frac{1}{C_s m}\right) R t^{\frac{3}{2}}$$
(3.2)

For the super-cooling technique, the layer thickness is the linear combination of equations (3.1) and (3.2),

$$d = \left(\frac{D}{\pi}\right)^{\frac{1}{2}} \left(\frac{1}{C_s m}\right) \left(2\Delta T t^{\frac{1}{2}} + \frac{4}{3} R t^{\frac{3}{2}}\right)$$
(3.3)

where D is the diffusion coefficient of the solute in the solvent at the growth temperature,  $C_s$  is the molar fraction of the solute in the growing solid, m is the slop of the liquidus  $dT/dC^L$ , R is the cooling rate, and t is the growth time.

# **3.1.3 LPE growth systems**

Although several LPE growth systems have been developed, all the growth systems are based on three basic systems: a tipping system, a dipping system, and a horizontal sliding system.

The tipping system (figure 3.4a) is the earliest LPE growth system invented by Nelson in 1963 [78]. In Nelson's tipping system, a quartz furnace tube is set to be tilted slightly about a horizontal axis. A graphite boat which contains the substrate and the solution sits at the center of the tube. Before growth, the solution locates in a lower position away from the substrate at a higher position. To start the growth, the furnace is tilted so that the substrate lies at the lower position and the solution submerges the substrate. To stop the growth, the furnace is tilted back to its original position to roll the solution off the substrate. All the furnace, quartz tube and graphite boat have to be tilted and only single layers are grown in the original tipping system.

The dipping system (figure 3.4b) was explored by Rupprecht in 1967 [91]. In the dipping system, the quartz furnace tube is fixed vertically. The solution is held in a crucible with the thermocouple probe located under the crucible to monitor the temperature. The substrate is clamped in a holder which can move vertically to dip into or move away from the solution. Dipping systems are widely used in the growth of oxide materials [92]. The attraction of the dip system is that the substrate can be kept in the cool upper part of the furnace tube prior to the growth, which is important if the

substrate contains a volatile constituent. The main drawbacks are the requirements of a relatively large amount of solution is required (up to 1 kg [93]) and the non-uniformity of the layer thickness. Also, only single layers are grown as the original tipping system discussed above.



Figure 3.4 Schematics of the three basic LPE growth systems. The tipping system (a), the dipping system (b), and the horizontal sliding system (c) [98].

The horizontal sliding system (figure 3.4c) is the most versatile and the most universally used system, representing an innovation in LPE, because multilayers structures can be achieved. In the horizontal sliding system, the quartz tube and furnace are fixed horizontally. The graphite boat

consists of a substrate holder with substrate located in a recess and multiple wells with different composition solutions hold in each well. The substrate is transported from one solution well to the next by pulling the substrate holder. A thermocouple probe is inserted at the back of the graphite boat to measure the temperature. The biggest advantage of sliding boat is that multilayered structures can be achieved as the boat is designed with multiple wells which can hold different solutions, which makes it widely used for the growth of laser diodes [94], solar cells [20, 95] and double heterostructure LEDs [96, 97]. A major drawback it that the depth of the recess for the substrate needs to be well designed based on the desired layer thickness. If the recess is too deep, solution carry-over will be a problem. If the recess is too shallow, scratches occur on the substrate when pulling the sample away from the solution.

Various designs of the graphite boats have been developed in order to control the layer thickness, improve the thickness uniformity and the throughput of the LPE. Many diverse slideboat designs for these purposes are introduced by Mauk [99]. Also, many other types of LPE boats have been reported. In 1974, Bauser [100] developed a graphite crucible which can be rotated 90° forward or backward around the longitudinal axis to bring the solution onto or off the substrate (figure 3.5a). In his design, only the quartz tube and the graphite crucible are rotated and the rotation is around the longitudinal axis which reduce the complexity in Nelson's design; however, the growth is single-layer growth as well. In 1997, Kaufmann [101] developed a graphite boat with the combination of the rotatable boat and the sliding boat (figure 3.5b). The boat has several solution chambers and the solution is brought onto or off the substrate by rotating the boat 90° forward or backward like the Bauser's. The substrate is mounted on a slider and is moved from one compartment into the next by pulling the slider while the solution and the substrate are not contact. The advantages of this boat are it allows multilayers growth and overcomes the problems of

solution carry-over and substrate scratching in the conventional sliding boat shown in figure 3.4c. Also, they improved the boat to allow several multilayer-samples growth which could mount multiple substrates and rotate 360° (figure 3.5c) [82]. However, the rotatable and sliding graphite boats (figures 3.5b and 3.5c) are very complex since they require rotation and translational movement. Scheel [102] in 1977 represented a screw graphite boat as shown in figure 3.6. In the screw boat, different composition solutions are held in separate chambers and the substrates are fixed. The solutions are moved separately from one chambers to the next by rotating the boat around a horizontal axis. This screw boat allows multilayers growth without having the problems of solution carry-over and substrate scratching which normally occur in the conventional horizontal sliding boat.



Figure 3.5 Schematics of rotatable LPE boats. Bauser's boat (a) and Kaufmann's boats (b) and (c) [82].



Figure 3.6 Schematic of the screw graphite boat [102].

# **3.2 LPE SiGe growth**

There are few reports about growing SiGe using LPE compared to CVD and MBE. Almost all the research work we found are reported by the researchers at Max-Planck-Institut für Feskörperforschung, Stuttgart, Germany in 1990s [20, 60, 84, 89, 103-113] and Institut für Physik, Humboldt-Unversitiät zu Berlin, Newtonstrasse, Berlin, Germany in 2000s [114-119]. The former concentrates on SiGe layers growth, whereas the latter are mainly about SiGe islands growth. In 1997, Gutjahr published an important paper about SiGe layers grown by LPE [20]. Gutjahr grew SiGe layers on Si (111) substrates by cooling saturated SiGeIn solutions from the saturation temperature 950 °C to 650 °C, which is the equilibrium-cooling technique introduced in section 3.1.2. In was used as the solvent and about the LPE solvents used for SiGe growth will be provided in section 3.2.1. The solution composition was Si<sub>0.02</sub>Ge<sub>0.08</sub>In<sub>0.9</sub> at 950 °C and different cooling rates were employed. The composition profile of the SiGe layers as the function of thickness were measured by energy-dispersive X-ray analysis which is shown in figure 3.7. Regardless of the different cooling rates, the Ge content of the SiGe layers continuously increases with increasing thickness and the slope of composition vs. thickness increases as well. This means SiGe grown in LPE by cooling a solution from high to low temperature becomes Ge-rich. In other words, if a SiGe layer is grown by LPE cooling process, the layer is a compositionally graded buffer. In addition, the larger the growth temperature interval, the range between the started temperature and ended temperature, the higher the final Ge content in the deposited SiGe. Therefore, LPE has the potential to well serve SiGe graded buffers growth.



Figure 3.7 Ge content as a function of layer thickness [20].

The task of growing SiGe graded buffers by LPE cooling techniques now can be broken into two steps. First, the growths should start with a 2D film growth. Second, the growth should keep the layer-by-layer growth mode during the LPE cooling process. In Gutjahr's report, the substrates used are Si (111) which are more suitable for 2D planar growth especially under the condition near equilibrium since {111} planes have lower surface energy [111] but extended stack faults are easier to occur which are detrimental to the device performance [120]. For Si (001) substrates, stack faults are sufficiently prevented and dislocation gliding in SiGe graded buffers is able to be engineered to reduce the threading dislocation density which was introduced in section 2.3 of chapter 2. At present, SiGe graded buffers are mostly grown on Si (001) substrates. Since 2D planar growth is not easy to proceed on Si (001) near equilibrium condition, appropriate LPE growth conditions including solvent, solution composition, temperature and cooling rate are significantly important to be chosen in order to grow desired SiGe planar films on Si (001).

# **3.2.1 The LPE solvents**

The LPE solution for SiGe growth contains a small quantity of Si and Ge as the solutes and a large quantity of solvent. The solvent used generally is the metal in groups III, IV or V of the periodic table such as Al, Ga, In, Sn, Pb, As, Sb, and Bi. In 1990, Trah [105] calculated the solubility of Ge and Si in different solvents (figure 3.8). The solubility of Ge in any solvent shown in figure 3.8 is always two or three orders of magnitude higher than that of Si. Also, the solvent elements deposit into the solid SiGe which is called doping. The solubility of different solvents in the solid SiGe were calculated by Fleurial [121] in 1990 (figure 3.9). For solid SiGe have the same Ge content, the solid SiGe contains more Ga impurity when Ga is used as the solvent; thus, Ga is an outstanding solvent for doping purposes [105, 106, 122]. In addition, it is favorable to use In, Sb, Bi or Pb as solvent if one wants to grow SiGe layer with low impurity content [103, 105, 106]. Among all the LPE SiGe reports we found, In is the most frequent solvent used due to its low solid solubility in the layer and low vapor pressure and only one kind of solvent is used except Healy's report that a mixed solvent, 60% Bi and 40% Au, is used [123]. The choice of solvent also affects the solid SiGe composition which will be provided in the next part 3.2.2.



Figure 3.8 Solubility of Si (solid lines) and Ge (dashed lines) in different metals [105].



Figure 3.9 Solubility of different solvents as a function of solid SiGe composition [120].

# 3.2.2 Si-Ge-metal phase diagram

The LPE solution for SiGe growth is a Si-Ge-M (metal) ternary system. Reliable Si-Ge-M phase diagram data are important to properly choose the solution composition, the saturation temperature, and to predict the solid composition. In 1987, Alonso [103] reported a method to calculate the phase diagram Si-Ge-In and Trah [105] in 1990 applied this method to any Si-Ge-M (M=Ga, In, Sn, Pb, Sb, Bi) system. Since Si-Ge-M phase diagram is important for the determination of solution composition at a desired saturation temperature and for the anticipation of the deposited composition in LPE growth, the calculation process is given in detail.

The calculation of Alonso and Trah is based on: (I) each Si-Ge-M phase diagram consists of two simple eutectic systems Si-M and Ge-M as shown in figure 3.1 and one binary solid-solution Si-Ge system as shown in figure 2.2 and (II) the following basic assumptions:

(1) The solubility of the metal in the solid phase  $x_M^s$  is zero; thus, the solid phase is Si and Ge, that is,  $x_{Si}^s + x_{Ge}^s = 1$ , where  $x_{Si}^s$  and  $x_{Ge}^s$  are the mole fraction of Si and Ge in the solid phase, respectively.

- (2) The binary interaction parameter between Si-M or Ge-M in the liquid  $\lambda_{i,M}$  is given by  $\lambda_{i,M} = a_i b_i T_s$ , where i = Si,Ge,  $T_s$  is the saturation temperature, a and b are the thermodynamic parameters and their values collected by Trah from various work for different solvents are listed in Table 3.1.
- (3) The binary interaction parameter between Si and Ge in the liquid  $\lambda_{Si,Ge}$  and in the solid

 $\Omega_{Si,Ge}$  in the Si-Ge system is zero,  $\lambda_{Si,Ge} = \Omega_{Si,Ge} = 0$ .

(4) Strain energy arising from the lattice-mismatch between the Si substrate and the SiGe epilayer is not taken into account.

Table 3.1: Values of the thermodynamic parameters a and b for different solvents collected by Trah from various work used to calculate the binary interaction parameter $\lambda_{i,M} = a_i - b_i$ , where *i* is Si or Ge [105].

	М	а	b		М	а	b
Si	Ga	3250	0.83	Ge	Ga	150	0
	In	9374	1.70		In	992	0.49
	Sn	8145	1.50		Sn	1680	1.08
	Pb	19830	4.58		Pb	8780	4.08
	Sb	3290	-1.61		Sb	2640	1.98
	Bi	11854	-0.178		Bi	5505	1.49

Based on above assumptions, the liquidus surface of the Si-Ge-M system can be described by the following equations:

$$\Delta H_{Ge}^{F}\left(1-\frac{\mathrm{T}_{\mathrm{s}}}{\mathrm{T}_{Ge}^{F}}\right)+RT_{\mathrm{s}}\ln\left(\frac{(1-x_{M}^{l})}{x_{Ge}^{s}(1+\rho)}\right)-\frac{x_{M}^{l}}{1+\rho}\left[\lambda_{\mathrm{Si},\mathrm{M}}\rho(1-x_{M}^{l})-\lambda_{\mathrm{Ge},\mathrm{M}}(\rho+x_{M}^{l})\right]=0$$
(3.4)

$$\Delta H_{Si}^{F} \left( 1 - \frac{T_{s}}{T_{Si}^{F}} \right) + RT_{s} \ln \left( \frac{\left( 1 - x_{M}^{l} \right) \rho}{\left( 1 - x_{Ge}^{s} \right) \left( 1 + \rho \right)} \right) - \frac{x_{M}^{l}}{1 + \rho} \left[ \lambda_{\text{Ge,M}} \rho (1 - x_{M}^{l}) - \lambda_{\text{Si,M}} (1 + \rho x_{M}^{l}) \right] = 0$$
(3.5)

where  $\Delta H^F$  is the enthalpy of fusion,  $T^F$  is the melting point,  $x^l$  is the mole fraction in the liquid phase, R is the universal gas constant, and  $\rho = \frac{x_{Si}^l}{x_{Ge}^l}$ . The values of  $\Delta H^F$  for Si and Ge are  $\Delta H_{Si}^F = 12082$  cal/mol and  $\Delta H_{Ge}^F = 8830$  cal/mol.

Equations of (3.4) and (3.5) can be solved by numerical iteration; however, the most important aspect concerned in LPE growth is the solid composition as a function of saturation temperature and as a function of solution composition. Since the solubility of Si in a metal is always considerably lower than the solubility of Ge at the same temperature in the same metal for all the binary systems Si-M and Ge-M (figure 3.7) which means  $x_{Si}^l(T) \ll x_{Ge}^l(T)$ , Alonso and Trah made the following assumptions:

$$x_{Ge}^l + x_M^l \cong 1 \tag{3.6}$$

$$\rho \equiv \frac{x_{Si}^l}{x_{Ge}^l} \cong 0 \tag{3.7}$$

With the above assumptions, the solid composition  $x_{Ge}^s$  as a function of liquid composition  $x_{Ge}^l$ and saturation temperature  $T_s$  can be written from equation (3.4):

$$x_{Ge}^{s} \approx x_{Ge}^{l} \exp\left\{\frac{1}{RT_{s}}\left[\Delta H_{Ge}^{F}\left(1 - \frac{T_{s}}{T_{Ge}^{F}}\right) + \lambda_{Ge,M}\left(1 - x_{Ge}^{l}\right)^{2}\right]\right\}$$
(3.8)

Figures 3.10 and 3.11 show the calculated results of solid composition  $x_{Ge}^s$  as a function of liquid Ge composition  $x_{Ge}^l$  and as a function of saturation temperature  $T_s$  with different solvents using equation 3.8. As figure 3.10 shown, the solid Ge content increases with increasing Ge content in the liquid for any solvent with fixed saturation temperature. In figure 3.11, we see that the solid composition  $x_{Ge}^s$  increases continuously as the saturation temperature decreases for any solvent with fixed liquid Ge composition. Thus, the solid composition is controlled by the liquid composition and the saturation temperature for any solvent. LPE SiGe growth normally starts at

temperatures higher than 900 °C in order to remove the native dioxide layer from the surface of the Si substrates [108, 113, 114, 119]. As discussed in previous, section 2.2 of chapter 2, the growth mode of a uniform composition SiGe on Si (001) depends on the Ge content and the growth temperature. The higher the growth temperature, the lower the Ge content required to proceed layer-by-layer growth. From this viewpoint, the initial Ge content of the solid SiGe deposited on Si (001) from the LPE solution should be relatively low in order to start 2D film growth. Based on the results shown in figure 3.10 that the lower the Ge content in the solution, the lower the Ge content deposited in the solid SiGe, the Ge content in the LPE solution should be relatively low in order to start 2D film growth on a Si (001) substrate.



Figure 3.10 Calculated solid composition  $x_{Ge}^s$  as a function of liquid Ge composition  $x_{Ge}^l$  in Si-Ge-M ternary systems. The calculations are done using equation (3.8) and the saturation temperature is fixed to 950 °C.



Figure 3.11 Calculated solid composition  $x_{Ge}^s$  as a function of saturation temperature in the Si-Ge-M ternary systems. The calculations are done using equation (3.8) and the Ge content in the solution is fixed to  $x_{Ge}^l = 0.02$ .

Also, as shown in figures 3.10 and 3.11, for the same liquid Ge composition and saturation temperature, the solid Ge composition is higher if Bi or Pb is used as the solvent compared to other solvents and the difference of solid Ge composition between using Bi or Pb as the solvent and using the other solvents becomes larger with decreasing saturation temperature. It is thus favorable to use Bi or Pb as a solvent if one wants to grow Ge-rich SiGe with a high Ge gradient. As discussed above, in order to grow SiGe films on a Si (001) substrate, the initial Ge content of the solid deposited on the substrate should be relatively low. If one wants to grow a film using Bi or Pb as the solvent temperature is a solvent of the liquid should initially be lower or the saturation temperature

should be really higher than using other solvents. As shown in the first two lines of Table 3.2, the solid Ge composition using Bi as a solvent is 0.083, about four times more than that of In (0.02) for a fixed liquid Ge composition at 0.02 and saturation temperature of 950 °C. If one wants to get the same solid Ge composition using Bi and In as a solvent and keeps the saturation temperature at 950 °C, the liquid Ge composition of using Bi as a solvent is 0.005, four times less. In order to get sufficiently small Ge mole fraction in the solution, practically we need to use a lot of Bi. Alternatively, we could start the growth at the saturation temperature of 1300 °C, which is too high for LPE furnace.

solvent	Liquid Ge composition	Saturation	Solid Ge composition	
sorvent	(mole fraction)	temperature (°C)	(mole fraction)	
In	0.02	950	0.022	
Bi	0.02	950	0.083	
Bi	0.005	950	0.022	
Bi	0.02	1300	0.023	

Table 3.2: Calculated data using equation (3.8).

It is emphasized that the calculated curves of solid Ge composition as a function saturation temperature with fixed liquid Ge composition such as the curves shown in figure 3.11 apply to predict the initially deposited composition when the growth starts from the saturation temperature. During LPE process of cooling a saturated solution from its saturation temperature to low temperature, more Ge is deposited from the solution when the temperature decreases (figure 3.7). For dilute Si-Ge-M solutions, we can assume that the solution amount is approximately equal to the solvent amount, that is, the solution amount does not change during the LPE cooling process. In this case, the solution becomes more Si-rich as the temperature decreases during the LPE cooling process. Therefore, the solid Ge composition as a function of temperature deviates negatively from the calculated curve using equation 3.8 with the liquid Ge composition fixed at

the actually, initially saturated Ge composition and the deviation becomes larger with decreasing temperature.

A bit sum up so far. If we want to grow SiGe graded buffers with as much high-Ge-content as possible by one LPE cooling step, the growth temperature interval should be quite large. Also, the liquid solution must have a relatively low Ge content, so the initially deposited SiGe on Si (001) has a relatively low Ge content; a low-Ge-content film is required in order to grow a 2D planar film on Si (001). In addition, although Bi and Pb are the solvents which can grow Ge-rich SiGe with a high Ge gradient, it is not time to use either as the solvent to grow SiGe graded buffers. The reasons for this include those discussed above that a large amount of Bi or Pb is required and a relatively high saturation temperature is required at which growth starts. Another important reason is that there are rare experimental data as reference to decide what an appropriate initial solid composition and the corresponding liquid composition are to start 2D film growth. We just know generally that a relatively low solid Ge content is required to start 2D film growth and thus a relatively low liquid Ge content but this is not enough. We need to know the actual values of these initial SiGe composition that start 2D film growth on Si (001) substrates. Considering all these above, we decide to use In as the solvent currently as it is the most common solvent used in LPE SiGe growth.

## 3.2.3 LPE SiGe surface morphology

LPE SiGe layers on Si (001) are characterized with crosshatch morphology, a set of ridges and troughs, as the CVD- or MBE- grown SiGe layers discussed in section 2.2 of chapter 2. Albrecht [107] in 1995 investigated the morphology and strain relaxation at different growth stages of LPE Si<sub>0.97</sub>Ge<sub>0.03</sub> layers. The growths were carried out in a tilting and sliding boat from In solutions

started at 900 °C with a cooling rate of 10 °C/h. Albrecht found that the formation of crosshatch morphology due to strain relaxation consists of four stages:

- 1) Elastic strain is partially relaxed by surface ripples along <100> directions.
- 60° misfit dislocations are first observed nucleated at the edge of the substrate because of the highly local stress concentration. Subsequently, misfit dislocations nucleation and glide extend towards the center of the substrate.
- 3) Growth rates at where misfit dislocations are underlying are higher than other areas and thus result in ridges formed. The surface of the layer is characterized with a set of ridges and troughs along <110> directions, which is so-called crosshatch morphology.
- 4) During further growth, dislocations favor to be nucleated in the troughs due to the local stress concentration. The preferred formation of dislocations again enhances growth rates in the troughs and thus results in smooth surface.

SK growth mode is energetically favorable in the growth of high-Ge-content SiGe on Si (001) substrates which leads to the formation of islands for partially elastic strain relaxation. Hanke [118] studied the SiGe island evolution during the LPE growth. The islands start with rather shallow lense-like islands without any faceting as labeled with 1 in figure 3.12a. Then, the islands are faceted as the one labeled with 2 in figure 3.12a. Afterwards, the islands become truncated pyramid with four {111} side facets and an (001) top facet such as the one labeled with 3 in figure 3.12a and a prevalent vertical growth takes place after the (001) top facet is present. It was reported by Hanke [114] that SiGe islands grown on Si (001) substrates tend to be self-organized along <100> directions. Hanke attributed this configuration to the strain energy distribution around the SiGe islands. The strain energy around a single SiGe island decreases fastest in all <100> directions, which favors further island nucleation. Hanke [117] also reported that lateral growths occur on the

islands along the {111} side faces as displayed in figure 3.12b that additional {111} facets appear on a SiGe island. Misfit dislocations will be formed for strain relaxation eventually as mentioned in section 2.2 of chapter 2.



Figure 3.12 The evolution of Si<sub>0.81</sub>Ge<sub>0.09</sub> islands grown on Si (001) (a) [118] and lateral growth observed on a completely developed Si<sub>0.91</sub>Ge<sub>0.09</sub> island (b) [117].

# 3.2.4 The LPE cooling rates

The properties of LPE grown SiGe layers are remarkably affected by the cooling rates. Sembian [110, 112] varied the cooling rates from 20 °C/h to 500 °C/h to grow Si<sub>0.966</sub>Ge<sub>0.034</sub> layers from In solution with a temperature interval of 930-750 °C in a tipping boat. The wavelength of undulation and etch pit density of the SiGe layers as a function of cooling rate were studied shown in figure 3.13. We can see that a high cooling rate in LPE results in a small wavelength of undulation and a high etch pit density. Sembian [110] explained this phenomenon with the growth kinetics involved in the LPE process. High cooling rates cause increased supersaturation and thus lead to enhanced growth rate. Meanwhile, high cooling rates decrease the surface mobility of the solutes on the substrate. The combination of the enhanced growth rate and the reduced surface mobility may lead to local accumulations of the solute materials which could cause local strain on the layer. Thus, more misfit dislocations are required to be nucleated to relax the strain. Since the morphology of ridges and troughs is due to the locally high growth rate induced by the underlying misfit
dislocations, as more misfit dislocations are generated, more ridges and troughs will be formed and thus results in a small wavelength of undulation. More misfit dislocations generated also leads to a high threading dislocation density which is displayed by the high etch pit density, a measurement of threading dislocation density.



Figure 3.13 Wavelength of undulation and etch pit density of the Si0.966Ge0.034 layers grown using different cooling rates [110].

The cooling rates also influence the composition gradient of SiGe layers (Figure 3.7). It was reported by Gutjahr [20] that a higher Ge concentration gradient in the SiGe layer was observed when a higher cooling rate is used. In this study, we decide to use a cooling rate of 500 °C/h. As discussed previously that a large growth interval helps to grow high-Ge-content SiGe, it will take ~28h to cover a whole growth interval of 950-400 °C if the cooling rate is 20 °C/h. Also, a high cooling rate leads to a larger Ge composition gradient as suggested by figure 3.7. Growths of different cooling rates will be carried out in the future. Currently, we choose the highest cooling

rate reported, 500 °C/h. The etch pit density of SiGe layers grown with 500 °C/h is higher than those grown with low cooling rates but it is still below  $\sim 10^6$  cm<sup>-2</sup>.

## 3.2.5 Growth challenges of LPE SiGe films

Since the two main challenges we had in our LPE growth are the completely removal of native oxide layer on the Si (001) substrates and the solution residue when removing the substrate away from the solution, some background are provided here.

## 3.2.5.1 Removal of native oxide layer

There is a native SiO<sub>2</sub> layer with thickness of 10-50 Å on the Si substrates [124]. The SiO<sub>2</sub> layer prohibits the liquid solution Si-Ge-M wetting the surface of the Si substrates and no growth happens if the SiO<sub>2</sub> layer remains. Bergmann [125] found that partial removal of SiO<sub>2</sub> layer on the Si (001) substrates could lead to the formation of SiGe pyramidal islands. As shown in figure 3.14, as small localized holes are opened in the SiO<sub>2</sub> layer on the Si (001) substrates, solution can only wet these areas and SiGe pyramidal islands grow from these small openings.



Figure 3.14 Formation of SiGe pyramidal islands due to localized removal of SiO<sub>2</sub> layer on Si (001) [125].

The native  $SiO_2$  layer must be removed completely for continuous SiGe films growth which is normally taken by two steps in LPE process. The first step is to dip the Si substrates into the HF solution before loading into the LPE furnace and the reaction is:

$$SiO_{2(s)} + 6HF_{(l)} \rightarrow H_2SiF_{6(aq)} + 2H_2O_{(l)}$$

The second step is to bake the Si substrates under a pure  $H_2$  atmosphere at temperature higher than 900 °C in the LPE furnace and the reaction is:

$$SiO_{2(s)} + H_{2(v)} \rightleftharpoons SiO_{(v)} + H_2O_{(v)}$$

In addition, there are reports [126, 127] about adding a bit amount of high purity Al (0.3 wt.%) to the metallic solution can help remove the  $SiO_2$  layer and the reaction is:

$$4Al_{(l)} + 3SiO_{2(s)} \to 2Al_2O_{3(s)} + 3Si_{(l)}$$

### **3.2.5.2 Solution entrainment**

Solution entrainment occurs commonly in the growth of using a horizontal sliding boat when the solution is not completely removed from the substrate as shown in figure 3.15. Solution entrainment is detrimental to the desired growth because it can affect the layer thickness, composition and morphology [128]. When it happens in the multilayer growth, partial solution could be carried over into the next solution chamber when transporting the substrate and thus changes the composition of the subsequent solution. When it happens at the end of the growth of removing the substrate away from the solution, deposition from the entrained solution continues while cooling the substrate to the room temperature. The continued growth from the entrained solution will make it hard to determine the results from the desired experiment. Wilson [129] investigated the solution entrainment during the LPE growth and found it depends on the slit height, S, between the surfaces of the substrate and the slider, the solution height, h, the substrate moving speed and the surface morphology of the grown layer. Wilson found the amount of entrained

solution can be reduced by decreasing the slit height. However, if the slit is too small, abrasion on the surface of the substrate or the grown layer will happen which could lead to growth defect. It was suggested that the optimized slit height should be in the range of 20~100 µm [82]. Wilson also found that lowering the solution height helps reduce the entrained solution since the solution pressure is proportional to the solution height and it could force the solution into the channel between the well and the substrate. In addition, fast moving speed and smooth surface morphology result in reduced solution entrainment.



Figure 3.15 Schematic of solution entrainment in the horizontal sliding boat.

## **Chapter 4**

# Liquid-Phase Epitaxy System

This chapter describe the LPE system we developed, the growth procedure as well as the main improvements of the growth condition to grow non-entrained, continuous film.

### 4.1 LPE system assembly

The LPE system developed is the horizontal sliding system. The schematic diagram of the LPE system is shown in figure 4.1. A quartz tube is fixed horizontally with quartz-to-meal seals sealed at both end. A high purity and fine grinded graphite boat which carries the solutions and the substrates for the crystal growth is located inside the quartz tube. The graphite boat has thermocouple probes inserted at one side to measure the temperature of crystal growth and has a pushrod inserted at the other side to transport the substrates. The quartz tube including the graphite boat sits inside a three-zone cylinder furnace. Each furnace has a controller to control its own set point of temperature and a thermocouple probe inserted on the top of each furnace to measure the actual temperature. The furnace can move laterally with wheels mounted underneath and the moving speed is controlled precisely by a stepper motor installed underneath the furnace via a ball-screw. The controllability of the furnace temperature and furnace moving speed allows a desired



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cooling rate for the crystal growth.

Ultrapure  $H_2$  or  $N_2$  is flowing through the system all the time to keep a clean and dry environment for crystal growth. Ultrapure  $H_2$  is flowing when the furnaces are operating to remove any regrown oxide layer on the substrates during the loading process. When the furnaces are not operating, ultrapure  $N_2$  is flowing for its low-cost and safety. The ultrapure  $H_2$  or  $N_2$  is obtained by filtering the 99.999% pure  $H_2$  or  $N_2$  with a gas purifier and the flow rate is controlled by a mass flow controller. For safety, a  $H_2$  detector with an alarm installed is operating all the time. A portable  $H_2$ detector is used to check along the LPE system every time after a few minutes of flowing  $H_2$  and before operating the furnace to make sure there is no  $H_2$  leak. A hygrometer installed close to the gas inlet of the quart tube to monitor the moisture inside the system. A metal trap installed close to the gas outlet of the quart tube to remove any vaporized metals before exhausted.

The schematic diagram of the designed horizontal sliding graphite boat is shown in figure 4.2. The graphite boat is essentially composed of four parts: a graphite holder, a graphite slider, a graphite well-block, and a graphite lid. The graphite well-block is the part to hold the metallic solutions which contains two separately rectangular wells with a size of  $1.28 \text{ cm} \times 1 \text{ cm}$ . Two thermocouple holes are created at one side of the well-block. Each hole corresponds to one individual well and goes close enough to the well to measure the temperature accurately for the crystal growth. The graphite slider is the part to hold the saturation wafers and the growth substrates. It has two sets of saturation wafer recess—growth substrate recess corresponding to each well which allows two growths in one single experiment. The size of the each recess is  $1.2 \text{ cm} \times 1.2 \text{ cm}$  and the depth of the recess is  $500 \text{ }\mu\text{m}$ . A hole for pushrod inserted is created at the edge of the slider. Noted that the pushrod hole and the thermocouple holes are located at different sides of the graphite boat.

graphite holder is cylindrical outside with well-machined slots inside to hold the slider, the wellblock, and the lid. The graphite lid is the part to cover the well-block to help confine the vaporized metals inside the well. The holder, the well-block, and the lid are assembled by two quartz pins and the slider lies between the holder and the well-block which is able to slide. A minimized gap of 20  $\mu$ m is designed to exist between the well-block and the slider to help reduce the solution residue as much as possible.



Figure 4.2 Schematic diagram of the custom-designed graphite boat showing the components and assembly.

### **4.2 Growth procedure**

The desired amounts of Ge and solvent, In, are precisely massed and homogenized at ~1000 °C for 4 h in the LPE system under ultrapure H<sub>2</sub> atmosphere. The Ge is 99.999% pure, -325 mesh powder and the In is 99.999% pure, 3-6 mm shots or -325 mesh powder. The saturation wafers are Si (001) and the growth substrates are Si (001) or CVD-grown Si<sub>0.9</sub>Ge<sub>0.1</sub>/Si (001). The Si (001) wafer has a thickness of 500  $\pm$  25 µm and a misorientation of  $\pm$ 0.3°. The CVD Si<sub>0.9</sub>Ge<sub>0.1</sub> film is grown in Massachusetts Institute of Technology. The Si (001) and CVD-grown Si<sub>0.9</sub>Si<sub>0.1</sub> wafers are cleaned in a 1:1::H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> (volume), self-heating, piranha solution for 15 min to remove any organic impurities followed by a 1:1:6::HC1:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O (volume) solution at 80 °C for 15 min to remove any metallic impurities [130, 131]. The wafers are rinsed by distilled water and cut into 1.2 cm × 1.2 cm pieces along <110> directions.

The saturation Si wafer and the growth substrate are dipped into 5% HF for 30 s to remove the native SiO<sub>2</sub> layer and then immediately loaded into the saturation wafer recess and the growth substrate recess of the graphite boat, respectively with the homogenized GeIn alloy loaded in the well. The graphite boat is immediately put into the quart tube from the gas outlet to prevent the regrowth of SiO<sub>2</sub> layer. After sealing the quartz tube, the gas flowing inside the system is switched from ultrapure N<sub>2</sub> to ultrapure H<sub>2</sub>. The H<sub>2</sub> leak of the LPE system is checked by using a portable H<sub>2</sub> detector. After making sure there is no H<sub>2</sub> leak, the temperature is heated to the saturation temperature,  $T_s = 950$  °C, for 1 h to preheat the Ge-In alloy and bake the saturation wafer and growth substrate to remove any remaining SiO<sub>2</sub> layer. Then, the saturation Si wafer is introduced to the GeIn solution for 3 h [132] to saturate the GeIn solution with Si. After that, the growth substrate is introduced to the SiGeIn solution and the temperature is reduced by 500 °C/h immediately. When the temperature reaches the final temperature,  $T_f$ , the substrate is removed

from the solution and then cooled to room temperature. The growth temperature range, the starting temperature to the final temperature, i.e.  $T_s$  to  $T_f$ , is called temperature interval. The schematic of growth procedure explained as temperature vs. time as well as the status of the graphite boat are shown in figure 4.3.



Figure 4.3 Temperature vs. time showing the growth procedure as well as the status of the graphite boat at each step. The orange rectangle represents the metallic solution and the black rectangles represent the saturation wafer and the growth substrate.

### **4.3 Growth condition improvements**

The two main problems during our initial LPE growth are the removal of oxide layer on the substrate and the solution entrainment. Failure in the removal of the oxide layer will not produce any growth or will result in pyramidal islands. Failure in the preventing of solution entrainment will cause second growth which is detrimental to the desired growth. The following describes the strategies explored to grow non-entrained and continuous film.

### 4.3.1 Removal of native oxide layer

Since low-Ge-content SiGe favors planar growth, a low-Ge-content LPE solution is require for film growth as discussed in chapter 3. The Si-Ge-In solution used initially contains ~2%Ge and

the initial deposition at the saturation temperature, 950 °C, should contain 2.2%Ge based on the calculation using equation 3.8. Such low-Ge-content deposition is supposed to be planar growth. Our initial growths were carried out with a growth temperature interval of 950-900 °C under 99.999% H<sub>2</sub> atmosphere. After growth, the growth substrate as well as the saturation wafer took out from the LPE system were shining as a mirror as the bulk Si wafer. X-ray diffraction (XRD) proved that no growth happened on the growth substrate since SiGe peak was not detected. The cause of this is that the substrate was all covered with SiO<sub>2</sub> layer so that the metallic solution cannot wet the substrate and thus did not produce any growth. Even for the saturation wafer, the surface of the wafer was flat and its thickness was 500  $\mu$ m, the same as its original thickness, which indicates saturation did not happen. The same reason for this, that is, the saturation wafer was all covered with SiO<sub>2</sub> layer so that the surface to dissolve Si. As described in the growth process above, the SiO<sub>2</sub> layer was first removed by HF etching and the reaction is:

$$SiO_{2(s)} + 6HF_{(l)} \rightarrow H_2SiF_{6(aq)} + 2H_2O_{(l)}$$

After HF wet etching, a H-terminated surface is formed on both saturation wafer and growth substrate and this H-terminated surface could be stable for approximately 15 min in air [133]. So, after HF etching, the saturation wafer and the growth substrate with the homogenized alloy were loaded into the LPE system as quickly as possible. To load the boat, the quart-to-metal seal at the downstream of the quart tube had to be opened and  $N_2$  was flowing during the whole loading process. After placing the boat into the quart tube, the thermocouple probe was adjusted to insert into the boat and so was the push rod; then the tube was sealed. This whole loading process was normally taken ~12 min which was under the effective time of the H-termination (15 min).

Afterwards, the LPE furnace was heated to the saturation temperature 950 °C under H<sub>2</sub> flowing and stayed at this temperature for 1h to bake the saturation wafer and the growth substrate. H<sub>2</sub> was supposed to etch any regrown SiO<sub>2</sub> layer at high temperature with the following reaction:

$$SiO_{2(s)} + H_{2(v)} \rightleftharpoons SiO_{(v)} + H_2O_{(v)}$$

However, both the saturation wafer and the growth substrate were all covered with  $SiO_2$  layer suggests the reaction between  $SiO_2$  and  $H_2$  was suppressed and the oxidation of Si was promoted.  $SiO_2$  layer was regrown after loading the graphite boat into the LPE system.

Multiple strategies were performed in order to remove the regrown  $SiO_2$  layer. The first strategy was to add a bit amount (0.3 wt.%) of Al into the metallic solution which was reported to help remove the  $SiO_2$  layer and the reaction is [126, 127]:

$$4Al_{(l)} + 3SiO_{2(s)} \rightarrow 2Al_2O_{3(s)} + 3Si_{(l)}$$

Following the same growth process, the sample took out from the LPE system were covered all with residual solution. After selectively etching In by HCl, the surface morphology of the sample observed by scanning microscopy image (SEM) is shown in figure 4.4a. Instead of no growth happened, pyramidal SiGe islands were grown. By observing the cross section (figure 4.4b), we only saw SiGe islands on the Si substrate and did not see any continuous film. This indicates that adding Al helped etch the SiO<sub>2</sub> layer but only opened localized holes in the SiO<sub>2</sub> layer to result in pyramidal islands growth [125]. Further adding more amount of Al into the metallic solution did not improve the growth significantly and made the metallic solution adhere strongly to the graphite boat which leads to scratching on our boat in order to get the metals off.



Figure 4.4 SEM images showing pyramid islands due to localized holes opened in the oxide layer. Plan view (a) and cross-sectional view (b).

The second strategy was to grow SiGe directly on the saturation wafer with a bit amount of Al (0.3 wt.%) added into the metallic solution. The atomic force microscopy (AFM) image of sample surface shown in figure 4.5a. A continuous film was grown but the film has multiple steps and a high density of pits which probably due to the rough surface after saturation. The growth of a continuous film indicates the SiO<sub>2</sub> layer was all removed and the ability of removing the SiO<sub>2</sub> layer is probably because of the combination of Al etching and solution dissolution. Once Al helps open large numbers of localized holes in the SiO<sub>2</sub> layer, the solution which is unsaturated with Si will

immediately dissolve Si starting from these holes and the dissolution will diffuse under the  $SiO_2$  layer layer. As the dissolution keeps going on, the solution wets more area of Si below the  $SiO_2$  layer which will be able to soak the layer off the substrate piece by piece. The schematic diagram of the dissolving process from localized openings in the  $SiO_2$  layer on the Si wafer is shown in figure 4.5b.



Figure 4.5 AFM image of SiGe film grown on a saturation wafer with aid of Al added in the metallic solution (a) and schematic of dissolving Si from localized openings in the SiO<sub>2</sub> layer on a Si wafer.

The third strategy was to further reduce the contamination of  $O_2$  and  $H_2O$  in the LPE system which brought the success of growing crosshatch film as shown in figure 4.6. Two methods were employed: (1) A Micro-Torr gas purifier was installed in the  $H_2$  and  $N_2$  line, respectively, which is able to remove  $H_2O$  and  $O_2$  impurities down to 100 part-per-trillion. (2) Heaters were adhered to the gas lines to bake the gas lines periodically to remove any adhere moisture. With the combination of gas filtering and gas line baking, the gas moisture was significantly reduced, which was observed from the hygrometer that the dew point was reduced from around -70 °C to below -120 °C (the detect limitation of the hygrometer is -120 °C). It was found that the dew point was required to be below -100 °C to get film growth. Further reducing  $O_2$  and  $H_2O$  contaminations successfully provides a SiO<sub>2</sub>-free surface on the substrate, which is the critical step for heteroepitaxial SiGe film growth. In addition, to avoid moisture, the graphite boat was always stored in the quart tube under ultrapure  $N_2$  atmosphere whenever it was not use. Moreover, the graphite boat and the quartz tube were baked periodically at temperature above 1000 °C under ultrapure  $H_2$  atmosphere to remove any moisture.



Figure 4.6 SEM image of the crosshatch film grown after further reducing O<sub>2</sub> and H<sub>2</sub>O contaminations.

#### 4.3.2 Minimization of solution entrainment

Solution entrainment is detrimental to the desired growth in LPE process. When solution entrainment occurs at the termination of the desired growth, growth continues as cooling to the room temperature. This could affect the surface morphology, film thickness and composition of the desired growth. Figure 4.7a shows a typical surface morphology during our LPE growth when solution entrainment occurs and figure 4.7b is the cross-sectional backscattered SEM image. Highly ordered and dense islands locate on a continues film. The island has ~70% Ge and the film has ~3% Ge which were determined by energy-dispersive X-ray spectroscopy (EDS). The low-Ge-content film is the result of the desired experiment occurred at high temperature and the high-Ge-content islands are the deposition from the entrained solution occurred at low temperature. Such high Ge content in the islands is because the entrained solution depletes of Si and LPE growth at low temperature favors high-Ge-content deposition. Because of the large misfit between the high-Ge-content SiGe and the low-Ge-content SiGe film, the high-Ge-content SiGe are grown following the SK growth mode. The arrangement of islands along <110> directions is due to dislocation network underlying the low-Ge-content film [134-136]. The low-Ge-content film is partially relaxed by the nucleation and gliding of  $60^{\circ}$  dislocations oriented along <110> directions. These dislocations create strain fields in the low-Ge-content SiGe film upon which the islands preferentially nucleate.



Figure 4.7 SEM images of highly ordered and dense Si<sub>0.3</sub>Ge<sub>0.7</sub> islands on a Si<sub>0.97</sub>Ge<sub>0.03</sub> film due to solution entrainment. Plan-view image (a) and cross-sectional view image (b). For image b, the sample was tilted to show the islands.

To reduce the solution entrainment, three strategies were carried out based on the discussion in section 3.2.5 of chapter 3. The first strategy was to set the gap between the substrate surface and the graphite boat at 20 µm which is the minimum of the suggested height range. The second strategy was to use a small amount of solution to reduce the solution height and thus reduce the solution pressure that could cause solution entrainment. The solution amount cannot be too small; otherwise, it cannot cover the whole substrate. In Hansson's LPE growth, the solution used has a thickness of 5 mm [106]. We chose to use the same thickness for our growth and the amount of solution determined was 3 g which was sufficient enough to cover the whole substrate. The third strategy was to pull the substrate away from the solution quickly. By accomplishing the three strategies above, solution entrainment is able to be prevented effectively and non-entrained SiGe films could be obtained. It was found that the surface morphology is the main factor for the solution entrainment after setting up the first two strategies. If the film surface is smooth, solution entrainment barely occurs regardless of the pulling speed. If the film surface is too rough or the growth is 3D island, solution entrainment will definitely occur no matter how quickly to pull the substrate away from the growth solution.

## Chapter 5

## **Characterization Methods**

The characterization methods used in this study are described in this chapter. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to characterize the surface morphology. Energy-dispersive X-ray spectroscopy (EDS) line scan in SEM was used to measure the composition profile and determine the layer thickness. Preferential defect etching is the primary technique to determine the threading dislocation density by measuring the etch pit density (EPD). Transmission electron microscopy (TEM) was also used to determine the threading dislocation density for partial samples. High-resolution triple-axis X-ray diffraction was used to determine the composition and strain state.

### 5.1 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to characterize the surface morphology and cross section of the SiGe layers with the energy-dispersive X-ray spectroscopy (EDS) for compositional analysis. SEM imaging was performed on a Hitachi SU3500 scanning electron microscopy using 20 kV accelerating voltage and ~10 mm working distance. Secondary electron (SE) mode was employed for the surface morphology characterization. Backscattered electrons compositional

(BSE COMP) mode was employed for the cross section imaging in which low atomic number elements (for example Si) appear dark and high atomic number elements (for example SiGe) appear bright. EDS line scan in the BSE COMP mode was performed to profile the Ge content of the epitaxial layer as the function of layer thickness. Before the profile, samples were prepared by grinding the cross section using progressively finer SiC paper (320, 500, 1200, and 4000 grit sizes) and then polished using 0.3 µm alumina powder suspensions. The samples were rinsed following water, acetone, and isopropanol.

### 5.2 Atomic force microscopy

Atomic force microscopy (AFM) was employed to measure the topography of the SiGe layers. The AFM imaging was performed on an Asylum MFP-3D atomic force microscopy at the Centre for Self-Assembled Chemical Structures (CSACS), Department of Chemistry, McGill University. A contact mode was used for all the AFM imaging. The AFM images were analyzed using software Gwyddion to calculate the surface roughness and extract line profiles for crosshatch morphology analysis.

### **5.3 Transmission electron microscopy**

Transmission electron microscopy (TEM) was used to measure the threading dislocation denisty from plan view. TEM imaging was performed on a FEI Tecnai G<sup>2</sup> F20 200 kV Cryo-STEM at the Facility for Electron Microscopy Research, McGill University. The observation was achieved by monitoring Kikuchi patterns and tilting an electron transparent sample to maintain a (220) reflection under two-beam condition using double tilting stage.



Figure 5.1 Gatan Disc Grinder used for TEM sample preparation. Top view (a), down view (b), and specimen mount (c).

For TEM observation, an electron transparent sample with thickness typically less than 100 nm was required [137]. The TEM sample was prepared using a Gatan Disc Grinder (figure 5.1) and ion beam milling. A piece of  $3 \text{ mm} \times 3 \text{ mm}$  was cut from the bulk sample and mounted with face side (laver surface) down onto the specimen mount using a low melting point Crystalbond wax (figure 5.2). The specimen mount was placed into the grinder after zero calibration and was adjusted using the control knob until the sample surface was flush with the polishing surface. The sample thickness was reduced by progressively grinding. A small increment of the sample was rolled out of the polishing surface and was grinded by SiC paper until the sample surface was flush with the polishing surface. Another small increment of the sample was rolled out of the polishing surface and was grinded by a finer SiC paper in the direction perpendicular to the previous grinding. This grinding process was repeated until the wax around the sample was all gone and the edge of the sample was smooth. The series of SiC paper used were 320, 500, 1200, and 4000 grit sizes. The sample was then polished using  $0.3 \mu m$  alumina powder suspensions to obtain a highly polished surface. After polishing, the sample was rinsed with water to remove the alumina powder. A 3 mm diameter copper grid with 2 mm  $\times$  0.6 mm slot was glued onto the sample using epoxy and then heated on a hot plate to melt the wax and thus to remove the sample from the specimen

mount. The sample was dipped into acetone to dissolve residual wax followed with isopropanol rinsing. The sample as shown in figure 5.3a was ready for ion beam milling. The ion beam milling was performed on a Gatan Precision Ion Polisher system (PIPS) at the Facility for Electron Microscopy Research, McGill University. The sample was placed into the sample holder of the PIPS and milled at the back side by two Ar ion guns at 4 keV with an incident angle of 6° until a small hole appeared as shown in figure 5.3b. The area around the small hole was electron transparency and TEM observation was carried out by examining this electron transparent area. One much be aware of is that TEM has a lower limit of threading dislocation detection due to the very small sampling area, which is roughly 10<sup>7</sup> cm<sup>-2</sup> for plan-view TEM [63].



Figure 5.2 Schematics of sample amounted on the specimen mount. Cross-sectional (a) and top view (b).



Figure 5.3 Schematics show the top view of TEM sample before (a) and after (b) ion milling.

### 5.4 Etch pit density

Preferential defect etching is a useful technique to measure the threading dislocation density. It involves using an appropriate chemical solution to etch the epitaxial layer. Since the dangling bonds increase the surface energy when a threading dislocation ends at the surface, the etch rate at where a threading dislocation locates is faster than other areas; thus resulting in a pit. For Si-rich SiGe layers, the most notable etch is the Schimmel etch which consists of 1(1M CrO<sub>3</sub>): 2HF (weight ratio) [138]. In the Schimmel etch, CrO<sub>3</sub> is used as the oxidizing agent to oxidize Si and HF is the dissolving agent to dissolve the oxidized Si. The etch rate depends on the composition, layer thickness and Cr concentration [139]. Considering the low-Ge-content of the SiGe layers in this study, a 1.5 times diluted Schimmel solution was used which was composed of 1 g CrO<sub>3</sub>, 20 mL HF and 35mL H<sub>2</sub>O.

Optical microscope was used to imaging the etch pits. Under optical microscope, the etch pits appear black dots as indicated by the arrow in figure 5.4. It was noted that etch time must be accurately controlled until the etch pits became clearly visible and individually distinguishable under optical microscope observation. Otherwise, over etching will lead to inaccurate result about the dislocation density. It has been observed that two close pits such as the two circled in figure 5.4 would be enlarged and eventually becomes one pit if over etching. This results in underestimation of the actual dislocation density. Depending on the composition and layer thickness, the etch time was different for different samples ranging from 2~15 min. The etch pit density (EPD) was determined by counting the pits imaged by optical microscopy using software ImageJ. For each sample, at least 0.2 mm<sup>2</sup> total area were examined after appropriate etching to determine the average EPD.



Figure 5.4 An example of optical microscopy image of etched sample showing etch pits.

### 5.5 High-resolution triple-axis X-ray diffraction

High-resolution triple-axis X-ray diffraction is the primary technique to determine the composition and strain states. All measurements were performed on a Bruker D8 triple-axis diffractometer at École Polytechnique, University of Montreal. The diffractometer was equipped with 4-bounce Ge (220) channel-cut monochromator and 1mm circular or linear slit to produce a high-resolution measurement. Symmetric (004) and glancing-incidence asymmetric ( $\overline{224}$ ) reciprocal space maps (RSMs) were recorded. In the following, theory about reciprocal space maps as well as the determination of composition and strain state are introduced.

### 5.5.1 Fundamental of X-ray diffraction

When X-ray waves impact on a crystal with atoms arranged in a periodic array, constructive X-ray diffraction happens if the incident angle upon the crystal plane and the path difference of the waves between two neighboring planes follow the Bragg's law:

$$n\lambda = 2d\sin\theta \tag{5.1}$$

where *n* is an integer,  $\lambda$  is the wavelength of the incident X-rays, *d* is the inter-planar spacing between diffracting planes, and  $\theta$  is the incident angle between the incident X-ray and the diffracting plane. Figure 5.5 schematically shows the constructive X-ray diffraction to illustrate the Bragg's law.



Figure 5.5 Schematic of the constructive X-ray diffraction [140].

Depending on the diffraction plane with respect to the surface plane, the diffraction geometry is sorted into two categories: symmetric diffraction geometry and asymmetric diffraction geometry. In symmetric diffraction geometry, the diffracting plane is such one family planes that is parallel or nearly parallel to the sample surface (figure 5.6a). The sample is not tilted and the incident angle between the X-ray and the surface plane,  $\omega$ , is equal to  $\theta$ . In asymmetric diffraction geometry, the sample is tilted and Bragg diffraction happens on other planes. If the sample is tilted towards a lower  $\omega$  value, the diffraction geometry is called glancing incidence (-) (figure 5.6b). If the sample is tilted towards a higher  $\omega$  value, the diffraction geometry is called glancing exit (+) (figure 5.6c). A symmetric diffraction geometry only collects the information from perpendicular lattice constants while an asymmetric diffraction geometry collects information from both the perpendicular and in-plane lattice constants. For an epilayer, if its composition is known, strain relaxation can be determined from the symmetric collection. If the epilayer is fully relaxed, composition can be determined from the symmetric collection as well. If neither is known, both symmetric and asymmetric collections are required.



Figure 5.6 Symmetric diffraction geometry (a) and asymmetric diffraction geometries of (b) the glancing incidence and (c) the glancing exit.

### 5.5.2 Reciprocal space mapping

Reciprocal space mapping is a the most powerful technique to analyze composition and strain states of graded buffers or multilayers [141-144]. A triple-axis X-ray diffractometer is required to produce high-resolution for reciprocal space mapping. A schematic diagram of the triple-axis Xray diffractometer is shown in figure 5.7. The triple-axis refers to the monochromator, sample, and analyzer. A monochromator allows to eliminate unwanted X-ray wavelengths,  $CuK_{\alpha_2}$  and  $CuK_{\beta}$ lines, and only leaves the highest intensity  $CuK_{\alpha_1}$  to impact on the sample [145, 146]. A slit may be placed between the monochromator and the sample to control the height and width of the X- ray beam. The sample stage is capable of moving in X, Y, and Z directions as precisely as 0.0001 mm to locate the beam position. The sample stage is also able to rotate ( $\varphi$ ) and tilt ( $\psi$ ) with a high degree of precision (~0.0001°) to orientate the sample. When the monochromatic CuK<sub> $\alpha_1$ </sub> X-rays strike on a sample, different diffracted angles, 2 $\theta$ , are produced. Instead of receiving several different 2 $\theta$ , an analyser crystal placed before the detector constrains the 2 $\theta$  angle to be received as shown in figure 5.7. The detector and the analyzer can move in a circle around the sample to cover all the angles of interest. This allows the ability of precisely distinguishing different diffracted angles [145, 146].



Figure 5.7 Schematic of triple-axis diffractometer [146].

X-rays incident on a crystal will be diffracted by planes of atoms and the diffraction pattern on a (001) oriented crystal is shown in figure 5.8. The diffraction pattern is made up of a series of reciprocal lattice points (RLPs), in which each RLP represents a set of equivalent lattice planes (*hkl*). Each RLP has a reciprocal lattice vector,  $g_{hkl}$ , pointing from the origin (000) to the RLP.

The incident beam and the diffracted beam are represented by the wave vector  $k_{inc}$  and  $k_{diff}$ , respectively as shown in figure 5.8. The diffraction vector K is defined as [147]:

$$\mathbf{K} = k_{\rm diff} - k_{\rm inc} \tag{5.2}$$

Constructive diffraction happens when a RLP lies on the Ewald sphere surface and satisfies with the diffraction vector K equals to the reciprocal lattice vector  $g_{hkl}$ . In figure 5.8, constructive diffraction is shown for (115) plane.

The scan directions of  $\omega$ , 2 $\theta$ , and  $\omega/2\theta$  scans in reciprocal space are depicted in figure 5.8. In  $\omega$  scan, that is, the sample is rotated around its  $\omega$  axis, the intensity is collected along a circle centered the origin (000) (arrow "b"). In 2 $\theta$  scan, that is, the detector is moved with the sample being fixed, the intensity is collected along the Ewald sphere (arrow "c"). In  $\omega/2\theta$  scan, the sample is rotated while the detector is moved at twice the rate as the sample, the scan direction is radial from the origin (000) (arrow "a"). Reciprocal space mapping collects several  $\omega/2\theta$  scans at different  $\omega$  setting. The direct output is intensity distributions plotted by  $2\theta$  vs. relative  $\omega$  but it is very useful to express the intensity distributions by the RLP coordinates. This is because the relative RLP positions between the layer and the substrate could directly provide information about the strain states and the presence of lattice tilt which will be introduced in section 5.5.3. The conversions are given by [147]:

$$q_{x} = \frac{2}{\lambda} \sin \frac{2\theta}{2} \sin (\frac{2\theta}{2} - \omega) = \frac{1}{\lambda} \{\cos \omega - \cos(2\theta - \omega)\}$$
(5.3)

$$q_z = \frac{2}{\lambda} \sin \frac{2\theta}{2} \cos(\frac{2\theta}{2} - \omega) = \frac{1}{\lambda} \{\sin \omega - \sin(2\theta - \omega)\}$$
(5.4)

where  $q_z$  is the component of the RLP in the crystal orientation, which is inversely proportional to the perpendicular lattice constant, and  $q_x$  is the component of the RLP in the horizontal direction, which is inversely proportional to the in-plane lattice constant [142].



Figure 5.8 Reciprocal lattice points of a (001) orientated crystal [142].

## 5.5.3 Interpreting RSMs of uniform composition SiGe layer

To determine the composition and strain state of an epitaxial layer, symmetric and asymmetric RSMs are required. For SiGe layers on Si (001), the symmetric RSM is typically collected in the (004) diffraction and the asymmetric RSM is in (224) diffraction. In this study, the asymmetric RSM was collected in the  $(\overline{224})$  diffraction, which is in the same family plane with (224). The positions of (004), (224), and  $(\overline{224})$  RSMs are marked in figure 5.8. The RLP position of SiGe with respect to Si depend on the perpendicular and in-plane lattice constants. Figure 5.9 schematically shows the relative RLP positions of SiGe and Si in symmetric (004) and asymmetric ( $\overline{224}$ ) RSMs. Since SiGe always has a larger perpendicular lattice constant than Si, the SiGe RLP locates below Si. As symmetric (004) RSM only collects the information from the perpendicular lattice constant, the SiGe (004) RLP lies directly below Si on the vertical [001] axis. Asymmetric ( $\overline{224}$ ) RSM collects information from both in-plane and perpendicular lattice constants. A fully

strained SiGe has its in-plane lattice constant been matched to Si, so fully strained SiGe  $(\overline{22}4)$  RLP (SiGe<sub>str</sub>) locates directly below Si. The  $(\overline{22}4)$  RLPs of fully relaxed SiGe and Si both lie on the  $[\overline{22}4]$  reciprocal lattice vector since they both have the cubic structure and their asymmetric planes are all parallel to each other [142, 143]. For SiGe layers have the same composition, the perpendicular lattice constant of the fully strained SiGe is larger than the fully relaxed SiGe; thus, fully strained SiGe RLP lies below fully relaxed SiGe. Arrows in figure 5.9 indicates the relaxation path from fully strained to fully relaxed SiGe layers. For a partially relaxed SiGe layer, the RLP lies between the SiGe<sub>str</sub> and SiGe<sub>rel</sub>.



Figure 5.9 Schematic of reciprocal space of SiGe on Si (001) [142].

The relative RLP positions of SiGe and Si introduced above is for a SiGe layer has the same crystal orientation to the Si substrate. If the crystal orientation of the layer is not parallel to the substrate,

that is, lattice tilt occurred, the layer RLPs are tilted as well [148]. The cause of lattice tilt is not clear but probably due to the miscut of the substrate [149-151]. France [149] investigated the misfit dislocation glide plane distribution of step-graded GaInAs and GaInP grown on (001) GaAs substrates with a miscut of 2° toward ( $\overline{1}11$ ) plane and found the miscut towards the ( $\overline{1}11$ ) plane creates an asymmetry in the resolved mismatch stress on the ( $\overline{1}11$ ) and ( $1\overline{1}1$ ) glide planes which makes dislocations prefer to glide on the ( $\overline{1}11$ ) plane rather than the ( $1\overline{1}1$ ) plane; thus, the epilayer has a systematic tilt relative to the substrate. The presence of lattice tilt can be directly observed on the symmetric RSM that epilayer (004) RLP no longer lies directly below the substrate on the vertical [001] axis if lattice tilt occurs. The effect of lattice tilt has to be corrected to determine the composition and strain state. Figure 5.10 schematically show the principle of tilt correction. A tilt angle is given by [120]:

$$\eta = \operatorname{arctg}\left(\frac{q_{x,e}^{0.04}}{q_{z,e}^{0.04}}\right)$$
(5.5)

where  $(q_{x,e}^{004}, q_{z,e}^{004})$  is the epilayer (004) RLP coordinate. The epilayer (004) and  $(\overline{2}\overline{2}4)$  RLPs indicated by the circles in figure 5.10 are rotated by the tilt angle,  $\eta$ , around the origin (000). After tilt correction, epilayer (004) RLP lies directly below the substrate on the vertical [001] axis and  $q_{z,corr}^{004}$  and  $q_{z,corr}^{\overline{2}24}$  are equal as shown by the black dots in figure 5.10.



Figure 5.10 Principle of tilt correction. Circles represent lattice tilted SiGe RLPs and black dots represent SiGe RLPs after tilt correction [152].

The in-plane  $(a_{\parallel})$  and perpendicular  $(a_{\perp})$  lattice constants of the epilayer could be determined

from the RLP coordinates after tilt correction [153]:

$$\frac{a_{\parallel} - a_s}{a_{\parallel}} = \frac{|q_{x,corr}^{\overline{224}} - q_{x,s}^{\overline{224}}|}{|q_{x,s}^{\overline{224}}|}$$
(5.6)

$$\frac{a_{\perp} - a_s}{a_{\perp}} = \frac{|q_{z,corr}^{004,\overline{22}4} - q_{z,s}^{004,\overline{22}4}|}{|q_{z,s}^{004,\overline{22}4}|}$$
(5.7)

Where  $(q_{x,s}^{\overline{224}}, q_{z,s}^{004,\overline{224}})$  is the coordinate of the Si substrate RLP which is (-0.5208, 0.7365) [153] and  $(q_{x,corr}^{\overline{224}}, q_{z,corr}^{004,\overline{224}})$  is the coordinate of the epilayer RLP after tilt correction. Following the elasticity theory, Ge content of the epilayer  $(X_{Ge})$  can be determined by solving equations (5.8) - (5.12): Chapter 5. Characterization Methods

$$X_{Ge} = \frac{a_r - a_s}{a_{Ge} - a_s} \tag{5.8}$$

$$a_r = \frac{a_\perp + (\nu a_\parallel)}{1 + \nu} \tag{5.9}$$

$$\nu = \frac{2C_{12}}{c_{11}} \tag{5.10}$$

$$c_{11} = c_{11,Ge}^0 X_{Ge} + c_{11,Si}^0 (1 - X_{Ge})$$
(5.11)

$$c_{12} = c_{12,Ge}^{0} X_{Ge} + c_{12,Si}^{0} (1 - X_{Ge})$$
(5.12)

where  $a_r$  is the lattice constant of a fully relaxed layer of the measured composition,  $a_{Ge}$  is the lattice constant of bulk Ge,  $c_{11}$  and  $c_{12}$  are the corresponding elastic constant. At 300K, elastic constants of Si and Ge are [21]:  $c_{11,Ge}^0 = 1.29 \times 10^{12}$ GPa,  $c_{11,Si}^0 = 1.66 \times 10^{12}$ GPa,  $c_{12,Ge}^0 = 4.83 \times 10^{11}$ GPa,  $c_{12,Si}^0 = 6.40 \times 10^{11}$ GPa.

The In-plane strain ( $\epsilon_{\parallel}$ ) and strain relaxation (*R*%) of the epilayer can be determined:

$$\epsilon_{\parallel} = \frac{a_{\parallel} - a_r}{a_r} \tag{5.13}$$

$$f = \frac{a_r - a_s}{a_r} \tag{5.14}$$

$$R\% = \left(1 - \frac{|\epsilon_{\parallel}|}{|f|}\right) 100$$
 (5.15)

### 5.5.4 Interpreting RSMs of SiGe graded buffer

The RSM of a compositionally graded buffer has a continuous intensity distribution because of its varying composition, and thus, varying lattice constant as an example shown in figure 5.11. The RLPs of the Si substrate are located at  $q_z||[001] = 0.7365 \text{ Å}^{-1}$ ,  $q_x||[110] = 0 \text{ Å}^{-1}$  in (004) RSM and at  $q_z||[001] = 0.7365 \text{ Å}^{-1}$ ,  $q_x||[110] = -0.5208 \text{ Å}^{-1}$  in ( $\overline{224}$ ) RSM, respectively [153]. For some of our (004) and ( $\overline{224}$ ) RSMs, the RLPs of the Si substrate were shifted slightly

to their accepted  $q_z$  and  $q_x$  values in both 004 and  $\overline{22}4$  due to a small misalignment. The data were adjusted by shifting the RLPs of the Si substrate to its accepted values. Since the continuously varying lattice constants and the depth dependent strain states, the analysis of a compositionally graded buffer RSM is complicated. The Bauer group [142, 153, 154] developed a way to analyze the RSMs of compositionally graded buffer. The analysis process adapted from Bauer group is described as following.

First, we cut the graded buffer (004) and  $(\overline{2}\overline{2}4)$  RSMs into n equal, thin slices along the direction perpendicular to its diffraction vector, respectively. (004) RSM was cut in the direction perpendicular to [001] and  $(\overline{2}\overline{2}4)$  RSM was cut in the direction perpendicular to  $[\overline{2}\overline{2}4]$ . In figures 5.11a and b, the line labeled "cutting line" is an representative to show the cutting direction for (004) and  $(\overline{2}\overline{2}4)$  RSMs, respectively. The positon of the slice in (004) or  $(\overline{2}\overline{2}4)$  RSM with respect to the substrate was labeled as j (j=1, 2, 3, ..., n) started with the one closet to the substrate. Slices in (004) and  $(\overline{2}\overline{2}4)$  RSMs which were labeled the same number, j, correspond to the same  $j^{th}$  sublayer of the graded buffer.

Second, we extracted the  $(q_{x,j}^{004}, q_{z,j}^{004})$  values at the maximum intensity of each slice in (004) RSM which is the vibrating line in figure 5.11a. These data were then smoothed by non-linear fitting which is the red line in figure 5.11a. Similarly, we extracted and smoothed the data of  $(q_{x,j}^{\overline{22}4}, q_{z,j}^{\overline{22}4})$  values at the maximum intensity of each slice for ( $\overline{22}4$ ) RSM which is represented by the vibrating and red line, respectively in figure 5.11b. The RLP values of  $j^{th}$  sublayer after smooth were labeled as  $(q_{x,j,smoo}^{004}, q_{z,j,smoo}^{004})$  for (004) RSM and  $(q_{x,j,smoo}^{\overline{22}4}, q_{z,j,smoo}^{\overline{22}4})$  for ( $\overline{22}4$ ) RSM, respectively.

Third, we corrected the smoothed RLP values of the  $j^{th}$  sublayer in both (004) and ( $\overline{22}4$ ) RSMs. The  $(q_{x,j,smoo}^{004}, q_{z,j,smoo}^{004})$  and  $(q_{x,j,smoo}^{\overline{22}4}, q_{z,j,smoo}^{\overline{22}4})$  values were rotated around the origin (000) by the corresponding tilt angle:

$$\eta = \operatorname{arctg}\left(\frac{q_{x,j,smoo}^{004}}{q_{z,j,smoo}^{004}}\right)$$
(5.16)

The correction principle is shown in figure 5.10. The black lines in figures 5.11 are the data after tilt correction. The RLP values of  $j^{th}$  sublayer after correction were labeled as  $(q_{x,j,corr}^{004}, q_{z,j,corr}^{004})$  for (004) RSM and  $(q_{x,j,corr}^{\overline{224}}, q_{z,j,corr}^{\overline{224}})$  for ( $\overline{224}$ ) RSM, respectively. After correction,  $q_{x,j,corr}^{004} = 0$  and  $q_{z,j,corr}^{004} = q_{z,j,corr}^{\overline{224}}$ .

The composition, in-plane strain, strain relaxation of  $j^{th}$  sublayer were determined following equations (5.6) - (5.15) using the corresponding RLP values after correction. The whole analysis process of graded buffer RSMs was programmed using Matlab.



Figure 5.11 An example of (004) and  $(\overline{22}4)$ RSMs of a compositionally SiGe graded buffer grown on Si (001) substrate. The vibrating black lines represent the original RLP data extracted from the highest intensity along the diffraction vector, the red lines are the data after smoothed and the black line are the data after correction.
### **Chapter 6**

## Characterizations of SiGe Graded Buffers during LPE Cooling Process

SiGe deposited by cooling a liquid solution, Si-Ge-M ternary system, from high to low temperature becomes Ge-rich during the LPE process [20]. The larger the cooling interval, the higher the Ge content in the SiGe film. From this viewpoint, a large growth temperature interval helps to grow high-Ge-content SiGe. In chapter 4, we successfully grew a continuous SiGe film on Si (001) from a solution with ~2%Ge. In this chapter, we keep the composition of the liquid solution constant, ~2%Ge, but grow SiGe films in varying and sometimes large temperature intervals up to 500 °C to capture and study the initial and intermediate growth stages. Starting with a growth temperature of 950 °C, the final growth temperature was varied to values of 940 °C, 850 °C, 750 °C, 650 °C, and 550 °C. The surface morphology, composition profile, strain state, and threading dislocation density of each sample are studied, which enable a detailed construction of the growth evolution during the LPE cooling process.

#### **6.1 Experimental**

SiGe layers are grown on Si (001) substrates using a custom-designed LPE system. All growths are carried out in a horizontal slide graphite boat with an ultrapure H<sub>2</sub> atmosphere. The desired amounts of Ge and In (used as solvent) are precisely massed and homogenized at ~1000 °C for 4h. Si substrates are cleaned in a 1:1::H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> (volume), self-heating, piranha solution for 15 min followed by 1:1:6::HCl:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O (volume) solution at 80 °C for 15 min. Before growth, Si substrates are dipped into 5% HF for 30 s to remove the native SiO<sub>2</sub> and then immediately loaded into the graphite boat with the homogenized GeIn alloy. The homogenized GeIn alloy is preheated at the saturation temperature,  $T_s = 950$  °C for 1 h. Then, a Si wafer (the saturation wafer) is introduced to the GeIn solution for 3 h to saturate the GeIn solution with Si. After that, the Si substrate (the growth substrate) is introduced to the SiGeIn solution and the temperature is reduced by 500 °C/h. When the temperature reaches the final temperature T<sub>f</sub>, the sample is removed from the solution and then cooled to room temperature. The final temperature is varied to 940 °C, 850 °C, 750 °C, 650 °C, 550 °C, or 450 °C while the solution composition is constant and at ~2%Ge for all the growths. The growth temperature range, the starting temperature to the final temperature, i.e. T<sub>s</sub> to T<sub>f</sub>, is called temperature interval. The surface morphology of each sample is characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Composition profiles and film thicknesses of each sample are measured with a line scan along the film cross section using energy-dispersive X-ray analysis (EDS) in an SEM. The composition and strain state are investigated by high-resolution triple-axis X-ray diffraction. The threading dislocation density of each sample is studied by plan-view TEM and preferential defect etching with a solution 2HF: 1(1M) CrO<sub>3</sub>:1.5H<sub>2</sub>O (weight ratio) followed by optical microscopy observations and use of the ImageJ software to calculated the etch pit density.

#### 6.2 Results and discussion

#### **6.2.1 Surface morphology**

Figures 6.1 shows the surface morphologies of samples 2SiGe<sup>950-940</sup>, 2SiGe<sup>950-850</sup>, 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup> (The sample notation indicates the liquid solution composition Ge%, here 2% for all the samples in this chapter, and the growth temperature interval, for example 950-940 °C). Samples 2SiGe<sup>950-940</sup> (figure 6.1a), 2SiGe<sup>950-850</sup> (figure 6.1b), and 2SiGe<sup>950-750</sup> (figure 6.1c) have the characteristic crosshatch morphology along the two orthogonal <110> directions due to the underlying  $60^{\circ}$  dislocations which partially relax the elastic strain by gliding along the <110>directions [107, 110]. When a SiGe film is grown on a Si (001) substrate, the film is elastically strained initially and then misfit dislocations glide and/or are nucleated at the film/substrate interface lying at the two orthogonal <110> directions when the film thickness exceeds the critical thickness. Growth in the vicinity of misfit dislocations is faster since these areas are more relaxed and result in ridges. Eventually, the film surface forms a set of ridges and troughs along the two orthogonal <110> directions, which displays the crosshatch morphology. For sample 2SiGe<sup>950-650</sup> that has a larger temperature interval, the crosshatch morphology is observed as well as the presence of circles indicated by arrow I in figure 6.1d. As the temperature interval is increased to 950-550 °C, sample 2SiGe<sup>950-550</sup> (figure 6.1e) still has the crosshatch morphology; however, a denser circular morphology arises,  $\sim 8.7 \times 10^4$  cm<sup>-2</sup> in the area shown in figure 6.1e, which is five times more dense than that of sample  $2\text{SiGe}^{950-650}$ ,  $\sim 1.6 \times 10^4$  cm<sup>-2</sup> of the area shown in figure 6.1d. Besides the circular morphology, there is also the presence of an X-shaped morphology as indicated by arrow II in figure 6.1e presents on sample 2SiGe<sup>950-550</sup>. The circular and X-shaped morphology will be discussed further when we present the surface morphology of sample 2SiGe<sup>950-</sup> 450



Figure 6.1 SEM images of samples 2SiGe<sup>950-940</sup> (a), 2SiGe<sup>950-850</sup> (b), 2SiGe<sup>950-750</sup> (c), 2SiGe<sup>950-650</sup> (d), and 2SiGe<sup>950-550</sup> (e).

Table 6.1:	Characterizations	of	crosshatch	morphology	of	samples	grown	with	different
temperatur	re intervals.								

Sample	2SiGe <sup>950-940</sup>	2SiGe <sup>950-850</sup>	2SiGe <sup>950-750</sup>	2SiGe <sup>950-650</sup>	2SiGe <sup>950-550</sup>
Thickness (µm)	1.1	6.7	9.4	11.4	14.0
Surface ridge width (µm)	5±1	15±3	22±5	20±4	20±4
Surface ridge height (nm)	13±5	41±18	69±31	143±76	259±124
Surface ridge density (cm <sup>-1</sup> )	747±60	615±42	511±29	513±36	512±48
RMS of surface roughness (nm)	5±1	25±8	35±7	71±7	110±14

Table 6.1 lists the height, width, and density of surface ridges as well as the root mean square (RMS) of surface roughness of samples 2SiGe<sup>950-940</sup>, 2SiGe<sup>950-850</sup>, 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup>. The surface ridge height, width and RMS of surface roughness of each sample is determined from the AFM scans and the ridge density of each sample is determined from the SEM images. Here, we take sample 2SiGe<sup>950-940</sup> as an example to illustrate the analysis process applied

to all samples. Figures 6.2a and b show an AFM image of sample 2SiGe<sup>950-940</sup> and a line profile corresponding to the black line in figure 6.2a from left to right. These narrow, bright stripes shown in figure 6.2a are the crosshatch ridges as they are higher compared to the field. The peak labeled "I" in figure 6.2b corresponds to the ridge labeled "I" in figure 6.2a. The ridge height, h<sub>r</sub>, is the distance between the ridge top and the ridge bottom while the ridge width, w<sub>r</sub>, is the bottom width of the ridge. The value of ridge height and ridge width of each sample listed in table 6.1 is the average value measured over several different areas in each sample. Each area is 90  $\mu$ m  $\times$  90  $\mu$ m and at least  $6.5 \times 10^4 \,\mu\text{m}^2$  were examined for each sample to determine these average values. The surface roughness RMS value of each sample listed in table 6.1 is also the average value measured over a 90  $\mu$ m  $\times$  90  $\mu$ m area. The surface ridge density is defined as the number of ridge intersections per unit length. For example, in sample 2SiGe<sup>950-940</sup>, the AFM scan shows that these crosshatch lines, such as those marked by arrows in figure 6.1a are elevated ridges as they are higher under AFM imaging (figure 6.2a). For each sample, the surface ridge density is taken at different areas in both orthogonal <110> directions and the value listed in table 6.1 is the average over many scans.



Figure 6.2 AFM image (a) and line profile (b) of sample 2SiGe<sup>950-940</sup>.

As shown in table 6.1, the surface ridge width of sample 2SiGe<sup>950-940</sup> is the smallest, 5 µm. As the temperature interval increases, that is, as the film thickness increases, the surface ridges becomes broader up to 22  $\mu$ m for sample 2SiGe<sup>950-750</sup>. The broadening of the surface ridges occurs because of the coalescence of smaller ridges. As the film thickness increases, the surface ridge width plateaus as we can see since samples 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup> are similar, ~20 um. While the width plateaus, however, the surface ridge height continues to increases, from 13 μm in sample 2SiGe<sup>950-940</sup> to 259 μm in sample 2SiGe<sup>950-550</sup>. The increasing height difference between the ridge crest and the trough  $(h_r)$  results from an increasing strain in the trough [155]. Once ridges and troughs are formed, the strain in the trough is high. This high strain field makes atoms prefer to diffuse towards the ridge crest; thus results in a high growth velocity at the ridge crest and low growth velocity in the trough. As the ridge becomes higher, the strain in trough becomes higher as well. Thus, the growth velocity at the ridge crest keeps accelerating while the growth velocity in the trough keeps decelerating and this results in an increasing ridge height. The surface ridge density generally has an inverse variation to the surface ridge width as the total area becomes covered with surface ridges, schematically samples 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup> and 2SiGe<sup>950-550</sup> in figure 6.3. As the film thickness increases, the surface ridge density decreases from 747 cm<sup>-1</sup> in sample 2SiGe<sup>950-940</sup> to 511 cm<sup>-1</sup> in sample 2SiGe<sup>950-750</sup> and is roughly constant for the larger growth intervals. The RMS film roughness increases from 5 nm in sample 2SiGe<sup>950-940</sup> to 110 nm in sample 2SiGe<sup>950-550</sup> displaying a similar trend as the surface ridge height. Figure 6.3 schematically shows the evolution process of the ridges during the growth process.



Figure 6.3 Schematic of evolution process of ridges during LPE growth process.

Sample 2SiGe<sup>950-450</sup>, which is grown with the largest temperature interval (950-450 °C) studied, has both a circular morphology and an X-shaped morphology distributed everywhere. Figure 6.4a shows an area with the X-shaped morphology. It is clear that each X-shaped is located inside a square/rectangle with edges oriented along <110>-type directions and all these X-squares are arranged along <110> directions. Figure 6.4b is a higher magnification image to show an individual X-shaped morphology, the one circled in figure 6.4a. Upon closer inspection, the Xshape has two frames: a large, outer frame marked by the dashed square "a" and a small, inside frame marked by the dashed square "b". The X is confined within the large, outer frame and surpasses the small, inside frame. A little square (labeled with "c") with edges oriented along the <110> directions is located at the center of the X-shape. In addition, the X has brighter SEM contrast than other areas inside its large, outer frame which suggests the X has a higher Ge content and this is proved by the EDS line scan (figure 6.4c). The EDS line scan follows the black-blueorange line in figure 6.4b starting from left to right. The orange lines represent scanning on the Xshape itself and the blue lines correspond to the scanning on the areas around the X-shape. The result of EDS line scan is shown in figure 6.4c plotted with Ge content as a function of scan distance. The data plotted in orange and blue correspond to the orange lines and blue lines in figure 6.4b, respectively. Apparently, the X-shape has about 6~7%Ge which is higher than other areas inside its large, outer frame, 5.5~6%Ge (We should note that since the EDS data samples a couple of microns, the actual Ge enhancement in the X-shape could be significantly higher). The AFM imaging of X-shaped morphology (figure 6.4d) shows it is actually a pyramid with base edges oriented along the <110> directions and with an X on top of the pyramid edges. The size of the pyramid is about 17 (± 2.3)  $\mu$ m × 17 (± 2.3)  $\mu$ m with a height ranging from 400 to 700 nm. While the X-shaped is located on top of a square pyramid, for example the one circled in 6.4d, if the pyramid such as the one marked by dashed rectangle in figure 6.4d. The formation of the X-shape or two V-shapes probably occurred because hi-Ge-content growth is energetically favorable to happen at the four edges of the pyramid island since there are more degrees of freedom for the lattice-mismatched material here. Either forming X-shape or two V-shapes appear to be related to the base is square or rectangular.



Figure 6.4 X morphology of sample 2SiGe<sup>950-450</sup>. SEM image (a), SEM image of an individual X-square (b), EDS line scan (c), and AFM image (d).

Figure 6.5 shows an AFM image of the circular morphology in samples 2SiGe<sup>950-650</sup> and 2SiGe<sup>950-</sup> <sup>450</sup> to illustrate the evolution process of the circular morphology during growth. The AFM image of the circular morphology in sample  $2SiGe^{950-650}$  (figure 6.5a) indicates that it is a truncated ridge. While some of the circular plateaus tend to be limited to the regions between crosshatch valleys such as the one labeled 1 in figure 6.5a, some extend over these valleys; for example, the circular plateau labeled 2 which crosses a valley between the two arrows and combines with the circular plateau labeled with 3. Unlike the circular morphology in sample 2SiGe950-650, the circular morphology in sample 2SiGe<sup>950-450</sup> (figure 6.5b) tends to have its own base with edges oriented along <110>-type directions. For example, circle 4 has a base aligned with the <110>-type directions and is separate from circle 5. The circular morphology in sample 2SiGe<sup>950-450</sup> often seems like a "volcano" since there is a higher rim which surrounds the inner circle. In addition, some of the circular "volcanos" are joined as shown in figure 6.5b where "volcanos" 4, 6 and 7 are joined together and we can see each of them has formed on a rectangular base. Note also that "volcano" 8 has a circle on top and what appears to be the X-like ridges extend from the circle ridge towards the corners of the underlying rectangle. This morphology may represent the transition from the circular "volcano" towards the X-shape. Similar morphological transformations from a spherical morphology (similar to the circular morphology seen here) to an eight-pointed star morphology (similar to the two dimensional the X-shape observed here) was reported in precipitates in a nickel-based single-crystal and the reason for this is probably due to the loss of coherency during the precipitation [156]. Presumably, the formation of three-dimensional growth, circular "volcano" or X shape is due to the low final growth temperature and helps to relieve some of the lattice mismatch strain which is not sufficiently relaxed from dislocation glide since the dislocation glide velocity is proportional to exp (-1/T) [29].





Figure 6.5 AFM images of the circular morphology. 3D image of sample 2SiGe<sup>950-650</sup> (a) and sample 2SiGe<sup>950-450</sup> (b).

#### 6.2.2 Cross-sectional Ge profile

EDS cross-sectional line scans were performed to investigate the composition profiles of samples 2SiGe<sup>950-940</sup>, 2SiGe<sup>950-850</sup>, 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-650</sup>. As an example of the analysis technique employed here, we take sample 2SiGe<sup>950-650</sup> as an example. Figure 6.6a is the cross-sectional SEM image of sample 2SiGe<sup>950-650</sup> where the SiGe film has a slightly brighter contrast than the underlying Si substrate. The EDS line scans for all samples started within the Si substrate and went through the film following the arrow as depicted in figure 6.6a. Figure 6.6b is the resulting Ge composition profile where the Ge content starts at 0%Ge on the left within the Si substrate. Then, the Ge content increases rapidly at point "a" indicating where electrons from the probe started interacting with the film. In the scan from the Si substrate through the film the substrate and film; hence, the beam sampled part of the substrate and part of the film. The transition from the beam fully sampling the substrate (solid circle in figure 6.6a) to fully sampling the film (circle with "x" in figure 6.6a)

occurred between arrows "a" and "b" shown in figure 6.6b. The film/substrate interface is halfway between positions indicated by arrows "a" and "b" in figure 6.6b. After the beam reached the film surface at the position indicated by arrow "c", the resulting scan is very noise. The data between arrows "b" and "c" are the data in which we are primarily interested. By designating the position of the substrate/film interface as "x=0", we get the Ge content as the function of the film thickness.



Figure 6.6 An example of EDS line scan. (a) SEM image and (b) original Ge profile.

Figure 6.7 shows the Ge content as the function of film thickness for samples 2SiGe<sup>950-940</sup>, 2SiGe<sup>950-850</sup>, 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup>. As the temperature interval increases, the Ge content of the film increases, which means that the LPE-deposited, SiGe film is a compositional graded buffer. The final growth temperatures and total film thicknesses are labeled in the figure 6.7 for different samples. It is clear that the Ge content increases only slightly for film whose

thicknesses are less than 6.7  $\mu$ m. As the film continues to grow, however, the composition vs. film thickness slope increases as well. In other words, the Ge composition gradient increases as the cooling interval increases which occurs because the solution becomes Ge-rich during the cooling process. Knowing that EDS compositional values are not very accurate without careful calibration, we only discuss the general compositional trends. We later discuss the actual compositional values when we discuss the XRD results (section 6.2.3) since XRD results are more accurate.



Figure 6.7 EDS cross-sectional composition profiles of samples 2SiGe<sup>950-940</sup>, 2SiGe<sup>950-850</sup>, 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup>.

Sample 2SiGe<sup>950-450</sup> is not included here because it was grown using a different graphite boat which affected its overall thickness, 10.8  $\mu$ m, and therefore did not follow the thickness trend as the other samples. The well of the graphite boat used for sample 2SiGe<sup>950-450</sup> is 1.74 cm × 0.87 cm, which is 0.23 cm<sup>2</sup> larger than that used for the other samples, 1.28 cm × 1 cm. Therefore, using the same amount of In solvent resulted in a shorter liquid height and Moon [157] and Konuma [158] reported

that the growth solution height affects the LPE layer thickness. Konuma found that the LPE layer thickness increases linearly upon increasing the solution height and will plateau when the diffusion length of solute atoms reaches the solution height [158]. Consequently, we only discuss the surface morphology evolution of sample 2SiGe<sup>950-450</sup> and not its composition profile, strain state, and threading dislocation density since all of these characterization results will be displayed as the function of film thickness.

#### 6.2.3 Composition and strain states

Figure 6.8 shows side-by-side the ( $\overline{224}$ ) and (004) RSMs of samples 2SiGe<sup>950-940</sup>, 2SiGe<sup>950-850</sup>, 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup>. The top peak in each sub figure represents the Si substrate while the bottom peak(s) corresponds to the SiGe film which has a larger lattice constant; therefore, its RLP appears below that of the Si substrate. In each ( $\overline{224}$ ) RSM, the vertical and inclined dashed lines show the RLP peak locations of pseudomorphic and fully relaxed films, respectively [144]. If the  $(\overline{2}\overline{2}4)$  film peak lies on the vertical dashed line, the film is fully strained; if the  $(\overline{2}\overline{2}4)$  film peak lies on the inclined dashed line, the film is fully relaxed; if the  $(\overline{2}\overline{2}4)$  film peak lies between the two dashed lines, the film is partially relaxed as long as there is no epilayer lattice tilt with respect to the substrate; otherwise, the effect of lattice tilt has to be corrected in order to measure the strain state of the film. The lattice tilt is observable in the (004) RSM; if lattice tilt between the film and the substrate is present, the (004) film peak will not lie directly below the substrate peak. The cause of lattice tilt has not been examined here but is probably due to the small miscut of the substrate,  $\pm 0.3^{\circ}$ . France [149] found that a miscut of 2° away from the (001) substrate towards the  $(\overline{1}11)$  plane creates an asymmetry in the resolved mismatch stress on the  $(\overline{1}11)$  and  $(1\overline{1}1)$  glide planes and this asymmetry causes a preference for dislocations glide on the  $(\overline{1}11)$  plane which results in a systematic tilt of the epilayer relative to the substrate.



Figure 6.8 (224) and (004) reciprocal space maps of samples 2SiGe<sup>950-940</sup> (a), 2SiGe<sup>950-650</sup> (b), 2SiGe<sup>950-850</sup> (c), 2SiGe<sup>950-750</sup> (d), and 2SiGe<sup>950-550</sup> (e).

The RSMs of samples  $2\text{SiGe}^{950.940}$  (figure 6.8a) and  $2\text{SiGe}^{950.850}$  (figure 6.8b) have one relatively symmetric film peak suggesting that both samples have rather uniform composition corroborated to the EDS line scans in which the Ge content only marginally increases in the first ~6.7 µm (figure 6.7). The strain relaxation of these two samples is determined at the film peak. Since the (004) film peak of samples  $2\text{SiGe}^{950.940}$  (figure 6.8a) and  $2\text{SiGe}^{950.850}$  (figure 6.8b) lie directly below the substrate peak, no significant film tilt occurred for both samples; thus, their ( $\overline{22}4$ ) RSM shown in figure 6.8a and figure 6.8b are sufficient to use to measure the strain states of the films. In figure 6.8a, sample  $2\text{SiGe}^{950.940}$ , the ( $\overline{22}4$ ) film peak is located directly below the substrate peak, indicating the film is fully strained. In figure 6.8b, sample  $2\text{SiGe}^{950.850}$ , the ( $\overline{22}4$ ) film peak is located between the two dashed lines, which suggests the film is partially relaxed, ~41%.

Instead of having one film peak like samples  $2SiGe^{950-940}$  and  $2SiGe^{950-850}$  (figures 6.8a, b), the RSMs of samples  $2SiGe^{950-750}$  (figure 6.8c),  $2SiGe^{950-650}$  (figure 6.8d), and  $2SiGe^{950-550}$  (figure 6.8e) show a continuous intensity distribution in the film because the film has a graded composition suggested by EDS line scans (figure 6.7) that the Ge content of these three samples increases obviously and thus a varying lattice constant. No significant lattice tilt observed of these three graded buffers since the ( $q_x$ ,  $q_z$ ) values extracted from the (004) RSM of each graded buffer oscillates only slightly along the vertical [001] dashed line as an example shown in figure 5.11a in chapter 5, likely due to noise; therefore the ( $\overline{22}4$ ) RSMs shown in figure 6.8c, figure 6.8d, and figure 6.8e are sufficient to measure the composition and strain states of the graded buffers. For each graded buffer, the ( $\overline{22}4$ ) peak closest to the substrate lies around the inclined dashed line which indicates the initial film is nearly fully relaxed. This occurs because there is enough time at high temperature for sufficient misfit dislocation glide to relax the film. Also, the film becomes thicker as the temperature interval increases which provides a larger driving force for dislocation

glide to relax the initial film. However, the films making up the graded buffer further from the substrate are only partially relaxed since their  $(\overline{2}\overline{2}4)$  peaks are located between the two dashed lines. This probably occurs because (1) the temperature is low when these layers are grown which slows misfit dislocation glide velocity and (2) dislocation nucleation is difficult at low temperatures. Figure 6.9 shows the profile of the in-plane strain (figure 6.9a) and strain relaxation (figure 6.9b) as a function of Ge content for the graded buffers 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup> (the analysis process was described in section 5.5.4 of chapter 5). For graded buffers 2SiGe<sup>950-750</sup> and 2SiGe<sup>950-550</sup>, the in-plane strain of the whole buffer is less than or equal to zero indicating both experience compressive strain. The strain relaxation of graded buffer 2SiGe950-750 decreases from the 100% to 56% as the Ge content increases from 0.73% to 2.8% and the strain relaxation of graded buffer 2SiGe<sup>950-550</sup> varies from 100% to 21% as the Ge content increases from 0.62% to 6.4%. For graded buffer 2SiGe950-650, the layers close to the substrate have a positive inplane strain (the part plotted in purple in figure 6.9a), which indicates the initial layers are under tension. This probably occurred because the layers were fully relaxed at high temperature but as the temperature cooled to room temperature the lattice constants of the layers reduced faster than the Si substrate due to the higher SiGe coefficient of thermal expansion [159, 160]. The upper layers of the sample 2SiGe<sup>950-650</sup> experience compressive strain as the in-plane strain is negative (the part plotted in orange in figure 6.9a). Strain relaxation of the graded buffer 2SiGe<sup>950-650</sup> increases from 64% to fully relaxed and then decreases to 52% as the Ge content varies from 0.94% to 4.3%. The value of the strain relaxation is determined by the absolute values of in-plane strain and misfit, so the value of strain relaxation is always less than 100% regardless if the strain is tensile or compressive.





Figure 6.9 In-plane strain (a) and strain relaxation (b) as a function of Ge content of samples 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup>.

Subsequently, the Ge content as a function of film thickness is determined based on the RSM results and the end thickness of each sample labeled in figure 6.7. While the thickness came from figure 6.7, the composition was determined using the black dot in each of the ( $\overline{22}4$ ) RSM for each sample in figure 6.8. For example, the composition determined at the end of the RSM of sample 2SiGe<sup>950-850</sup> (marked by the black dot in figure 6.8b) is 1.8%Ge. The corresponding position of this composition is the total film thickness of sample 2SiGe<sup>950-850</sup>, 6.7 µm (the orange curve in figure 6.7). This was how we determined the points shown in figure 6.10 except the first point. The composition at the first point is the average composition determined at the beginning of the RSMs of all samples (marked by the circle of each ( $\overline{22}4$ ) RSM in figure 6.8) and the error bar in figure 6.10 represents the standard deviation. As shown in figure 6.10, the Ge content increases with increasing thickness and the composition vs. thickness slope increases as well from thickness 1.1 µm (the second point) to 14 µm (the last point), and has a similar trend as the EDS cross-section

line scan (figure 6.7). The more accurate XRD results are systematically higher than the compositions determined by EDS.



Figure 6.10 Ge content as a function of film thickness determined from the RSMs.

Based on the in-plane strain/strain relaxation as the function of Ge content (figure 6.9) and using the Ge content as the function of film thickness (figure 6.10), we determined the in-plane strain/relaxation as the function of film thickness for samples 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup>, shown in figure 6.11, in order to study the evolution of the strain state during the growth. Both the in-plane strain and strain relaxation curves as a function of thickness for samples 2SiGe<sup>950-940</sup> and 2SiGe<sup>950-850</sup> are included in figures 6.11a and 6.11b, respectively. Since the RSMs of both samples 2SiGe<sup>950-940</sup> and 2SiGe<sup>950-850</sup> have one film peak, it is not accurate to use the graded buffer RSM analysis method, cutting the film RSM into n thin, equal slices, for these two samples. Therefore, we assumed that the strain was constant for the whole thickness of the sample and represented these two samples with a black and red horizontal line, respectively. As shown in

figure 6.11, when the temperature interval is 950-940 °C, the film 2SiGe<sup>950-940</sup> is about 1.1 µm thick and fully strained. As noted earlier some misfit dislocations were present in sample 2SiGe<sup>950-</sup> <sup>940</sup> since ridges were observed on the surface (figure 6.1a), which suggests the film should be more relaxed but the XRD data suggest the film is fully strained (figure 6.8a). As shown in figure 6.8a, there is a small tail towards to the inclined dashed line suggesting a variation of strain relaxation across the film and the greatest relaxation at the end of the tail (the arrow end) is 67%. Strain relaxation is localized (~micrometers) to the vicinity of misfit dislocations [161]; however, the average separation between misfit dislocations of sample  $2SiGe^{950-940}$  is  $13.3 \pm 5.6 \ \mu m$ , which is too large to relieve significant strain for most of the film while the film around the misfit dislocations is partially relaxed. As the temperature interval increases to 950-850 °C, sample  $2SiGe^{950-850}$  is 6.7 µm thick and ~41% partially relaxed due to more misfit dislocations nucleated and gliding longer distances. As the temperature gets larger to 950-750 °C, sample 2SiGe<sup>950-750</sup> is 9.4 thick. The initial film on this sample at the film/substrate interface is fully relaxed since larger amounts of high-temperature exposure as well as thicker film drive misfit dislocation glide; however, the film becomes less relaxed from this initial film and the strain relaxation decreases to 56%. The decreasing strain relaxation with increasing thickness is probably because the glide velocity of misfit dislocation becomes slower as the growth temperature decreases. As the temperature interval increases to 950-650 °C, sample 2SiGe<sup>950-650</sup> becomes 11.4 µm thick and the part of the film thinner than 7.3 µm are fully relaxed at high temperature and will experience tensile strain as the sample is cooled to room temperature (the part plotted in purple in figure 6.11a). The strain relaxation of this sample varies from 69.4% at the interface to 100% at 7.3 µm thick (the part plotted in purple in figure 6.11b). The upper layers with thickness at the range of 7.3~11.4 µm experience compressive strain and the strain relaxation changes from 100% at 7.3 µm to 52% at the surface. Finally, for a temperature interval 950-550 °C, the thickness of sample  $2\text{SiGe}^{950-550}$  is 14.0 µm. The initial layer at the interface is fully relaxed and the strain relaxation of the film changes from 100% to 20%. We are not clear why the strain changed back to compressive from tensile as the temperature interval increases from 950-650 °C to 950-550 °C but might be the compressive film on top puts some compression on the underlying films since the top is so compressive and it is thick.



Figure 6.11 In-plane strain (a) and strain relaxation (b) as a function of film thickness. The points at each figure are some of representative points we picked up from figure 6.9.

#### 6.2.4 Dislocation density

#### 6.2.4.1 Plan-view TEM

Plan-view TEM was employed to study the threading dislocation density of samples  $2SiGe^{950-940}$ ,  $2SiGe^{950-850}$ ,  $2SiGe^{950-750}$ ,  $2SiGe^{950-650}$ , and  $2SiGe^{950-550}$ . For each sample we observed at least 4100  $\mu m^2$  area and only one threading dislocation was found for sample  $2SiGe^{950-850}$  and two for sample  $2SiGe^{950-750}$ . For the other samples, we did not find any threading dislocations. This implies the

threading dislocation density of all these five samples is less than  $10^7 \text{ cm}^{-2}$  [63]. Figure 6.12 shows a plan-view TEM of sample  $2\text{SiGe}^{950-750}$  to illustrate the very low threading dislocation density of our samples. The area shown in figure 6.12 of sample  $2\text{SiGe}^{950-750}$  is  $353 \,\mu\text{m}^2$  and there is only one threading dislocation (TD).



Figure 6.12 Plan-view TEM image of sample 2SiGe<sup>950-750</sup>.

#### 6.2.4.2 Etch pit density

Since very few threading dislocations were found by plan-view TEM, this suggests a low threading dislocation density for all samples; therefore, preferential etching of defect was employed to study the threading dislocation density. Figure 6.13 plots the EPDs of samples 2SiGe<sup>950-940</sup>, 2SiGe<sup>950-850</sup>, 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup> as a function of film thickness. A result observed from

figure 6.13 is that the average EPD of the samples grown at different temperature interval is around  $10^6 \text{ cm}^{-2}$  and is somewhat constant or has a modest decreasing slope with increasing thickness. In other studies, threading dislocation density decreases as film thickness increases because the dislocations interact and can annihilate [162, 163]. As the dislocation density decreases, the likelihood of the dislocations interacting decreases as well and the dislocation density vs. thickness levels off [162, 163]. For samples 2SiGe<sup>950-940</sup>, 2SiGe<sup>950-850</sup>, 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup>, the dislocation density starts low ~10<sup>6</sup> cm<sup>-2</sup> making coalescence of threading dislocations difficult. This is why the EPD remains roughly constant or only slightly decreases as film thickness increases. The error bars in figure 6.13 represent the standard deviation of the measurements taken which are large because the distribution of threading dislocation is non uniform. Also, for each sample at least 0.2 mm<sup>2</sup> were examined to create figure 6.13.



Figure 6.13 Etch pit density of samples 2SiGe<sup>950-940</sup>, 2SiGe<sup>950-850</sup>, 2SiGe<sup>950-750</sup>, 2SiGe<sup>950-650</sup>, and 2SiGe<sup>950-550</sup>.

For some CVD- or MBE-grown SiGe graded buffers, the threading dislocation density is ~10<sup>6</sup> cm<sup>-</sup> <sup>2</sup> as our LPE-grown SiGe graded buffers and this density of dislocation is sufficient to relax the whole buffer [17, 65]; however, for our LPE-grown SiGe graded buffer, this density of dislocation could only relax the initial film as the growth time is long enough but not the upper layers of the buffer (figure 6.11). This happens because the growth temperature of the CVD- or MBE-grown SiGe graded buffers is normally  $\geq$  800 °C and at this high growth temperature the glide velocity of dislocation is fast which could result in sufficiently long misfit dislocation to relax the whole buffer but for our LPE-grown SiGe graded buffers the growth temperature of the upper layers is low which means the glide velocity of the dislocation is slow and this result in short misfit dislocations that could not relax the upper layers of the graded buffer.

#### 6.3 Conclusion

SiGe graded buffers were grown on Si (001) substrates from a relatively low-Ge-content solution,  $\sim 2\%$ Ge. All growth started from 950 °C but ended at different final temperatures 940 °C, 850 °C, 750 °C, 650 °C, 550 °C, and 450 °C in order to study the evolution of surface morphology, composition profile, strain states, and threading dislocation density. Results show that the growth initiates with a characteristic crosshatch morphology and transfers into more three-dimensional growth. During the cooling process, the surface morphology becomes broader and higher; however; when the temperature is lower than 750 °C, the surface ridge only increases vertically with constant width. Meanwhile, circle plateaus appear lying along the surface ridges. As the temperature further decreases, the circle plateau will have its own base with edges oriented along <110> directions and will split with its adjacent surface ridges, which looks a "volcano". As the film thickens, the circle size decreases leaving a high-Ge-content X-shape or two V-shapes on the surface depending on if the base is square or rectangle. The formation of three-dimensional circular "volcano" and X

pyramid is due to the low growth temperature, which makes dislocation glide prohibitively slow such that the film cannot relieve enough strain; therefore, the growth turns to three-dimensional growth to enable some relaxation.

The Ge content of the film continues to increase with increasing thickness and the grading rate becomes faster. The composition of the initial film deposited at the substrate is 0.81%Ge. As the temperature decreases to 940 °C, the film is about 1.1 µm thick and fully strained with Ge content increased to 1.6%. When the temperature decreases to 850 °C, the film becomes 6.7 µm thick and ~41% partially relaxed with a Ge content of 1.8%. As the temperature decreases to 750 °C, the thickness of the film is about 9.4 µm and the final Ge content is 2.8%. The film at the interface is fully relaxed and the film becomes more strained from the interface to the top. As the temperature decreases to 650 °C, the film is about 11.4 µm thick and the final Ge composition increases to 4.3%. The film with thickness less than 7.3 µm is fully relaxed at the high temperature and will experiences tensile strain as it is cooled to room temperature due to the higher thermal expansion coefficient of SiGe than Si. The upper layers of the film with thickness ranging from 7.3~11.4 µm experience compressive strain and the strain relaxation changes from 100% to 52%. When the temperature drops to 550 °C, the film becomes 14.0 µm thick with a final Ge content of 6.4%. The film at the film/substrate interface is fully relaxed however the film becomes more strained further from the interface. The long growth temperature interval helps to relax the initial film close to the film/substrate interface; however, the top part of the film is partially strained and becomes more strained as it becomes thicker and more Ge-rich.

In addition to the strain and surface morphologies, the dislocations of the sample were studied and the etch pit density of all the films is around  $10^{-6}$  cm<sup>-2</sup> and barely changes with increasing thickness. This is somewhat surprising given the larger surface morphology changes observed. Moreover,

the Ge content of the film does increase with increasing thickness as we increase the temperature interval but the final Ge content is only 6.4% which is grown from a relatively large temperature interval 950-550 °C. This is because the growth solution has relative low-Ge-content, 2%Ge. It is necessary to increase the Ge content of the growth solution in order to enhance the final Ge content.

# Chapter 7 SiGe Films Grown from Different Composition Solution

During the LPE growth process, SiGe deposited from the liquid solution becomes Ge-rich by cooling the solution from high temperature to low temperature. In the previous chapter, we grew SiGe starting at temperatures as high as 950 °C from a relatively low-Ge-content solution, ~2%Ge, and deposits while cooling. The growth is initially a two-dimensional film and transforms into a more three-dimensional film with increasing thickness and Ge content when the final cooling temperature goes lower than 650 °C. Similar change from two-dimensional to more three-dimensional films occur if we increase the Ge content in the solution which increases the Ge content of the initial film. Since low-Ge-content SiGe directly grown on Si (001) favors two-dimensional growth while high-Ge-content SiGe directly grown on Si (001) favors three-dimensional growth. In this chapter, we vary the solution composition from low-Ge-content to high-Ge-content and grow SiGe at a very short temperature interval (950-940 °C) in order to determine the highest Ge content of the initial deposition which maintains two-dimensional growth and three initial deposition which maintains two-dimensional growth and its corresponding liquid composition. Properties of these initial deposition such as surface

morphology, composition, strain state and threading dislocation density are characterized. In addition, SiGe graded buffers are grown at a comparatively large temperature interval (950-750 °C) to compare their properties with their own initial film. Surface morphology, composition, strain state and threading dislocation density of these graded buffers are characterized as well.

#### 7.1 Experimental

SiGe layers are grown on Si (001) substrates using a custom-designed LPE system. All growths are carried out in a horizontal slide graphite boat with an ultrapure  $H_2$  atmosphere. The desired amounts of Ge and In (used as solvent) are precisely massed and homogenized at ~1000 °C for 4 h. Si substrates are cleaned in a 1:1::H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> (volume) followed by 1:1:6::HCl:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O (volume) at 80 °C. Before growth, Si substrates are dipped into 5% HF for 30 s to remove the native SiO<sub>2</sub> and then loaded into the graphite boat with the homogenized GeIn alloy immediately. The homogenized GeIn alloy is preheated at the saturation temperature,  $T_s = 950$  °C for 1 h. Then, a Si wafer (the saturation wafer) is introduced to the GeIn solution for 3 h to saturate the GeIn solution with Si. After that, the Si substrate (the growth substrate) is introduced to the SiGeIn solution and the temperature is reduced by 500 °C/h. When the temperature reaches the final temperature T<sub>f</sub>, the sample is removed from the solution and then cooled to room temperature. Either the solution composition ( $\sim 2\%$ Ge,  $\sim 4\%$ Ge,  $\sim 5\%$ Ge, and  $\sim 6\%$ Ge) or the growth temperature range, T<sub>s</sub>-T<sub>f</sub> (950-940 °C and 950-750 °C) is varied. The surface morphology of each sample is characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Composition and strain states are studied by high-resolution triple-axis X-ray diffraction. The threading dislocation density of each sample is studied by preferential etching with a solution 2HF:

1(1M) CrO<sub>3</sub>:1.5H<sub>2</sub>O (weight ratio) followed by optical microscopy observation and use of the ImageJ software to calculate the etch pit density.

#### 7.2 Results and discussion

#### 7.2.1 Initial growth

#### 7.2.1.1 Growth appearance

Based on our LPE growth experiments, if the grown film is too rough or has three-dimensional islands, the sample will remain partially or all covered with residual (entrained) SiGeIn solution when it is removed from the growth solution. When this occurs, as the entrained solution on the sample cools, because of continued etching and growth (typically Ge-rich, micron-sized islands are the last material deposited), it is hard to determine the results of the desired experiment and results in a sample with significant roughness and uncontrolled Ge content and thickness. Consequently, one standard here is to grow a non-entrained SiGe and then to do the characterization.

Table 7.1: Growth appearance of samples grown with different composition solution from temperature interval 950-940 °C.

Solution composition (Ge%)	~2%	~4%	~5%	~6%
Sample	2SiGe <sup>950-940</sup>	4SiGe <sup>950-940</sup>	5SiGe <sup>950-940</sup>	6SiGe <sup>950-940</sup>
Growth appearance	non-entrained	non-entrained	non-entrained	entrained

Note: The sample name notation indicates the initial Ge content (Ge%) in the solution and the growth temperature interval. For example, sample 2SiGe<sup>950-940</sup> means the initial Ge% is 2% and the growth temperature interval is 950-940 °C.

Table 7.1 shows the appearance (entrained or non-entrained) of samples grown with different initial Ge content solutions for a temperature interval of 950-940 °C (The temperature interval notes the initial temperature, in this case 950 °C, followed by the final temperature, here 940 °C). As table 7.1 shown, non-entrained SiGe are obtained when the solution composition is ~5%Ge or

lower. When the solution composition is increased to ~6%Ge, the sample is completely entrained with InGeSi uncovering a surface with high-Ge-content (~70%Ge by EDS) SiGe islands after it is etched with HCl at 80 °C to selectively remove the In.

#### 7.2.1.2 Surface morphology

Figure 7.1 shows the surface morphology of sample 2SiGe<sup>950-940</sup>. This sample has the characteristic crosshatch pattern along the two <110> directions and partial crosshatch lines are marked with black lines in figure 7.1a. The crosshatching is formed due to the underlying misfit dislocations along the two orthogonal <110> directions. When the SiGe film is grown on a Si (001) substrate, the film is elastically strained first. As the film thickness exceeds the critical thickness, misfit dislocations are nucleated at the film/substrate interface lying at the two orthogonal <110> directions. Growth in the vicinity of misfit dislocations is faster since these areas are more relaxed and result in ridges. The AFM scan proves these so-called crosshatch lines as marked in figure 7.1a are the ridges. As it is shown in figure 7.1b, crosshatch lines have brighter contrast than other areas proving these crosshatch lines are higher. The RMS Surface roughness determined from sampling an area of 90  $\mu$ m × 90  $\mu$ m shown in figure 7.1b is 3.8 nm. Also, the crosshatch lines of sample 2SiGe<sup>950-940</sup> are straight and long, which suggests long misfit dislocations [57].



Figure 7.1 Surface morphology of sample 2SiGe<sup>950-940</sup>. SEM image (a) and AFM image (b).

Figure 7.2a is an AFM image of sample  $4\text{SiGe}^{950-940}$  and this sample has a crosshatch pattern as well. Comparing figure 7.2a to figure 7.1b, it is clear that sample  $4\text{SiGe}^{950-940}$  has higher ridge density,  $\sim 1.8 \times 10^3$  cm<sup>-1</sup>, than sample  $2\text{SiGe}^{950-940}$ ,  $\sim 7.5 \times 10^2$  cm<sup>-1</sup>, which suggests the higher misfit dislocation density of sample  $4\text{SiGe}^{950-940}$ . The RMS surface roughness measured over the 90 µm × 90 µm area shown in figure 7.2a is 64.1 nm which is 17 times rougher than the sample  $2\text{SiGe}^{950-940}$  about 3.8 nm. In addition to the crosshatch pattern, circular hillocks are observed on sample  $4\text{SiGe}^{950-940}$  as indicated with the arrow labeled "a" in figure 7.2b and the density of these circular hillocks is  $\sim 1 \times 10^4$  cm<sup>-2</sup>. The circular hillock labeled "b" in figure 7.2c, a three-dimensional AFM image, shows that this hillock lies along a cross hatch ridge but is even higher than the ridge which is higher than the surrounding field.



Figure 7.2 Surface morphology of sample 4SiGe950-940. AFM image (a), SEM image (b), and three-dimensional AFM image (c).

For sample 5SiGe<sup>950-940</sup>, its surface has a crosshatch pattern as well as shown in figures 7.3a and 7.3b. Besides the crosshatch pattern, the sample surface has several different types of square morphologies which takes one of four different morphologies: Morphology (1) shows a square whose contrast at the center is darker (in SEM) than that of its edges as indicated by arrow I in figure 7.3a. AFM imaging of square morphology (1) (figure 7.3c) shows circular pit with square walls oriented along <100> directions. The square walls refer to the part between the dashed circle and the dashed square as shown in figure 7.3c and we call them walls because they are higher than the bulk film (we use the wall terminology to describe the next three morphologies as well). The depth of the circular pit (the distance between the pit bottom and the film surface) shown in figure 7.3c is  $\sim 100$  nm and the bulk film thickness is about 1  $\mu$ m suggesting the circular pit is very shallow and does not reach the substrate surface. Schematics for the top and the cross-sectional views of square morphology (1) is shown in figure 7.3d. Square morphology (2) is highlighted by arrow II in figure 7.3b which has darker contrast at the center compared to the circular pit in square morphology (1). AFM imaging (figure 7.3e) of the second square morphology shows a pit with a bottom base (marked with the dashed square 1 in figure 7.3e) and top base (marked with the dashed square 2) are both orientated along <110> directions and this square pit has a square wall (the part between the dashed square 2 and the dashed square 3) oriented along <100> directions. The depth of the square pit shown in figure 7.3e is  $\sim 0.85 \,\mu m$  which is much deeper compared to the circular pits (~0.1 µm) but does not reach the substrate surface, either. The top view and the cross-sectional view of the square pits are schematically presented in figure 7.3f. Square morphology (3) is shown by arrow III in figure 7.3a and shows a square with four <100> directional edges and a hillock locating at the center. AFM result (figure 7.3g) show the hillock is surrounded with a square wall (the part between dashed square 4 and dashed square 5) orientated along <100> directions.

Grooves exist evidently between the square wall the hillock and the groove depth (the distance between the groove bottom and the film surface) shown in figure 7.3g is  $\sim 0.5 \mu m$  which suggests the groove does not reach the substrate surface. The top view and the cross-sectional view of the hillocks are schematically presented in figure 7.3h. Finally, square morphology (4) is shown with arrow IV in figure 7.3b and highlights a square with four <100> directional sides enclosing a square with edges oriented along <110> direction and dark contrast at the center. AFM imaging on morphology square with this morphology (figure 7.3i) illustrates that the square located at the center seems to be a "volcano" with a square base oriented along <110> directions and the square "volcano" is surrounded by a wall (the part between the dashed square and the dashed circle in figure 7.3i) with a circular inner rim and square outer rim (marked with the dashed square) oriented along <100> directions. Strong grooves exist between the square "volcano" and its surrounded wall and the groove depth is  $\sim 1.0$  µm, the same as the bulk film thickness. This suggests the groove reached the original substrate surface; in other words, the square "volcano" splits completely with the bulk film resulting in uncovered Si substrate. The top view and the cross-sectional view of the square "volcano" are schematically shown in figure 7.3j.



Figure 7.3 Surface morphology of sample 5SiGe<sup>950-940</sup>. SEM images (a)(b)





Figure 7.4 Surface morphology of sample 5SiGe<sup>950-940</sup>. Circular pit (c)(d), square pit (e)(f), hillock (g)(h), and square "volcano" (i)(j). "d" is the pit depth in figure 7.3d and 7.3f or the groove depth in 7.3h and 7.3j.

Different shapes of pits in SiGe film/Si (001) have been reported including circular and square pits with edges oriented along <110> directions due to induced strain or impurities and defects at the substrate surface [164, 165]. We think the pits as well as the hillocks and square "volcano" on sample 5SiGe<sup>950-940</sup> are strain induced as misfit dislocations are hard to nucleate in LPE growth and cannot relieve the elastic strain sufficiently. However, we have not found any reference reports that the film around the pit is higher than the bulk film and oriented along <100> directions. On the other hand, Hanke [166] reported that they observed square islands surrounded by circle walls as shown in figures 7.4a and 7.4b but the square island is a truncated pyramid with four {111} side facets and an (001) top facet which is different with our square "volcano". A similarity between their morphology and our morphology is the presence of a grove that reaches the original Si surface. Hanke SiGe film growth started from a similar same temperature 930 °C but ended at different temperature to study the growth process. All growth was carried out in a LPE slide boat using In as a solvent at a cooling rate of 0.16 °C/min and the overall growth temperature interval is 930-920 °C. Hanke found that the growth initiates tiny surface undulations which are formed by discrete vertical steps as the circles shown in figure 7.4c. Then, the film shrinks to form circular dots (figure 7.4d). Eventually, the circular dots split into a central truncated pyramid ("d1" in figures 7.4a and 7.4e) with four {111} side facets and circularly shaped rim ("w" in figure 7.4e) exposing the bare silicon substrate (figure 7.4e). Hanke thought that the liquid solution becomes undersaturated in the course of dot nucleation. Material transports from the dots as well as the film back into the liquid solution subsequently resulting in central truncated pyramids and circular walls enclosing uncovered silicon substrate. Figure 7.4f illustrates the process from circular surface (figure 7.4c) into truncated pyramids surrounded by circular walls (figure 7.4e). Even though the square islands from Hanke's and ours (figure 7.3i) are different in shapes, we speculate the

uncovered Si substrate between the square islands and the circular or octagonal rims we observed is formed probably due to the material transformation back into the liquid solution as well. The grooves surrounding the hillock are also caused by materials redissolving into the liquid solution and will reach the substrate surface to form square islands with base sides oriented along <110> directions and circular inner rims. Similarly, the cavity of the square "volcano" might be a result of material redisolving into the liquid.



Figure 7.5 Surface morphology showing growth process of SiGe on Si (001) from Hanke [166]. Truncated pyramid surrounded by circular walls grown from 930-920 °C (a)(b), surface undulation from 930-929 °C (Ge content in the film is 10%) (c), circular dots from 930-928.5 °C (d), central truncated pyramid and circular walls enclosing uncovered silicon substrate formed from 930-925 °C (e), and schematics depicts the process from circular dots to pyramid islands in side and top view (f). The insets in figure 7.4d and figure 7.4e display dots assembled with preferential <100> directions transfer into pyramid ensembles surrounded by circular walls.

Crosshatch lines on samples 2SiGe<sup>950-940</sup> and 4SiGe<sup>950-940</sup> are very long; however, some of the crosshatch lines on sample 5SiGe<sup>950-940</sup> are short and seem to end/start close to a pit, hillock, or square "volcano". In figure 7.5a, arrow I highlights a ridge with a hillock at one end; arrow II

highlights a ridge that has a pit and a square "volcano" at either end; and arrow III indicates a category of ridges with a square "volcano" lying at one end. The ridge indicated with arrow III is broader than the other two. This ridge seems to end at a square "volcano" with a perpendicular groove which separates the ridge from the "volcano"; the other end of the ridge is rounded. This ridge, one of many sheathed ridges, has a surrounding wall which joins the wall around the square "volcano" and is schematically depicted in figure 7.5b. The width (w) of the sheathed ridges in figure 7.5a is 7.3  $\pm$  1.1 µm. Figure 7.5c is the AFM image of a sheathed ridge containing two overlapped images. Ridge A marked with an orange line is a segment of a ridge with brighter SEM contrast such as the one marked with the same color in figure 7.5a and ridge B is a segment of a sheathed ridge with darker SEM contrast such as the one marked with blue in figure 7.5a. The average height of ridge A is  $0.54 \pm 0.23$  µm, which is twice as high as ridge B,  $0.27 \pm 0.05$  µm. The average wall height of ridge A is  $0.11\pm0.02$  µm twice as high as that of ridge B,  $0.06\pm0.01$ µm. The bottom right schematic in figure 7.5c shows the cross-sectional view of sheathed ridges and labels the ridge height (h<sub>r</sub>) and wall height (h<sub>w</sub>). A trench lies between the ridge and the wall. Figure 7.5d plots the trench depth ( $d_r$  as labeled in the schematic of figure 7.5c) from point a to point b as indicated in figure 7.5c extracted from AFM line profiles. The positions of trench were determined by designating the position of point a as "0". The trench depth of the sheathed ridge segment B is uniform and about 0.15 µm (from point b to point c) while the trench depth of the sheathed ridge segment A (from point a to point c) is deeper than that of the sheathed ridge B. The trench depth for the first 15 µm along the path from point a to c is approximately 1.0 µm suggesting the trench is very close to or has already reached the original substrate surface. The trench depth of the sheathed ridge A becomes shallow as it is away from the square "volcano" (from point a to point c).


Figure 7.6 Surface morphlogy of sample 5SiGe<sup>950-940</sup>. SEM image (a), schematic diagram of sheathed ridge (b), AFM image of sheathed ridge (c), and trench depth profile (d).

# 7.2.1.3 Composition and strain states

Figure 7.6 shows the (004) and  $(\overline{22}4)$  RSMs of samples 2SiGe<sup>950-940</sup>, 4SiGe<sup>950-940</sup>, and 5SiGe<sup>950-</sup> <sup>940</sup>. Each sub figure has two peaks: the top peak represents the Si substrate while the lower one corresponds to the SiGe film due to its larger lattice constant. The vertical and inclined dashed lines in the  $(\overline{2}\overline{2}4)$  RSM show the RLP peak locations of pseudomorphic and fully relaxed films, respectively [144]. Since the (004) peak of each sample lies directly below the substrate peak, no significant film tilt occurred [148] for any of the samples; thus, the  $(\overline{2}\overline{2}4)$  RSM shown in figure 7.6 are sufficient to use to measure the strain states of the films. If the  $(\overline{2}\overline{2}4)$  film RLP lies on the vertical dashed line the film is fully strained and if the RLP lies on the inclined dashed line means the film is fully relaxed; otherwise, the film is partially relaxed. In figure 7.6a, sample 2SiGe<sup>950-</sup> <sup>940</sup>, the ( $\overline{2}\overline{2}4$ ) peak is located directly below the substrate peak, indicating that a significant portion of the film is fully strained. The small tail towards to the inclined dashed line highlighted with a black arrow suggests there is a variation of strain relaxation across the sample and the greatest relaxation at the end of the tail (the arrow end) is 67%. In figure 7.6b, sample 4SiGe<sup>950-940</sup>, the  $(\overline{2}\overline{2}4)$  peak (marked with the black dot) is located between the vertical and inclined dashed lines, which shows that most of the film is partially relaxed,  $\sim 30\%$ , though the strain relaxation of the film varies from fully strained to fully relaxed. Figure 7.6c, sample 5SiGe<sup>950-940</sup>, the peak is directly below the substrate peak, which indicates a significant portion of the film is fully strained. The tail towards the right to the inclined line suggests that a variation of strain relaxation is present in the sample. The highest relaxation at the tail end (the arrow end) is 61%. A significant portion of both 2SiGe<sup>950-940</sup> and 5SiGe<sup>950-940</sup> films is fully strained and this is due to their low misfit dislocation density,  $\sim 10^2$  cm<sup>-1</sup> for samples 2SiGe<sup>950-940</sup> and 5SiGe<sup>950-940</sup> compared to  $\sim 10^3$  cm<sup>-1</sup> of sample 4SiGe<sup>950-940</sup>. This low misfit dislocation density results in a large misfit dislocation spacing, the

average dislocation spacing of sample  $2SiGe^{950-940}$  and  $5SiGe^{950-940}$  is 13 µm and 24 µm, respectively, which cannot relieve significant strain for most of the film since strain relaxation is localized (~micrometers) to the vicinity of misfit dislocations [161].



Figure 7.7 ( $\overline{22}4$ ) and (004) reciprocal space maps of samples  $2SiGe^{950-940}$  (a),  $4SiGe^{950-940}$  (b), and  $5SiGe^{950-940}$  (c).

The Ge content of samples 2SiGe<sup>950-940</sup>, 4SiGe<sup>950-940</sup>, and 5SiGe<sup>950-940</sup> is calculated using the RSM peak and is 1.4%, 2.4%, and 3.1%, respectively. Since the growth temperature interval is only 10 °C and the Ge content of each sample varies slightly, we consider this composition calculated from the RSM peak is the composition of the initial deposition on Si substrate. Thus, in order to initiate two-dimensional film growth on Si (001), the Ge content of the initial deposition should be less than 3.1% for these growth conditions. Figure 7.7 plots our experimentally deposited composition and the calculated composition based on Alonso and Trah [103, 105]. The calculation is using equation (3.8) with temperature fixed at 950 °C. The experimental results are lower than the calculated results and the difference between these two results varies from 0.8% to 2.5% as the Ge content in the liquid solution increases from 2% to 5%. Alonso's experimental results of Si-Ge-In at 900 °C are also lower than the calculated results and he explained this is because of a missing contribution to the free energy of mixing in the calculation which should be added to the exponent of equation (3.8) [103].



Figure 7.8 Initial Ge content of SiGe deposited on Si (001).

## 7.2.1.4 Etch pit density

Figure 7.8 shows optical micrographs of samples  $2SiGe^{950-940}$ ,  $4SiGe^{950-940}$ , and  $5SiGe^{950-940}$  after preferential etching highlighting etch pits most due to dislocations. Sample  $2SiGe^{950-940}$  has few etch pits (figure 7.8a) corresponding to its long and low density of misfit dislocations. Sample  $4SiGe^{950-940}$  (figure 7.8b) has significantly more etch pits than sample  $2SiGe^{950-940}$ , which corresponds with the increased misfit dislocation density. It is obviously that the etch pits on sample  $4SiGe^{950-940}$  are arranged along <110> directions, which results from dislocation glide terminating in the vicinity of another dislocation whose glide direction is perpendicular [62]. Sample  $5SiGe^{950-940}$  (figure 7.8c) has significantly more etch pits than sample  $2SiGe^{950-940}$  as well. The misfit dislocation density of sample  $5SiGe^{950-940}$  is lower than sample  $2SiGe^{950-940}$ ,  $3 \times 10^2$ cm<sup>-1</sup> compared to  $7.5 \times 10^2$  cm<sup>-1</sup>, but sample  $5SiGe^{950-940}$  still has higher EPD. This is because of its short misfit dislocations which results in a higher threading dislocation density.

Figure 7.8d shows another optical micrograph of sample  $5SiGe^{950-940}$  after preferential etching. Correlating this image with that of figure 7.5a, the squares shown in figure 7.8d have the square "volcano" morphology and regions like those between the two dashed lines, correlate with a sheathed ridge. The measured width of these stripes confirmed that these stripes are the sheathed ridges. For example, the width of the stripe between the two dashed lines is 7.5 µm, which is comparable to the measured width of the sheathed ridge talked previous,  $7.3 \pm 1.1$  µm. Etch pits on the sheathed ridges are few since the trenches which border them stop most dislocations from entering since they are too deep either going to the substrate surface or reducing the thickness to be below the critical thickness for nucleation glide [167]. The bulk film (areas between the sheathed ridges) is filled with a large number of etch pits.



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Figure 7.9 Optical microscopy images of samples after etching, 2SiGe<sup>950-940</sup> (270s) (a), 4SiGe<sup>950-940</sup> (130s) (b), 5SiGe<sup>950-940</sup> (80s) (c)(d) and the EPD of different samples (e).

Figure 7.8e displays the etch pit density (EPD) of all three samples (the blue columns). The average EPD of sample  $2SiGe^{950.940}$  is the lowest,  $1.36 \times 10^6$  cm<sup>-2</sup>, which is expected because of its long and low density of misfit dislocations. Comparing sample  $4SiGe^{950.940}$  to sample  $2SiGe^{950.940}$  as the Ge content of the film increases from 1.4% to 2.4%, the average EPD increases an order of magnitude, from  $1.36 \times 10^6$  cm<sup>-2</sup> to  $1.43 \times 10^7$  cm<sup>-2</sup>, which is comparable to the higher misfit dislocation density of sample  $4SiGe^{950.940}$  than sample  $2SiGe^{950.940}$  as discussed previous (figure 7.2 vs. figure 7.1,  $1.8 \times 10^3$  cm<sup>-1</sup> compared to  $7.5 \times 10^2$  cm<sup>-1</sup>). For sample  $5SiGe^{950.940}$ , the average EPD is  $1.56 \times 10^7$  cm<sup>-2</sup>, similar to that of sample  $4SiGe^{950.940}$ , probably because of the hard generation of misfit dislocation. The large deviation of EPD of sample  $5SiGe^{950.940}$  is caused by the significantly inhomogeneous distribution of the short misfit dislocations (figure 7.5a).

# 7.2.2 SiGe graded buffer

# 7.2.2.1 Surface morphology

Figure 7.9 shows the surface morphology of samples  $2SiGe^{950-750}$ ,  $4SiGe^{950-750}$ , and  $5SiGe^{950-750}$ . As the growth temperature interval increases to 950-750 °C for the same three initial Ge solution concentrations, samples  $2SiGe^{950-750}$  (figure 7.9a) and  $4SiGe^{950-750}$  (figure 7.9b) are still characterized with classic crosshatch morphology, in which the crosshatch lines are straight and long oriented along <110> directions, which suggests the long misfit dislocations of both samples [57]. However, the surface of sample  $5SiGe^{950-750}$  is wavy and only roughly oriented along the <110> directions (figure 7.9c), which is probably because of more three-dimensional growth discussed earlier (figures 7.3 and 7.5).





Figure 7.10 SEM images of samples 2SiGe<sup>950-750</sup> (a), 4SiGe<sup>950-750</sup> (b), and 5SiGe<sup>950-750</sup> (c).

# 7.2.2.2 Composition and strain states

Figure 7.10 shows the  $(\overline{224})$  and (004) RSMs of samples 2SiGe<sup>950-750</sup>, 4SiGe<sup>950-750</sup>, and 5SiGe<sup>950-750</sup>. Instead of having one peak (like that in all of the sub figures in figure 7.6), the RSMs of samples grown using a 950-750 °C temperature interval show a continuous intensity distribution in the film since the layer has a varying composition called graded buffer and thus a varying lattice constant [153]. Comparing these samples to their initial growth, the ones with a 950-940 °C growth interval (figure 7.10 vs. figure 7.6), the peak of the film (in the  $(\overline{224})$  RSM) closest to the Si substrate moves from around the vertical dashed line to the inclined dashed line which indicates the initial film is almost fully relaxed as the growth interval increase. This is able to occur probably because there is enough time at high temperature for sufficient misfit dislocation glide to relax the initial

film more. Also, the film becomes thicker as the temperature interval increases which provides a larger driving force for dislocation glide to relax the initial film. However, the layers of the graded buffer further from the substrate are strained since the intensity from these layers are located between the two dashed lines. It is probably because the temperature is low when these layers are grown and misfit dislocation glide velocity is slow in addition to the fact that dislocation nucleation is difficult at low temperature to relax the upper layers.



Figure 7.11 ( $\overline{22}4$ ) and (004) reciprocal space maps of samples  $2SiGe^{950-750}$  (a),  $4SiGe^{950-750}$  (b), and  $5SiGe^{950-750}$  (c).

Figure 7.11 shows the profile of the in-plane strain and strain relaxation as a function of Ge content for samples 2SiGe<sup>950-750</sup>, 4SiGe<sup>950-750</sup>, and 5SiGe<sup>950-750</sup> following the analysis process described in section 5.5.4 of chapter 5. For each sample, the in-plane strain of the film close to the Si substrate is positive (the part plotted with dark color of each sample in figure 7.11a), which indicates the initial film experiences tensile strain. This happens probably because the initial film was fully relaxed at high temperature but as the temperature cools to room temperature the lattice constants of the initial film reduces faster than the Si substrate due to the higher thermal expansion coefficient of SiGe and thus results in tensile strain [159, 160]. We calculated the thermal strain based on the thermal expansion efficiency [168] for each sample and the values are similar to our XRD results (the part plotted with dark color of each sample in figure 7.11a) which confirmed our assumption that causes the tensile strain. The upper layers of these three graded buffers all experience compressive strain as the in-plane strain are negative (the part plotted with bright color in figure 7.11a). Strain relaxation of each graded buffer increases to reach fully relaxed and then decreases (figure 7.11b). The value of the strain relaxation is determined by the absolute values of in-plane strain and misfit, so the value of strain relaxation is always less than 100% regardless if the strain is tensile or compressive. For the upper layers of the graded buffer (the part plotted with bright color of each sample in figure 7.11b), strain relaxation decreases with increasing Ge content, which probably occurs because the glide velocity of misfit dislocation slows as the temperature decreases and layer becomes more strained. By increasing the Ge content of the liquid solution from 2% to 5%, the final composition of the graded buffer grown from the same temperature interval becomes more Ge-rich, from 2.8% to 6.5%, as the initial deposition has more Ge content.



Figure 7.12 In-plane strain (a) and strain relaxation (b) as a function of Ge content.

# 7.2.2.3 Etch pit density

The etch pit density of samples  $2SiGe^{950-750}$ ,  $4SiGe^{950-750}$ , and  $5SiGe^{950-750}$  are plotted in figure 7.8 (the orange columns). The error bars represent the standard deviation of the measurements taken which are large because of the inhomogeneous distribution of threading dislocations. The EPD of these three samples will be discussed with their own initial EPD of the sample grown from temperature interval 950-940 °C (the blue column in figure 7.8e). The average EPD of sample  $2SiGe^{950-750}$  is  $9.36 \times 10^5$  cm<sup>-2</sup>, which is similar or a slight reduction from its initial value,  $1.36 \times 10^6$  cm<sup>-2</sup> in sample  $2SiGe^{950-940}$ . The average EPD of  $4SiGe^{950-750}$  and  $5SiGe^{950-750}$  is  $2.24 \times 10^6$  cm<sup>-2</sup> and  $2.16 \times 10^6$  cm<sup>-2</sup>, respectively, and reduces approximately one order of magnitude compared to their initial average EPD ( $1.43 \times 10^7$  cm<sup>-2</sup> of sample  $4SiGe^{950-940}$  and  $1.56 \times 10^7$  cm<sup>-2</sup> of sample  $5SiGe^{950-940}$ ). Threading dislocation density decreases with increasing film thickness due to the dislocation interaction and annihilation [162, 163]. As the dislocation density decreases, the likelihood of the dislocations interacting decreases as well; therefore, dislocation density vs.

thickness levels off [162, 163]. When the growth temperature interval increases from 950-940 °C to 950-750 °C, the film thickness increases from ~1  $\mu$ m to ~9.4  $\mu$ m. For samples 4SiGe<sup>950-750</sup> and 5SiGe<sup>950-750</sup>, the initial dislocation density is high, ~10<sup>7</sup> cm<sup>-2</sup>, which provides a great chance for dislocation interacting and annihilating to reduce the dislocation density. For sample 2SiGe<sup>950-750</sup>, the dislocation density starts low, ~10<sup>6</sup> cm<sup>-2</sup>, and this low dislocation density makes dislocations interaction rare; thus, its EPD just decreases slightly as the film thickness increases.

## 7.3 Conclusion

SiGe films were grown on Si (001) substrates with different Ge content solution (2%, 4%, 5%, and 6%) at a short temperature interval, 950-940 °C. Results show the growth turns from classic crosshatch film into more three-dimensional growth with increasing Ge-content in the solution. Films grown with 2% and 4% Ge-content solution have the classic crosshatch pattern. As the solution composition increases from 2% to 4%, more misfit dislocations are generated but the film becomes rougher. Films grown with 5% Ge-content solution not only have the crosshatch pattern but also have pits, hillocks and square islands probably due to the insufficiently strain relaxation by misfit dislocation. The highest Ge content of the solution to maintain two-dimensional film growth should be less than 5% and its corresponding Ge content of the initial film is less than 3.1%. The initial film is either fully strained for films grown with 2% or 5% Ge-content solution or ~30% partially relaxed for film grown with 4% Ge-content solution. Film grown with 2% Ge-content solution has the lowest etch pit density, ~10<sup>6</sup> cm<sup>-2</sup>.

SiGe graded buffers were then grown on Si (001) with different Ge content solution (2%, 4%, and 5%) at a larger growth interval 950-750 °C. Graded buffers grown from 2% and 4% Ge-content-solution maintain classic crosshatch pattern similar to the films with a 10 degree growth interval

from the same solutions; however, the film grown with 5% Ge content solution did not have a classic crosshatch morphology, and displayed a wavy morphology only roughly oriented along <110> directions probably because of the tendency for three-dimensional growth. As the Ge content of the liquid solution increases from 2%, to 4%, then to 5%, the final composition of the graded buffer grown from the same temperature interval becomes more Ge-rich, from 2.8%, to 5.9%, and then to 6.5%. Layers of the graded buffers close to the substrate experience tensile strain and relax more than the initial film since there is enough time for sufficient misfit dislocation glide to relax the initial film. The upper layers experience compressive strain and become more strained with increasing Ge content for each graded buffer because the temperature is low and misfit dislocation gliding velocity reduces. The etch pit density decreases with increasing thickness as the growth temperature interval increases. The etch pit density of graded buffers grown from 2% Ge solution is around ~9 ×10<sup>5</sup> cm<sup>-2</sup> and reduces slightly compared to its initial film while the etch pit density of graded buffers grown from the 4% and 5% Ge solutions reduce significantly, from ~10<sup>7</sup> cm<sup>-2</sup> to ~10<sup>6</sup> cm<sup>-2</sup> due to dislocation interaction and annihilation.

# Chapter 8 LPE SiGe Films Grown on CVD SiGe/Si (001)

In the previous chapter, SiGe films were grown on Si (001) using solutions with differing Ge contents and a short growth interval of 950-940 °C to study the morphology and composition of the initial deposition. Results showed that the growth starts with two-dimensional growth and moves towards a more three-dimensional growth as the Ge content in the solution increases. It was found that in order to maintain two-dimensional film growth, the largest Ge content in the film could be 3.1% and resulted in a film that was either fully strained or just ~30% partially relaxed. Larger Ge-content films are not possible on Si (001) probably because there are not sufficient misfit dislocations generated to relax the film causing three-dimensional growth. Therefore, increasing the dislocation density is necessary and since dislocation nucleation can be difficult in LPE (growth occurs close to equilibrium), introducing a larger dislocation density in the substrate could be helpful to increase the film relaxation and maintain two-dimensional growth. In this chapter, a SiGe graded buffer on Si (001) grown by CVD is used as the starting growth substrate of LPE growth because the large number of threading dislocations produced by CVD ( $8 \times 10^6$  cm<sup>-2</sup>). Similar to the previous chapter, SiGe are grown at temperature interval 950-940 °C by varying

the solution composition from low-Ge-content to high-Ge-content in order to determine the highest Ge content of the initial deposition that maintains two-dimensional growth; however this time the growth is on the CVD-grown SiGe film. Properties of the initial deposition such as surface morphology, composition, strain state, and threading dislocation density of each sample are studied. Since the CVD SiGe film is used as the growth substrate, the effect of 4 h annealing under the same conditions as that prior to LPE growth is also studied.

#### 8.1 Experimental

SiGe layers were grown on CVD SiGe/Si (001) substrates using a custom-designed LPE system. All growths were carried out in a horizontal slide graphite boat with an ultrapure H<sub>2</sub> atmosphere. The desired amounts of Ge and In (used as solvent) were precisely massed and homogenized at ~1000 °C for 4 h. The saturation wafer (Si) and CVD wafer were cleaned in 1:1::H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> (volume) followed by 1:1:6::HCl:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O (volume) at 80 °C. Before growth, the saturation wafer and a CVD wafer were dipped into 5% HF for 30 s to remove the native SiO<sub>2</sub> and then immediately loaded into the saturation groove and growth substrate groove in the graphite boat, respectively, with the homogenized GeIn alloy. The homogenized GeIn alloy was preheated at the saturation temperature,  $T_s = 950$  °C for 1 h. Then, the saturation wafer was introduced to the GeIn solution for 3 h to saturate the GeIn solution with Si. After that, the CVD substrate (the growth substrate) was introduced to the SiGeIn solution and the temperature was reduced by 500 °C/h. When the temperature reached the final temperature  $T_f = 940$  °C, the sample was removed from the solution and then cooled to room temperature. The solution composition used in this chapter was ~15%Ge, ~20%Ge, ~22%Ge, ~23%Ge, or ~24%Ge. The surface morphology of each sample was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Composition and strain states were studied by high-resolution triple-axis X-ray diffraction. The threading dislocation density of each LPE film as well as the CVD wafer were studied by preferential etching with a solution 2HF: 1(1M) CrO<sub>3</sub>:1.5H<sub>2</sub>O (weight ratio) followed by optical microscopy observation and using ImageJ software to calculate the etch pit density.

The CVD SiGe film, used as the growth substrate, was annealing at the saturation temperature for 4h before the LPE growth. The effect of 4h annealing was also studied following the experimental procedure above exactly except loading any saturation wafer and metallic solution. The resulting films and the CVD wafer were studied including their surface morphology by scanning electron microscopy (SEM) and the composition and strain states by high-resolution triple-axis X-ray diffraction.

#### 8.2 Characterization of CVD SiGe film

Figures 8.1 shows the SEM images of the CVD SiGe film before and after annealing. The left images are at a lower magnification and the right images are a higher magnification image of the area shown in the left. The CVD SiGe film is characterized with the classic crosshatch pattern oriented along the <110> directions (figures 8.1a, b). After annealing, islands, the white particles in figures 8.1c-f, appear all over the CVD SiGe film and EDS shows that these islands are SiGe with increased Ge content. Figure 8.1c shows an area of the annealed CVD SiGe film has densely aligned SiGe islands along <110>-type directions. A higher magnification image (figure 8.1d) indicates these SiGe islands seem to be two levels of Ge enrichment suggested by the brighter contrast, a high level (indicated by arrow I) and a lower level (indicated by arrow II) compared to the rest of the film. The size of these aligned islands (similar to the region demarcated by arrow II in figure 8.1d) as indicated by the doubled headed arrow in figure 8.1c is  $2.0 \pm 0.3 \,\mu$ m. Figure 8.1e shows another area of the heated CVD SiGe film has a sparse distribution of larger SiGe islands

such as indicated by arrow III and has numbers of tiny SiGe islands as indicated by arrow IV in figure 8.1f aligned along <110> directions. The size of these larger and smaller SiGe islands shown in figure 8.1e are  $1.5 \pm 0.3 \mu m$  and  $0.34 \pm 0.07 \mu m$ , respectively. Also, many places similar to that indicated by arrow V in figure 8.1e, have darker contrast compared to other places of the bulk film, appear to be Ge poor, and the bigger islands locate at some of these darker contrast places. These SiGe islands formed is probably due to the rearrangement of Si and Ge atoms during the heating process and the alignments of these SiGe islands probably result from Si and Ge atoms diffuse towards the ridges, high relaxed regions, due to the underlying misfit dislocations [169]. Also, the morphology shown in figure 8.1f may be between the morphologies of figure 8.1b and 8.1d as the Ge-rich islands are smaller in figure 8.1f and the background is more homogenous in shading.



Figure 8.1 SEM images of CVD SiGe film before and after annealing at 950 °C for 4h. Before annealing (a)(b), densely aligned SiGe islands (c)(d), and sparse SiGe islands and tiny aligned SiGe islands (e)(f).

Figure 8.2 shows the  $(\overline{2}\overline{2}4)$  and (004) RSMs of the CVD SiGe/Si (001) before and after annealing. RSM mapping were performed on both kind areas as shown in figures 8.1c and 8.1e of the annealed CVD SiGe film and are shown in figure 8.2b and figure 8.2c, respectively. The CVD SiGe film consists of a continuously graded buffer with a thicker cap layer on top. In each sub figure, the top peak represents the Si substrate while the lower one corresponds to the cap layer and the part with continuous intensity distribution between the two peaks is for the graded buffer. The vertical and inclined dashed lines in the  $(\overline{2}\overline{2}4)$  RSMs show where the RLP peaks would be located for pseudomorphic and fully relaxed films, respectively [144]. Since the (004) film peak (circled dot in (004) RSM) is not locating directly below the substrate peak, lattice tilt occurred during the CVD SiGe film growth and the effect of lattice tilt has to be corrected in order to determine the composition and strain relaxation of the film [142, 148, 152]. The position marked by circled dot in each sub figure highlights the RLP location of RSM film peak while the position marked by "X" shows the RLP location of the film after applying the required lattice tilt correction (The principle of lattice tilt correction was displayed in figure 5.10). The composition and strain relaxation determined from these "X" positions after tilt correction are listed in each figure. The composition of the annealed CVD SiGe film either in the area with densely aligned islands (figure 8.1c) or the area with sparsely bigger islands and tiny aligned islands (figure 8.1e) is same to the composition before annealing,  $\sim 12\%$ Ge; but the film becomes more relaxed, from 86% before annealing to  $\sim 95\%$ after annealing, which happens because dislocations are allowed to glide more during the annealing and thereby relieve more strain [29]. Strain relaxation in regions shown in figures 8.1c and 8.1e are similar, ~95%.



Figure 8.2 ( $\overline{22}4$ ) and (004) reciprocal space maps of CVD SiGe film/Si (001) before (a) and after 4h annealing (b)(c).

#### 8.3 Selection of growth solution and growth appearance

An important parameter to determine before growing LPE SiGe on the CVD SiGe/Si (001) is the appropriate solution composition. Since we are trying to grow higher-Ge-content LPE SiGe films on the CVD SiGe capping layer to study how dislocation nucleation sources on the substrate affect the properties of the initial LPE deposition and determine if a higher-mismatched film can be grown on the CVD capping layer since more dislocations are present, we need to choose an appropriate initial solution composition to grow a non-entrained film and then determine the maximum mismatch possible to maintain a two-dimensional film grown by LPE. Therefore, we would like to grow a film with 12% Ge or higher however there is very little experimental data to guide this. Alonso and Trah [103, 105] calculated the ternary phase diagram of Si-Ge-M (solvent) and figure 8.3 plots the solid composition as a function of liquid composition in the Si-Ge-In ternary system (equation 3.8) with a fixed temperature of 950 °C (the saturation temperature used in this study). The solid has similar composition to the liquid for Si-Ge-In ternary system at temperature 950 °C but our previous results (figure 7.7) showed that the experimentally solid composition is lower in Ge content than that calculated by Alonso and Trah (for example, 2.5%Ge lower of the experimental results compared to the calculated result for 5%Ge liquid solution). Therefore, we started with 15%Ge liquid solution whose calculated solid composition is 16.2%Ge as shown in figure 8.3. The sample grown with ~15%Ge liquid solution is non-entrained film and we kept increasing the Ge content in the liquid solution until the growth sample was entrained. Table 8.1 lists the liquid solution composition we used and its corresponding growth appearance (entrained or non-entrained). The sample grown with ~24%Ge liquid solution was entrained while others grown with ~15%Ge, ~20%Ge, 22%Ge, and 23%Ge were not.



Figure 8.3 Solid composition as a function of liquid composition in Si-Ge-In ternary system with temperature fixed at 950 °C calculated based on Alonso and Trah method [103, 105].

Table 8.1: Calculated solid composition, growth appearance, experimental results of samples grown with different Ge content solution from temperature interval 950-940 °C.

Sample	15SiGe <sup>950-940</sup>	20SiGe <sup>950-940</sup>	22SiGe <sup>950-940</sup>	23SiGe <sup>950-940</sup>	24SiGe <sup>950-940</sup>
Solution composition (Ge%)	~15	~20	~22	~23	~24
Calculated solid composition* (Ge%)	16.2	21.3	23.3	24.3	25.3
Growth appearance	non-entrained	non-entrained	non-entrained	non-entrained	entrained
CVD film composition (Ge%) (RSM)	11.7	13.8	~14.1	~14.9	
CVD film strain relaxation (%) (RSM)	92	95	~96	~98	
LPE film composition (Ge%) (RSM)	9.6	13.0	14.1	14.9	Not determined
LPE film strain relaxation (%) (RSM)	86	92	96	98	
LPE film strain	tensile	tensile	compressive	compressive	
EPD (cm <sup>-2</sup> )	$2.69 \pm 1.82 \times 10^{6}$	2.62±0.99×10 <sup>6</sup>	5.39±1.85×10 <sup>6</sup>	4.35±0.91×10 <sup>6</sup>	

Note: The sample name notation indicates the initial Ge content (Ge%) in the solution and the growth temperature interval. For example, sample 15SiGe<sup>950-940</sup> means the initial Ge% is 15% and the growth temperature interval is 950-940 °C.

\*calculated based on Alonso and Trah using equation (3.8) with temperature fixed at 950 °C.

#### 8.4 LPE growth on CVD SiGe/Si (001)

# 8.4.1 Surface morphology

Figure 8.4 shows the SEM images of the non-entrained samples,  $15SiGe^{950.940}$ ,  $20SiGe^{950.940}$ ,  $22SiGe^{950.940}$ , and  $23SiGe^{950.940}$ . All four samples are characterized with crosshatch pattern aligned along the <110> directions as shown in the left image (low magnification) of each sample. The right images are higher magnification and figure 8.4d shows that sample  $20SiGe^{950.940}$  has a large numbers of square morphologies as indicated with arrow I in figure 8.4d. AFM proves that these square morphologies, likely pits, with edges oriented along the <110> directions. We repeated the growth of sample  $20SiGe^{950.940}$  and achieved the same result with high-density pits ( $7.3 \times 10^8$  cm<sup>-2</sup> and a size (as marked by the double headed arrow) of  $129 \pm 26$  nm on the surface. No pits were observed on sample  $15SiGe^{950.940}$  as shown in figure 8.4b. Very few and small pits (verified by AFM) as indicated with arrow II in figure 8.4f and arrow III in figure 8.4h are observed on samples  $22SiGe^{950.940}$  and  $23SiGe^{950.940}$ . Also, deep valleys are observed on samples  $22SiGe^{950.940}$  as indicated by arrow "a" in figure 8.4e and arrow "b" in figure 8.4g, respectively.





Figure 8.4 SEM images of samples 15SiGe<sup>950-940</sup> (a)(b), 20SiGe<sup>950-940</sup> (c)(d), 22SiGe<sup>950-940</sup> (e)(f), and 23SiGe<sup>950-940</sup> (g)(h).

#### 8.4.2 Composition and strain states

Figure 8.5 shows (224) and (004) RSMs of samples 15SiGe<sup>950-940</sup>, 20SiGe<sup>950-940</sup>, 22SiGe<sup>950-940</sup>, and 23SiGe<sup>950-940</sup>. In each sub figure, the circled dot indicates the RLP position of the film peak and the "X" marks the RLP position after the correction of the lattice tilt. The RSMs of samples 15SiGe<sup>950-940</sup> (figure 8.5a) and 20SiGe<sup>950-940</sup> (figure 8.5b) have two film peaks: one represents the CVD film while the other is for the LPE film. For both 15SiGe<sup>950-940</sup> and 20SiGe<sup>950-940</sup> samples, the film represented by the peak closest to the substrate experiences tensile strain since each  $(\overline{2}\overline{2}4)$ peak after correction (marked with red "X" on the left sub figures of figure 8.5a and figure 8.5b) lies above the inclined dashed line and the film represented by the peak away from the substrate experiences compressive strain as its  $(\overline{2}\overline{2}4)$  film peak after correction (marked with black "X" on the left sub figures of figure 8.5a and figure 8.5b) lies between the two dashed lines. In this case, the film peak closes to the substrate, for samples 15SiGe<sup>950-940</sup> and 20SiGe<sup>950-940</sup>, correspond to the LPE film while the other peak away from the substrate correspond to the CVD capping layer because tensile strain in this growth system can only occur when a lower-Ge-content film is on top of a higher-Ge-content film. The composition and strain relaxation of the LPE and CVD film for samples 15SiGe<sup>950-940</sup> and 20SiGe<sup>950-940</sup> determined from the RSMs are listed in table 8.1. For samples 22SiGe<sup>950-940</sup> (figure 8.5c) and 23SiGe<sup>950-940</sup> (figure 8.5d), each RSM only has only one film peak. We performed the measurements on another spot of each sample and we had the same result. We even performed the measurements in a relatively large range and we did not find any other film peak. For both 22SiGe950-940 and 23SiGe950-940 samples, the film experiences tensile strain since each  $(\overline{2}\overline{2}4)$  peak after tilt correction (marked with red "X" on the left sub figures of figure 8.5c and figure 8.5d) lies below the inclined dashed line. The composition and strain relaxation determined from the RSM peak of sample 22SiGe<sup>950-940</sup> is 14.1%Ge and 96%,

respectively. The composition and strain relaxation determined from the RSM peak of sample 23SiGe<sup>950-940</sup> is 14.9%Ge and 98%, respectively.



Figure 8.5 ( $\overline{22}4$ ) and (004) reciprocal space maps for samples 15SiGe<sup>950-940</sup>, 20SiGe<sup>950-940</sup>, 22SiGe<sup>950-940</sup>, and 23SiGe<sup>950-940</sup>.

Figures 8.5c and 8.5d represent two samples in which there is only one apparent film peak in XRD, a surprising result since there should be both a CVD cap (1  $\mu$ m thick) and an LPE film on top. We believe these two peaks represent both the CVD film as well as the LPE film. One reason for this belief is that these singular XRD film peaks (in figures 8.5c and 8.5d) are broader than those in figures 8.5a and 8.5b. It is clear to see that each individual film RSM of sample 15SiGe<sup>950-940</sup> (figure 8.5a) and 20SiGe<sup>950-940</sup> (figure 8.5b) is thinner in the vertical direction for (004) RSM and the [ $\overline{22}4$ ] direction for ( $\overline{22}4$ ) RSM. Also, the peak (marked with the circled dot) is located at the center of each of the peaks in each of these sub figures (figures 8.5a and 8.5b). However, the film RSM of sample 22SiGe<sup>950-940</sup> and 23SiGe<sup>950-940</sup> is broader in the vertical direction for both the ( $\overline{004}$ ) RSMs and the [ $\overline{22}4$ ] direction for the peak. This suggests that the film RSM of sample 22SiGe<sup>950-940</sup> and 23SiGe<sup>950-940</sup> is actually an overlapped map of the LPE film and its capping layer which happens because the capping layer composition was similar to the LPE film.

A strong reason why these XRD peaks at least represent the LPE film, if not the CVD film, can be seen in the orange curve in figure 8.6 which plots the LPE film composition (as determined by XRD) as a function of Ge concentration within the LPE growth solution. From this curve there is a strong linear relationship between the Ge composition in the film and the Ge composition within the solution. The last two points with highest Ge content (from samples 22SiGe<sup>950-940</sup> and 23SiGe<sup>950-940</sup>) on this curve represent film composition of the films in figures 8.5a and 8.5b, respectively. The first three points are the results discussed in chapter 7 (figure 7.7). The fourth and fifth points are the LPE film composition of samples 15SiGe<sup>950-940</sup> and 20SiGe<sup>950-940</sup>. The blue line in figure 8.6 plots the corresponding calculated solid composition based on Alonso and Trah [103, 105] using equation (3.8) with temperature fixed at 950 °C. All the LPE experimental results

including the two points determined from the RSM peak of sample 22SiGe<sup>950-940</sup> and 23SiGe<sup>950-940</sup> increase linearly, which has the same trend to the calculated results. This suggests us that the composition determined from the RSM peak of samples 22SiGe<sup>950-940</sup> and 23SiGe<sup>950-940</sup> represents the LPE film composition. The experimental results are systematically lower than the calculated results and can be seen in the grey curve in figure 8.6 which is the difference between the orange and blue curves.



Figure 8.6 Experimental solid composition and calculated solid composition based Alonso and Trash method [103, 105].

Given that the XRD peaks are likely LPE films and that the peaks are broader than an LPE or CVD film by themselves (note all the XRD plots in figure 8.5 are on the same scale), we suggest that there is some variance in the CVD composition across the wafer which accounts for an overlap of the CVD and LPE films. The composition difference between the LPE film and the capping layer of sample 20SiGe<sup>950-940</sup> is 0.8%Ge as listed in table 8.1 and the two film RSMs are slightly

overlapped but still can be distinguished. This suggests that the composition difference of the LPE film and CVD for samples 22SiGe<sup>950-940</sup> and 23SiGe<sup>950-940</sup> is less than 0.8%Ge as only one peak is present. So, for the composition and strain relaxation of the capping layer of samples 22SiGe<sup>950-940</sup> and 23SiGe<sup>950-940</sup>, we put the values determined from the RSMs in table 8.1 and indicates some uncertainty by using a "~".

One initial hypothesis was that by growing an LPE film on a substrate with a higher dislocation density we could grow 2D LPE films with a larger lattice mismatch ( $\Delta Ge_{max}$ %) and have those films be more relaxed. However, due to the likelihood that the CVD capping was a similar composition to the film we could not determine  $\Delta Ge_{max}$ %. However, we can conclude is that the initial LPE film on the CVD film is much more relaxed than that directly grown on the bare Si. The initial LPE film on the CVD film is 86%~98% relaxed regardless the tensile strain or compressive strain while the initial films directly grown on bare Si is fully strained (see figure 7.6 chapter 7). This happens because threading dislocations of the CVD film are sources for misfit dislocations which glide and release most of the strain during the initial deposition; whereas, growth on bare Si has very few initial dislocations and in LPE growth dislocations are difficult to nucleate which results in highly strained films.

#### 8.4.3 Etch pit density

The etch pit density of samples  $15SiGe^{950-940}$ ,  $20SiGe^{950-940}$ ,  $22SiGe^{950-940}$ , and  $23SiGe^{950-940}$  are shown in Table 8.1. The average EPD of CVD SiGe film is  $7.88 \pm 1.34 \times 10^6$  cm<sup>-2</sup> and the average EPD of the other four samples are lower than the CVD film but they are all at the same order of magnitude of the CVD film,  $\sim 10^6$  cm<sup>-2</sup>. The slightly low EPD of LPE films compared to the CVD film is due to the dislocation interaction and annihilation during the LPE growth [162, 163]. The average EPD of samples  $15SiGe^{950-940}$  and  $20SiGe^{950-940}$  are similar at  $2.69 \times 10^6$  cm<sup>-2</sup> and  $2.62 \times 10^{-2}$  cm<sup>-2</sup> cm<sup>-2</sup> and  $2.62 \times 10^{-2}$  cm<sup>-2</sup> cm<sup>-2</sup>

 $10^6$  cm<sup>-2</sup>, respectively and the average EPD of samples  $22SiGe^{950-940}$  and  $23SiGe^{950-940}$  are  $5.39 \times 10^6$  cm<sup>-2</sup> and  $4.35 \times 10^6$  cm<sup>-2</sup>, respectively.

# 8.5 Conclusion

SiGe films were grown on CVD SiGe /Si (001) substrates with different Ge content solutions at a short temperature interval 950-940 °C to study the properties of the initial deposition on a substrate which could provide a generous number of dislocation nucleation sources. The purpose of this is to find the highest Ge content difference ( $\Delta Ge_{max}$ %) between the initial deposition and the CVD substrate that maintains two-dimensional growth and to compare this  $\Delta Ge_{max}$ % to that on the bare Si which was presented in previous chapter. As the CVD SiGe film will be annealed at the saturation temperature for 4h before growth, the surface morphology, composition and strain state of the CVD film were studied and the results show aligned SiGe islands distributed over it and the composition of the annealed CVD film constant before and after annealing; however, the film further relaxes after the annealing due to further misfit dislocation glide. For the LPE films with a small temperature interval on the CVD substrate, due to the possibility of the dissolution of the CVD capping layer, it is not applicable to compare the  $\Delta Ge_{max}$ % on the CVD substrate to that on the bare Si. We can conclude that the LPE initial film grown on CVD film is much more relaxed (≥86%) than that on the bare Si (fully strained) because existing dislocations inherited from the CVD capping layer are recycled to further relax the LPE film; while for the initial film on bare Si, misfit dislocations are hard to nucleate in LPE making relaxation difficult. Finally, the etch pit density of the LPE initial film is a bit lower than the initial CVD capping layer and on the order of  $\sim 10^{6} \text{ cm}^{-2}$ .

# **Chapter 9**

# **Conclusions and Future Work**

### 9.1 Conclusions

SiGe graded buffers are an effective technique to grow lattice-mismatched heteroepitaxial layers with low threading dislocation densities. The LPE technique is economical for heteroepitaixal growth and allows low dislocation density film growth on Si substrate. Also, SiGe grown by LPE from high temperature to low temperature results in a compositionally graded buffer. LPE has the potential to grow SiGe graded buffers with low threading dislocation densities. The drawback of LPE is that it is hard to get relaxed films as misfit dislocation maybe hard to nucleate at near equilibrium condition and it is hard to get high Ge compositions films as high-Ge-content growth in LPE favors 3D islands growth. In this study, an LPE system was developed which was described in chapter 4. The removal of Si native oxide layer and minimization of the solution entrainment are critical for the heteroepitaxial SiGe film growth.

In chapter 6, low-Ge-content SiGe graded buffers were grown on Si (001) from the same initial solution composition, ~2%Ge. All growths started from 950 °C but ended at different final temperatures 940 °C, 850 °C, 750 °C, 650 °C, 550 °C, and 450 °C to study the growth evolution during the LPE growth process. The growth started with the classic two-dimensional crosshatch morphology with ridges becoming broader and higher. As the temperature became lower than 750

°C, the ridges only increase vertically and three-dimensional-type growth started to appear when the temperature lower than 650 °C. The composition of the graded buffer increases from 0.81%Ge to 6.4%Ge with increasing grading rate. The film closest to the buffer/substrate interface is fully strained initially and becomes fully relaxed when the temperature drops to 750 °C. The Long growth interval helps to relax the initial film close to the interface but the top part of the film is partially strained and becomes more strained with increasing thickness and Ge content which both are products of the increased growth interval.

In chapter 7, SiGe films were grown with different solution compositions (2%Ge, 4%Ge, and 5%Ge) from a short temperature interval (950-940 °C) to study the properties of the initial deposition and determine the largest Ge content that maintains two-dimensional growth. Lower Ge solution compositions result in growth with a crosshatch morphology and become more threedimensional morphology with increasing Ge content in the solution. The greatest Ge content that maintains two-dimensional growth is 3.1%Ge. The initial film is either fully strained or 30% partially relaxed. In addition, SiGe graded buffers were grown on Si (001) with different composition solutions (2%, 4%, and 5%) at temperature intervals from 950-750 °C. Graded buffers grown from 2% and 4% Ge-content-solution maintain crosshatch morphologies but not graded buffers grown with 5% Ge content solution which is probably due to the tendency of threedimensional growth. Layers of each graded buffer close to the substrate are fully relaxed at high temperature since there is enough time for sufficient misfit dislocation glide to relax the initial film but experience tensile strain after being cooled to room temperature. The upper layers of each graded buffer become more strained with increasing Ge content and thickness because the low temperature makes misfit dislocation gliding velocity becomes slow. The threading dislocation density decreases with increasing thickness. The threading dislocation density of graded buffer grown from 2% Ge-content-solution is around ~9 ×10<sup>5</sup> cm<sup>-2</sup> and reduces slightly compared to its initial film (the film grown in the first ~10 °C growth interval). The threading dislocation density of graded buffers grown from 4% and 5% Ge-content-solution reduce an order of magnitude compared to its initial film, from 10<sup>7</sup> cm<sup>-2</sup> to 10<sup>6</sup> cm<sup>-2</sup>, because the high initial threading dislocation density provides a large opportunity of dislocation interaction and annihilation.

In chapter 8, SiGe films were grown on a CVD-grown Si<sub>0.88</sub>Ge<sub>0.12</sub>/Si (001) virtual substrate with different Ge content solutions using a short growth temperature interval (950-940 °C) to study the properties of the initial deposition on a substrate which could provide a generous number of dislocation nucleation sources. The initial LPE film grown on CVD film is much more relaxed ( $\geq$ 86%) than that on the bare Si (fully strained) since misfit dislocations are easier to nucleate by gliding from existing threading dislocations. The initial LPE film has a similar threading dislocation density to the CVD film.

#### 9.2 Future work

Since most applications of interest required high-Ge-content films, the most desired future work would try to significantly increase the Ge content in LPE SiGe graded buffers. One way to accomplish this is by using Bi or Pb solvents, instead of In, can result in the growth of SiGe films/buffers with higher Ge content as discussed in chapter 3. To grow SiGe graded buffers on Si (001), the first step is to initiate two-dimensional growth. Since the greatest Ge content on Si (001) that maintains two-dimensional growth determined in chapter 7 is 3.1%Ge, based on this greatest Ge content and equation (3.8), we can determine the corresponding Si-Ge-Bi composition to use

which is 0.7%Ge. For such a low Ge content solution (0.7%Ge), a large amount of Bi solvent is required to dissolve enough Si and Ge solutes for growth. The maximum solvent amount is limited to the graphite well volume. A small growth temperature interval (for example 10 °C) is necessary to make sure the initial growth is two-dimensional film growth first. If it is, we can then try a larger growth temperature interval or try grow with a higher Ge content solution.

Another interesting concept to pursue is to fully relax the graded buffer. As shown in the conclusions in chapters 6 and 7, the film close to buffer/substrate interface is fully relaxed; however, the film further from the interface is strained and has more strain with increasing thickness and Ge content. This happens because the growth temperature for these layers close to the interface are high at which dislocation glide velocity is fast and there is enough time for sufficient misfit dislocation glide long enough to fully relax the layers. For the upper layers, the growth temperature is low and misfit dislocation glide velocity is slow; so, the misfit dislocations do not glide enough to fully relax the layers. To extend the misfit dislocation length, annealing could be done. Multiple cooling-annealing steps could result in a graded buffer that is fully relaxed. The growth starts at the saturation temperature  $T_s$  and when the temperature drops to a certain temperature  $T_1$ , the temperature is maintained at  $T_1$  to anneal the grown layer to be relaxed more. Then, the temperature is dropped again to grow until another temperature  $T_2$  and the temperature is also maintained at  $T_2$  to preform annealing. This process could continue until the desired final temperature.

In addition, it would be interesting to do some electrical characterizations such as charactering the number and the type of carriers (e.g. Hall effect). Also, it is worth fabricating the metal-oxide-semiconductor field-effect transistor (MOSFETS) to study the mobility and making Photovoltaics (pn junction) to study the defect density.

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