ABSTRACT

BHARATHAN, JAYESH MOORKOTH. Germanium-on-Silicon Strain Engineered Materials for Improved Device Performance Grown by Chemical Vapor Deposition. (Under the direction of Dr. G. A. Rozgonyi).

The primary goal of this research is to develop a chemical vapor deposition process for growing epitaxial films of germanium on silicon (001) substrates with two-dimensional (2-D) morphology, and a low density of threading dislocations. Growth was carried out in a reduced-pressure chemical vapor deposition (RPCVD) system by a two-step growth technique.

An accurate knowledge of elastic constants of thin films is important in understanding the effect of strain on material properties. Residual thermal strain was used to measure the Poisson ratio of Ge films grown on Si(001) substrates, by the $\sin^2 \psi$ method and high-resolution x-ray diffraction. The Poisson ratio of the Ge films was measured to be 0.25, compared to the bulk value of 0.27. The result was found to be independent of film thickness and defect density, which confirmed that the strain is associated with the elastic response of the film. The study showed that the use of Poisson ratio instead of bulk compliance values yields a more accurate description of the state of in-plane strain present in the film.

The experimentally measured in-plane strain in Ge films was found to be lower than the theoretical calculations based on the differential thermal expansion coefficients of Si and Ge. The mechanism of thermal misfit strain relaxation in epitaxial Ge films grown on Si(001) substrates was investigated by x-ray diffraction, and transmission electron microscopy.
Lattice misfit strain associated with Ge/(001)Si mismatched epitaxy is relieved by a network of Lomer edge misfit dislocations during the first step of the growth technique. However, thermal misfit strain energy during growth is relieved by interdiffusion mechanism at the heterointerface. Two SiGe compositions containing 0.5 and 6.0 atomic percent Si were detected that relieve the thermal mismatch strain associated with the two steps of the growth process. This study discusses the importance of interdiffusion mechanism in relieving small misfit strains present during epitaxy.

The microstructural characteristics of Ge films were analyzed by x-ray diffraction, atomic force microscopy and transmission electron microscopy. The principal defects in the epitaxial films were determined to be threading dislocations and stacking faults. A unique defect appearing as a line during defect delineation was established to be a wide stacking fault arising from oxygen contamination during RPCVD epitaxy. A decrease in defect density by almost an order of magnitude was observed with increasing film thickness. Germanium films with a thickness of 3.5 µm exhibited the lowest threading dislocation densities of $5 \times 10^6$ cm$^{-2}$. The mechanisms of interactions between threading dislocations has been discussed with the aid of transmission electron microscopy to explain the reduction in the observed threading dislocation density.

A strong correlation was obtained between electrical performance of the devices and defect density. Thicker films with the lowest threading dislocation density of $5 \times 10^6$ cm$^{-2}$ also yielded devices with the lowest dark current density of ~ 5 mA/cm$^2$ (1 V reverse bias) and bulk resistivity of 30 Ω cm$^2$. All devices showed spectral response of up to 1.61 µm,
confirming a strain-induced shrinkage of the direct band gap by approximately 30 meV, which is in good agreement with theoretical models.

In summary, the structural, electrical, and optical properties of 2-D Ge films grown on Si(001) substrates by RPCVD has been investigated.
Germanium-on-Silicon Strain Engineered Materials for Improved Device Performance
Grown by Chemical Vapor Deposition

by
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DEDICATION

To my mother and father for their endless love and sacrifice.
BIOGRAPHY

Jayesh Bharathan was born in Bombay, the financial capital of India. He completed his Master of Science degree from the University of Bombay, in the field of Chemistry in the year 1995. In 1996, he started his graduate study at the Department of Materials Science and Engineering, at the University of California, Los Angeles. His research at UCLA was focused on polymer light-emitting diodes under the guidance of Dr. Yang Yang. His thesis was titled “Study on the Polymer-Metal Interface and Introduction to Hybrid Ink-Jet Printing for Patterning of Polymers”. After graduating with a Masters degree from UCLA in 1998, he worked for Cree Incorporated (1999 - 2005) in California and later at their North Carolina location, as a process development engineer. His work at Cree was focused on indium gallium nitride-based materials for light-emitting diode applications. In 2005 he started working at Nextreme Thermal Solutions, also in North Carolina, as an advanced process engineer. His work at Nextreme was focused on bismuth telluride-based thermoelectric materials. In June 2009, he started working for RTI International as a research engineer while simultaneously pursuing a doctoral program in the Department of Materials Science and Engineering at North Carolina State University. His research focused on the growth and characterization of germanium epitaxial films on silicon for near infrared detector applications.
I would like to begin by thanking Dr. Rozgonyi for being the inspiration behind my doctoral studies and for agreeing to serve as the committee chair. The extraordinary quality of his published research was my main motivation for pursuing a PhD program in his group. Returning to academia after ten years in the industry was a difficult and risky decision and he was very accommodating with my requests to make this transition a smooth one. I would like to thank Dr. Narayan, Dr. Cuomo, Dr. Ozturk, Dr. Reynolds, and Dr. Rama Venkatasubramanian for agreeing to serve on my committee and being available to guide me on my research. I am extremely grateful to Dr. Jagdish Narayan for his tremendous help in shaping my research and taking it to a conclusion. His door was always open for me. If I was to pick two papers that influenced my research they would be: (i) New mechanism of formation of stacking faults in Ge/(001)Si heterostructures, J. Narayan et al., Phil. Mag. A 72, 305 (1995) and (ii) Ultrahigh vacuum rapid thermal chemical vapor deposition of epitaxial silicon onto (100) silicon, M. C. Ozturk et al., J. Electrochem. Soc., 142, 3961 (1995). Both these papers addressed some of the technical challenges I was encountering and helped me plan future experiments. The references provided in these papers are a valuable guide for researchers engaging in the epitaxial growth and defect characterization of Ge thin films grown on Si.

I would like to thank Dr. Rama Venkatasubramanian for taking time out of his busy schedule to review my work and provide his thoughtful comments. Without his gracious support, I would have never been able to complete my PhD program. I would also like to
thank RTI International for supporting this research. I would like to thank my supervisor at RTI, Dr. Gary Bulman for being patient with me, reviewing my presentations, and for his constant encouragement. It must have been very difficult to him to accommodate my academic requirements, but he did so very elegantly. I would like to thank Dr. Honghui Zhou and Oak Ridge National Labs for assistance with the STEM micrographs presented in Chapter 5 of this thesis. A special thanks to Edna Deas from the Department of Materials Science and Engineering, who is one of the most caring and organized person I have ever met in the academic world.

I would like to thank my colleagues at RTI International for all their help. I am deeply indebted to Jackie Tapp from RTI International for expediting my processing requests. I would also like to thank Dr Mark Walters at Duke University for his help with the x-ray system. Special thanks goes to my friends, Jon, Geza, Sarabjit, Jessica (Nathu), Ruby, and Ashley for the fun times.

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CHAPTER 1: INTRODUCTION

1.1 Background

Heteroepitaxial growth of Ge on Si is a research topic of significant technological importance. This is primarily driven by the need for high-efficiency and high-bandwidth near infrared (NIR) photodetectors compatible with Si-based optoelectronic integrated circuits (OEICs), for fiber optical communications at the low-loss near infrared (NIR) wavelengths of 1.3 µm and 1.55 µm [1]. Complementary metal-oxide-semiconductor (CMOS) compatibility for discrete devices such as waveguides, modulators, and filters based on Si has been recently realized on Si substrates [2,3]. However, the fulfillment of NIR photodetectors remains an important challenge [4]. Despite the widespread interest, only two types of devices are available for NIR detection; solid-state InGaAs semiconductor diodes and vacuum tubes. Although InGaAs exhibits the best performances [5], its integration with Si CMOS technology is expensive [6]. Vacuum tubes, on the other hand, are fragile, expensive and relatively bulkier, and its applications are restricted to the high-end segment of NIR imaging such as military and scientific instruments. Since the band gap of Si is 1.1 eV [7], it cannot detect NIR wavelengths. On the other hand, SiGe alloys have been successfully used as detectors, but their operation is limited to a wavelength of 1.3 µm [8]. Hence, there exists a compelling need for the incorporation of pure Ge, with a direct band gap of 0.8 eV, to efficiently detect photons with wavelength of 1.55 µm. Germanium also offers the following advantages: (i) it has a very high absorption coefficient in the NIR range (about 10^4 cm^{-1} up to 1.55 µm) [9]; (ii) it has the same crystalline structure as Si, and can be grown by epitaxial
techniques such as chemical vapor deposition at low temperatures. Lastly, its compatibility with CMOS processing technology makes it very appealing as a low-cost, high-performance photodetector in Si OEICs.

1.2 Motivation

Ge epitaxial films on Si are commonly grown using molecular beam epitaxy or ultra-high vacuum chemical vapor deposition, using the two-step growth technique [10]. Although there have been some reports on the use of reduced pressure chemical vapor deposition (RPCVD) [11], and atmospheric pressure chemical vapor deposition (APCVD) [12] for Ge epitaxy, most of the available research has been performed primarily on ultra-high vacuum platforms [13,14] A comprehensive understanding of the impact of using RPCVD technique on the material and electrical properties of Ge epitaxial films is not fully understood.

1.3 Organization of Thesis

One of the primary goals of this thesis is to understand how to grow thick Ge epitaxial films on Si substrates with two-dimensional morphology, and a low density of threading dislocations, by the RPCVD technique. Chapter 2 reviews the fundamental issues associated with Ge epitaxy on Si and the methods utilized to mitigate these issues. It also introduces the two-step growth technique used to grow Ge films in this thesis. The impact of strain on the band gap of Ge has been discussed. Chapter 3 provides a detailed description on the CVD reactor used in this research. The importance of surface preparation and the growth conditions used to carry out Ge epitaxy have been discussed. In addition, materials
characterization tools utilized in this research have been described along with data from the epitaxial films. Chapter 4 introduces a novel technique of measuring the Poisson ratio of thin films using high-resolution x-ray diffraction (HRXRD) technique, which has been demonstrated on the Ge films grown in this research. Chapter 5 discusses the role of the Si/Ge interface on residual strain in Ge films. The importance of this interface on optoelectronic properties of the epitaxial film has been discussed. Chapter 6 presents the results from defect delineation studies on the films. Chapter 7 reviews the electrical performance of devices fabricated using these films, along with the method of device fabrication. Important performance parameters such as dark current and responsivity of the detectors have been presented.
References


CHAPTER 2: GERMANIUM EPITAXY ON SILICON

2.1 Introduction to Germanium-on-Silicon Mismatched Epitaxy

Silicon (Si) and germanium (Ge) form a solid solution over the entire composition range with a lattice constant that deviates only slightly from Vegard’s law [1,2].

\[ a_{SiGe} = a_{Si}(1-x) + a_{Ge}(x) \]  

At the extreme end of the alloy composition, pure Si and Ge have lattice parameters of 5.43Å [3] and 5.65Å [4] respectively, at 300 K. This gives rise to a large lattice mismatch of 4.2%, which causes two serious issues in Ge-on-Si mismatched epitaxy: (i) high surface roughness resulting from the Stransky-Krastanov (S-K) growth; and (ii) a high density of threading dislocations (TDs) in the Ge epitaxial layer.

Fig. 2.1: Schematic structure of (a) pseudomorphic growth and (b) strain relaxation via formation of misfit dislocations (adapted from Ref. 5).
High surface roughness hinders the process of integrating Ge devices with Si electronics because CMOS devices require planar processing. A high density of threading dislocations adversely affects the performance of Ge devices, due to the recombination centers introduced along the dislocations.

![Graph](image)

**Fig. 2.2:** Calculated critical thickness plotted against germanium fraction for pseudomorphic Si$_{1-x}$Ge$_x$ layers grown on bulk Si(001) substrates.

In the early stages of Ge epitaxial growth, the in-plane lattice constant of Ge is constrained by the Si substrate, resulting in the distortion of the cubic unit cell to a tetragonal cell. This growth mode is termed ‘pseudomorphic’ and is represented by Fig. 2.1a [6]. Beyond a critical thickness, $h_c$, it becomes energetically favorable to form misfit dislocations to relieve the strain energy in the epitaxial layer, which is given by [5]:

\[
E_{\text{strain}} = \begin{cases} 
\frac{1}{2} G b^2 h_c & \text{if } h < h_c \\
0 & \text{if } h \geq h_c
\end{cases}
\]
$h_c = \frac{G(1-\nu\cos^2 \alpha) \times (b/b_{\text{eff}}) \times [\ln(h_c / b) + 1]}{2Yf}$  \hspace{1cm} (2)

where $G$ is the average shear modulus of the interface, $\nu$ is the Poisson ratio, $\alpha$ is the angle between the dislocation sense vector and Burgers vector $b$, $b_{\text{eff}}$ is the in-plane component of the Burgers vector, $Y$ is the Young’s modulus and $f$ is the mismatch between the film and substrate. Since strain relaxation in Si-Ge system occurs via the nucleation of $a/2 <110> 60^\circ$ dislocations at the free surface [7,8], $\alpha$ is $60^\circ$, and $b/b_{\text{eff}}$ is 2.

The critical thickness for pseudomorphic growth of Si$_{1-x}$Ge$_x$ alloys on Si, calculated using Eq. 2, is shown in Fig. 2.2. In the case of Ge/Si heteroepitaxy, the critical thickness is approximately 1 nm [9], or seven monolayers of Ge.

2.2 Misfit Relaxation

Misfit strain relaxation in Ge/Si(001) heteroepitaxy commences with the nucleation of $60^\circ$ dislocation half-loops at the free surface, followed by glide to the interface [10]. The nucleation barrier for dislocations is relatively low and the process is glide limited, in contrast to the nucleation-limited mode observed in low-misfit materials [11]. The dislocation morphology consists of closely spaced misfit segments, with a high density of TDs on the order of $10^8$ - $10^9$ cm$^2$ [12]. Since the Burgers vectors of these dislocations are inclined at $60^\circ$ with respect to the interface, they are half as effective in relieving misfit strain at the interface, compared to a perfect $90^\circ$ misfit dislocation. The transformation from $60^\circ$ to $90^\circ$ misfit dislocation has been the subject of numerous investigations [13-16]. It was shown that perfect $90^\circ$ misfit dislocations are formed by the reaction between glissile $60^\circ$
dislocations with opposite screw components, at intersecting glide planes, for example, \(a/2[0\bar{1}\bar{1}]\) and \(a/2[\bar{1}01]\), on intersecting glide planes \((\bar{1}11), (\bar{1}1\bar{1})\) respectively (Fig. 2.3).

\[
\frac{a}{2}[\bar{1}01](\bar{1}1\bar{1}) + \frac{a}{2}[0\bar{1}\bar{1}](\bar{1}11) \rightarrow \frac{a}{2}[\bar{1}10](001), \quad \mathbf{b}_1^2 + \mathbf{b}_2^2 > \mathbf{b}_3^2
\]

As a result, a pure edge misfit dislocation is formed along the interface with its ends containing two triple nodes with reacted inclined 60° dislocations, also known as complementary dislocations. Subsequent studies showed that the nucleation of the second complementary 60° dislocation is influenced by the stress field of the existing 60° dislocation [77,17].

![Diagram](image)

**Fig. 2.3:** Formation of 90° misfit dislocation by the reaction between two glissile 60° dislocations (adapted from Ref. 18).
Such a reaction is energetically favored due to the reduction in the total energy of the dislocations. The total energy of a dislocation comprises of two components; (i) an elastic component associated with the strained bonds, and (ii) core energy of the dislocation. The elastic component is proportional to \(b^2\), where \(b\) is the magnitude of Burgers vector. The core energies of the 60° as well as the 90° dislocation have been estimated numerically using the Stillinger-Weber interatomic potentials [19,20]. The core structure of the 60° dislocation at the Ge-Si interface consists of an octaring (eight-atom ring), with the extra half-plane located in the Si substrate and a dangling bond every 3.84Å of the dislocation line. The calculated value of the core energy of the dislocation line was 1.13 eV/Å. On the other hand, the core structure of the 90° dislocation consists of a pentaring on the on the Si-side and a septaring on the Ge-side (five-atom and seven-atom ring, respectively) with a core energy of 0.56 eV/Å and no dangling bonds. Thus, the formation of 90° misfit dislocations results in the reduction of the elastic as well as core energy of the dislocations. The dangling bonds present along the core of the 60° dislocation have a profound effect on the electrical properties of Ge [21]. It is believed that these bonds create generation centers that contribute to the leakage currents in devices [22].

2.3 Germanium Epitaxy on Silicon

In the next sections, some of the important methods used to overcome the issues associated with Ge/Si(001) heteroepitaxy, discussed in the preceding sections, have been reviewed. The methods used for growing Ge on Si substrates can be broadly classified into: (i) growth using SiGe buffer layers; (ii) direct growth of Ge on Si; and (iii) selective growth.
2.3.1 Epitaxial growth using SiGe buffer layers

The first successful approach for growing epitaxial Ge layers on Si was reported by Luryi in 1984 [23]. This study made use of a graded SiGe buffer layer, grown in a molecular beam epitaxy chamber, to obtain a low density of threading dislocations in the Ge layer. This was later modified by Fitzgerald [24-26] by using optimized SiGe graded buffer layers grown by ultra-high vacuum chemical vapor deposition process. A grading rate of approximately 10% Ge per micron was adopted to minimize dislocation nucleation rates. The growth temperatures employed for different SiGe compositions enabled the film to relax by gliding existing threading dislocations. At 50% Ge composition, an ex situ chemical mechanical polishing step was used to remove crosshatch surface roughness and reduce the dislocation pile-up formation that hinders dislocation gliding. This approach successfully demonstrated Ge films with threading dislocation density less than $2 \times 10^6$ cm$^{-2}$, but required a 10 µm thick buffer layer.

2.3.2 Growth without SiGe buffer layers (two-step growth technique)

Direct epitaxial growth of Ge on Si has also been carried out without utilizing SiGe buffers layers. In this case, a two-step growth technique was used to prevent S-K growth of Ge, with subsequent annealing to decrease the density of threading dislocations in the film [27-29]. In the first growth step, a thin Ge buffer layer of thickness 30 - 60 nm is grown on Si at temperatures ranging from 320°C to 360°C. At such low growth temperatures, the low surface diffusivity of Ge is thought to suppress islanding of Ge. In the second step, growth temperature is increased to greater than 600°C to achieve higher growth rates and better
crystal quality. If the buffer layer is thick enough (> 27 nm), the Ge atoms are no longer influenced by the lattice mismatch and homoepitaxial Ge growth results, with two-dimensional morphology retained at elevated temperatures [30]. The threading dislocation density of the as-grown film is typically on the order of $10^8 - 10^9 \text{ cm}^{-2}$. In situ post-growth annealing is carried out at temperatures greater than 750$^\circ$C, which reduces defect density by up to two orders of magnitude. Different approaches for annealing, such single step [31,32], cyclic annealing [27] have been reported to give comparable results. This two-step growth technique was used to grow the epitaxial Ge films in this research.

2.3.3 Selective growth

Selective area epitaxy is the use of patterned silicon dioxide or nitride materials as masks to selectively grow Ge epitaxial films on the surface of Si. If the growth region is smaller than 40 µm, then this technique also reduces threading dislocation density, since dislocations are able to glide to the edge of the mesas and annihilate [33]. Using this approach Luan et al. demonstrated threading dislocation densities of $2.6 \times 10^6 \text{ cm}^{-2}$ [29].

To further reduce the defect density, selective growth was applied to epitaxial necking [34] as well as lateral overgrowth [35], wherein Ge epitaxy is carried out in high aspect ratio windows in the dielectric layer. In the case of the epitaxial necking, Ge was grown on Si through 100 nm diameter holes patterned in a silicon dioxide mask. It was found that the threading segments were effectively blocked by the oxide sidewall resulting in a defect-free Ge surface. The mechanism is suspected to be either due to the alteration of the stress state of Ge in the small holes, or due to the action of image forces that force defects to
glide to the sidewall. In the case of lateral overgrowth, a larger patterned window of 500 nm was used. It is believed that the presence of facets during growth direct dislocations towards the outer edges of the trenches where they are removed.

2.4 Band Structure of Silicon and Germanium

The presence of residual strain has a significant effect on mechanical [36], optical and electronic properties [37] of materials. Si and Ge both possess a diamond cubic unit lattice (Fig. 2.4a). This structure can be viewed as two interpenetrating face-centered cubic lattices displaced from one another by the translation (¼¼¼). Each atom in the diamond lattice is covalently bonded to four neighboring atoms. The first Brillouin zone of the reciprocal space of Si and Ge are shown in (Fig. 2.4b), which shows the high symmetry directions and points.

![Fig. 2.4: (a) Diamond cubic lattice of Si, Ge and (b) First Brillouin zone showing the high symmetry directions and points [38].](image_url)
Figure 2.5 depicts the band structure of Si and Ge, with energy plotted against the wave vector for some of the important directions in k-space. Both Si and Ge are indirect band gap materials with the valence band edge at the Γ point at $k = 0$ consisting of degenerate light-hole, heavy-hole and a split-off band. The conduction bands in Ge have a minima at the L-points of the Brillouin zone along the [111] directions. As there are eight $L$ points indicated by the hexagons in Fig. 2.4b, the conduction band minimum in Ge is eightfold degenerate. Since the conduction band in silicon has six minima along the [100] direction at the X-points, it is six fold degenerate.

**Fig. 2.5:** Calculated band energy structure of Si on the left and Ge on the right [38].

2.4.1 *Influence of strain*

There are two components of strain which changes the band structure of Ge: (i) hydrostatic strain arising due to the fractional volume change shifts the energy of a band; and
(ii) shear strain splits the degeneracy of bands e.g. the valleys in the conduction band and the
degenerate light and heavy hole valence band edge. The influence of these components on
the band structure and splitting of the degenerate valence bands (and of indirect conduction
bands) has been treated in detail using model-solid theory, by Van de Walle et al. [39,40]
and Pollak et al. [41]. Band calculations based on this theory indicate that in-plane tensile
strain decreases the direct as well the indirect band gap of Ge. In-plane compressive strain in
Ge, on the other hand, leads to the opposite effect of increasing band gap, which is
detrimental for longer wavelength detection capability [42].

2.5 Strained Germanium Epitaxial Films

Ge epitaxial films grown on Si have been found to have a residual in-plane strain that
is tensile in nature. Residual strain in thin films consists of three components: (i) lattice misfit
strain; (ii) thermal misfit strain; and (iii) defect strain. Since the critical thickness for
pseudomorphic epitaxial growth of Ge on Si is ~1 nm (Section 2.1), the misfit component is
expected to be fully relaxed for films grown at high temperatures. When cooled to room
temperature, tensile strain accumulates in Ge due to the difference in coefficient of thermal
expansion (CTE) between Si and Ge [43,44]. The in-plane thermal misfit strain is expected
to be unrelaxed since the mechanism of relaxation involves the nucleation of dislocations and
glide in a relatively thick film. The theoretically expected in-plane thermal misfit strain ($\varepsilon_{||}$)
can be calculated using [45]:

$$\varepsilon_{||} = \int \frac{\tau_{Ge}}{\tau_{Ge} - \tau_{Si}}\left[\alpha_{Ge}(T) - \alpha_{Si}(T)\right]dT$$  (3)
where $T_{RT}$ and $T_{GR}$ are the room temperature and growth temperature respectively, $\alpha_{Ge}$, $\alpha_{Si}$ are the thermal expansion coefficients of Ge [46] and Si [47] respectively, and are given by

$$\alpha_{Si}(T) = (3.725 \times \{1 - \exp[-5.88\times10^{-3}(T - 124)]\} + 5.548\times10^{-4}T)\times10^{-6}(K^{-1})$$ \hspace{1cm} (4)$$

$$\alpha_{Ge}(T) = 6.05\times10^{-6} + 3.6\times10^{-9}T - 0.35\times10^{-12}T^2 (C^{-1})$$ \hspace{1cm} (5)$$

Fig. 2.6: Experimental and calculated in-plane strain in Ge epitaxial films versus growth temperature (adapted from Ref. 44).

Figure 2.6 compares the theoretically calculated strain using Eq. 3, and the experimentally obtained in-plane strain reported in Ref. [44], for Ge films grown at different growth temperatures. The discrepancy between the theoretical and experimental strain is not
well understood. In-plane strain is generally calculated from the experimentally measured perpendicular strain and the elastic constants of the bulk counterparts using [45,48]

$$
\varepsilon_\perp = \frac{-2\nu}{(1-\nu)} [\varepsilon_\parallel] = \frac{-2C_{12}}{C_{11}} [\varepsilon_\parallel] 
$$

(6)

where $C_{12}$ and $C_{11}$ are the bulk elastic compliances and $\nu$ is the Poisson ratio of Ge. This is because in-plane strain cannot be measured directly using techniques such as XRD [49]. However, literature indicates that elastic and plastic properties of thin films can vary significantly from bulk materials [50,51]. Hence, a precise knowledge of the elastic constants such as the Poisson ratio of Ge films is required for accurate determination of in-plane strain.

Secondly, the low temperature Ge buffer layer at the Si/Ge interface serves as a 2-D growth template for the subsequent growth of the high temperature Ge layer. The characteristics of this layer can have a profound impact on strain and overall optoelectronic properties of the epitaxial film. Hence, it needs to be well characterized. The measurement of the Poisson ratio of Ge thin films using XRD is presented in Chapter 4, and experimental data characterizing the low temperature buffer layer and the Si/Ge interface is discussed in Chapter 5.
References


CHAPTER 3: MATERIALS GROWTH AND CHARACTERIZATION

3.1 Background

The first successful demonstration of germanium (Ge) epitaxy on silicon (Si) was reported by Luryi et al. [1], using molecular beam epitaxy (MBE). Although many universities still use MBE for basic research, it is not commonly used for mass production in comparison with chemical vapor deposition (CVD) techniques. Some important reasons for the dominance of CVD in commercial environments are: (i) traditionally, most fabrication plants have used CVD for Si epitaxy since the 1960s; (ii) high-purity gas sources for epitaxy are readily available; and (iii) MBE has the disadvantage of high particulate density, arising from material deposited on the walls of the chamber, which over time fall off creating particles.

3.2 CVD Reactor Design and Setup

Chemical vapor deposition is a thin-film growth technique, whereby a solid material is deposited from a vapor by a chemical reaction on a heated substrate. A number of different methods have been developed for materials growth, which can be conveniently classified into: (i) ultra-high vacuum chemical vapor deposition (UHVCVD) at growth pressures of less than 10 Pa [2,3]; (ii) low pressure vapor deposition (LPCVD) with pressures ranging from $10^1$ to $10^3$ Pa [4]; and (iii) reduced pressure vapor deposition (RPCVD) with pressures ranging from $10^3$ to $10^4$ Pa. UHVCVD was first proposed by Meyerson et al. [3] to enable epitaxial growths at lower temperatures, and is commonly used for growing Ge films on Si
Epitaxial growth of Ge has also been carried out using RPCVD [6], and low-energy plasma-enhanced chemical vapor deposition [7,8]. Germanium films studied in this research were grown in a commercially available RPCVD system. The following sections provide a description of this system.

### 3.2.1 Gas dispensing system

A schematic of the RPCVD system used in this research is shown in Fig. 3.1. The system is designed for recipe-driven automatic operation for unattended process runs. The gases flow through mass flow controllers (MFC) from the left into the reactor tube. The precursor used for Ge epitaxy was germane (GeH₄), which is readily available from several vendors. Germane can be diluted with argon, helium, hydrogen or nitrogen in order to provide concentrations of less than 100%. This study used a 1% germane-hydrogen mixture by volume. The flow rate of GeH₄ during growth was maintained at 50 standard cubic centimeters per minute (sccm). The other precursors connected to the CVD system are 10% silane-hydrogen mixture for the epitaxial growth of Si, 0.01% diborane-hydrogen mixture for boron doping, and 0.01% phosphine-hydrogen mixture for phosphorous doping. The diluted dopant-hydrogen mixtures permit p-type and n-type doping of Si and Ge in the range of 10¹⁷ cm⁻³ to 10¹⁹ cm⁻³. The main components of the gas delivery manifold are the carrier gas supply, inject/vent lines, and gaseous precursors. Precursor material was introduced into the reactor tube using hydrogen (H₂) as the carrier gas, through the inject line. Hydrogen was used as the carrier gas since it is known to passivate surfaces, rendering them inert to contaminants that would otherwise prevent epitaxy [9,10]. Furthermore, it is believed that H₂
may actually be beneficial for epitaxy, contributing to interface abruptness by reducing surface segregation and diffusion during growth [11].

Fig. 3.1: Schematic of the RPCVD system used in this research.

A H\textsubscript{2} flow rate of 2 standard liters per minute (slm) was constantly maintained in the tube through the inject line. Since H\textsubscript{2} is used ubiquitously during the growth process, its purity is of importance. Purification was achieved by passing H\textsubscript{2} through an in-line palladium
membrane purifier. Purifiers operate via pressure driven diffusion and provide less than one part-per-billion purity with any inlet gas quality. Impurities removed include oxygen, water, carbon monoxide, carbon dioxide, nitrogen and all hydrocarbons. Coupled with the inject line is a vent line, which is a path through which a reactant flow can be diverted, if it is not desired within the reactor tube at a particular time. A H₂ flow rate of 1 slm was constantly maintained in the vent line.

The gases from the reactor tube and vent line combine downstream and pass though a pyrolysis furnace that decomposes the hazardous material before they are released to the exhaust. During growth, it is important to ensure that flow of gases in the inject and vent line is properly balanced in order to prevent backstreaming into the reactor tube, which would cause undesirable effects such as gas phase nucleation and poor quality of epitaxial growth.

3.2.2 Reactor and gas flow dynamics

The reactor comprises of a quartz tube that houses a silicon-carbide coated graphite susceptor. The tube is surrounded by water-cooled radio frequency coils that are used to heat the susceptor. The temperature of the susceptor was monitored using an embedded thermocouple. The system does not have load-lock capability; substrates were manually loaded on the susceptor after venting the chamber to air. For growth of films of uniform thicknesses and composition, the gas flow patterns in the reaction chamber are of greatest importance. Since a complete description of the gas flow dynamics is beyond the scope of this thesis, it suffices to say that the gas flow in the RPCVD system was considered to be
laminar. Theoretically, laminar flow is characterized by the Reynolds number, \( R_e \), which is a dimensionless parameter.

\[
R_e = \frac{\rho \times V \times D}{\eta} \quad (1)
\]

where \( \rho \) is density of the gas, \( V \) is the velocity, \( D \) is the diameter of the tube and \( \eta \) is the viscosity. At \( R_e \) less than 1100 the flow is laminar, while at \( R_e \) greater than 2100 the flow is turbulent. The range 1100 to 2100 is characterized as mixed flow regime [12]. No specific experiments were carried out to determine the Reynolds number for the gas flows used during growth. The realization of good film morphology, established on the basis of materials characterization studies, confirmed the existence of laminar flow conditions. The pressure during growth was maintained at 40 Torr. The minimum pressure at which the system can operate is 10 Torr. The desired pressure in the tube was attained using a throttle valve in series with a mechanical pump and was monitored using gauge, G1.

3.2.3 Deposition sequence

When the appropriate precursor material, in this case \( \text{GeH}_4 \), reaches the heated substrate, thermal decomposition takes place, leading to the deposition of a thin film of Ge on the substrate. The sequence of events taking place during a CVD reaction is shown in Fig. 3.2 and can be summarized as follows:

1. Reactant gases enter the reaction chamber.
2. Diffusion of reactants through the boundary layer.
3. Contact of the reactants with heated substrate.
4. Chemical reaction on the surface of substrate.

5. Diffusion of the gaseous by-products away from the surface, through the boundary layer.

Fig. 3.2: Sequence of events during deposition and important reaction zones (adapted from Ref. 13).

3.2.4 Boundary layer

In the case of laminar flow, the velocity of the gas, concentration of the vapor species, and temperature profiles near the substrate surface differ from the main gas stream. Thus a velocity boundary layer, a concentration boundary layer, and a thermal boundary layer exist. The velocity and thermal boundary layers in a laminar flow are sketched in Fig. 3.3.
Fig. 3.3: Schematic of a reactor tube showing: (a) velocity boundary layer; and (b) temperature boundary layer at the surface of the substrate (adapted from Ref. 13).

A steep velocity gradient is noticeable in Fig. 3.3a, going from maximum velocity at the center of the tube to zero velocity at the surface of the wall. The temperature boundary layer is similar to the velocity layer (Fig. 3.3b). The flowing gases heat rapidly as they come in contact with the hot substrate, resulting in a temperature gradient. As the gases flow down the tube, they become gradually depleted giving rise to a concentration boundary layer. The boundary layer starts at the inlet of the tube and increases in thickness until the flow becomes stabilized. The precursor material has to diffuse through the boundary layer to reach the substrate surface and cause a reaction. The thickness of this boundary layer ($\Delta$) is inversely proportional to the square root of the Reynolds number and is given by [13]:

$$\Delta = \frac{x}{\sqrt{R_e}}$$  \hspace{1cm} (2)

where $x$ is the distance from the inlet in the flow direction. The thickness of the boundary layer decreases with decreasing pressure and temperature. The rate-limiting step in a CVD
reaction is generally determined by either surface reaction kinetics or by mass transport. In the case of control by surface reaction kinetics, the rate is dependent on the concentration of reactant gases. This usually occurs when the boundary layer is thin, the temperature is low, and there is a surplus of reactants. On the other hand, if the process is limited by mass-transport through the boundary layer, the rate limiting step is the diffusion rate of the reactants and by-products through the boundary layer. Since LPCVD and RPCVD reactors operate at pressures in the Torr range, the reactions are generally mass transport limited. Surface kinetic controlled reactions are observed when the pressure is in the millitorr range, such as in UHVCVD and MBE systems.

3.3 Silicon Surface Passivation

Each surface atom in <100>-oriented Si and Ge is bonded to two atoms beneath the surface layer with two dangling bonds pointing upwards. A clean Si surface reacts instantly with oxygen when exposed to air, forming a native oxide of thickness on the order of 1 nm. Such large concentration of interfacial oxygen prevents the growth of epitaxial layers, while smaller concentrations have been reported to cause nucleation of defects such as dislocations and stacking faults [14,15]. Surface passivation of Si is achieved by termination of the dangling bonds with hydrogen. A commonly used method for surface passivation is wet chemical treatment with hydrofluoric acid (HF). This treatment is a crucial step in the surface preparation of Si substrates [16,17]. The use of HF concentration of about 5% in water has been found to be optimal [18], whereas surfaces treated with higher concentrations of HF have a higher fluorine content, and are more easily oxidized in water. Furthermore, carbon as
well as oxygen concentration increase with HF concentrations lower or higher than 5% [19]. Carefully prepared surfaces have oxygen and carbon coverage of a few percent of a monolayer (ML) [20]. Such hydrogen passivated surfaces have been shown to have remarkable resistance against contamination in air for several minutes and vacuum for several hours [21]. Temperature programmed desorption experiments carried out by Meyerson et al. [22] in a UHVCVD system, established that the rate of hydrogen desorption from an HF-treated surface is thermally activated, with an activation energy of 59.4 kcal/mole and pre-exponential factor of $2 \times 10^{15}$. These values predicted a desorption rate of 0.005 ML/min of hydrogen at 400°C, with the rate increasing significantly above this temperature. The stability of hydrogen on a Si surface for temperatures up to 400°C provides a large time window for initiating epitaxy. Hence, in order to properly utilize hydrogen passivation, growth was initiated prior to hydrogen desorption. Using this approach, Meyerson et al. demonstrated low defect density, single crystalline Si and Si/Ge alloys on Si substrates, in the temperature range of 425°C to 650°C.

### 3.3.1 Surface preparation

The importance of surface passivation has been reviewed in the preceding section. This section describes the procedure that was followed to obtain such a surface. A typical surface preparation prior to epitaxial process started with an *ex situ* clean. The purpose of this clean was to remove organic and metallic impurities from the substrate surface. Hydrocarbon contaminants such as oils and organic residues may be removed by solvents which dissolves the contaminants. The substrate was rinsed sequentially in acetone followed by isopropanol.
The application technique involved spraying the solvent on the substrate for a few minutes each time. This was followed by a rinse in de-ionized (DI) water. Next the substrate was immersed in a heated piranha etch, consisting of a 1:1 mixture of sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂). This step removes organic residue from the Si wafers and also forms a 10 nm thick surface oxide. The substrate was then rinsed thoroughly in DI water to remove any traces of piranha etchant. The final step involved dipping the substrate in 5% aqueous hydrofluoric (HF) acid to remove the oxide and passivate the surface with hydrogen. Substrates used in this study were p-type, Si (001). The resistivity and thickness specifications of the substrate were 0.005-0.009 Ω-cm and 450-550 µm respectively. The procedure for surface preparation is summarized below:

1. Solvent clean using acetone and isopropanol.
2. De-ionized water rinse.
3. Ten minute dip in piranha etchant at 120-150°C.
5. Four minute dip in 5% aqueous HF acid at ambient temperature.

After the completion of step 5, the substrate was loaded into the reactor tube, which was immediately evacuated to a pressure of 40 Torr.

### 3.4 Epitaxial Structure and Growth Steps

Traditional CVD processes employed a high temperature *in situ* bake (> 1000°C) in H₂, prior to epitaxial growth. The purpose of this bake was to remove any carbon and oxygen contaminants on the Si surface that would cause the nucleation of interface defects. Ghidini
et al. [23,24] studied the oxidation of Si as function of the partial pressure of water and temperature in a UHV system (Fig. 3.4). Their results showed that an oxide-free surface could be maintained at lower temperatures, if the pressure in the chamber was reduced. Subsequently, the pioneering work of Meyerson et al. [9] demonstrated high quality epitaxial growth in a UHVCVD system without the high temperature bake, by taking advantage of the hydrogen surface passivation.

**Fig. 3.4:** Equilibrium conditions for the formation of an oxide-free Si surface in the presence of wafer vapor (adapted from Ref. 23).

Figure 3.4 indicates that as temperature decreases, surface oxide formation is favored in the presence of water vapor. However, the oxidation reaction is expected to be kinetically suppressed at 360°C due to the lower rate of H₂ desorption from the Si surface at this
temperature. Hence, based on the review of existing literature, it was felt that epitaxy should be initiated on a hydrogen passivated surface without using an *in situ* bake.

### 3.4.1 Growth structure

Figure 3.5 shows the epitaxial layers grown on Si and their respective growth conditions. After loading the substrate into the reactor tube, Ge epitaxy was carried out using the two-step growth technique. The structure comprised of three layers: (i) low-temperature Ge buffer layer; (ii) high-temperature Ge layer; and (iii) n-type Ge cap layer. In between steps (ii) and (iii), a high temperature anneal was carried out to reduce the density of threading dislocations (TDs) in the film.

![Fig. 3.5](image)

**Fig. 3.5:** (a) Schematic of the epitaxial structure grown on Si substrates and (b) thickness of each layer, and growth conditions used for the individual layers.
3.4.2 Low temperature Ge buffer

The Ge buffer was grown at a temperature 360°C, using a flow rate of 50 sccm of GeH₄. The thickness of the Ge films was measured using cross-sectional scanning electron microscopy. Figure 3.6 plots film thickness as a function of growth time for a series of Ge films, grown using the conditions discussed in the preceding section. The slope of the graph gives a growth rate of 8.7 Å/min, which was used to grow 50 - 60 nm thick buffer layers.

![Graph](image)

**Fig. 3.6:** Measured thickness of the Ge buffer layer as a function of growth time at 360°C.

An interesting feature of Fig. 3.6 is that the straight line fit does not pass through the origin, but intersects the x axes at about 20 min. This seeming delay in the initiation of epitaxial growth is known as incubation or induction time. Racanelli *et al.* [25] observed an incubation time of 10 min during Si₁₋ₓGeₓ epitaxy in a UHVCVD system, and proposed that this was related to the presence of an interfacial oxide layer. Since GeH₄ is known to react
with silicon dioxide to form the volatile species GeO$_x$ [26], it was suggested that epitaxial growth initiated only after the volatilization of the interfacial oxide was complete. Halbwax et al. [27] studied Ge growth in situ, by reflection high-energy electron diffraction (RHEED) patterns. They observed that the growth rate of Ge during the first 15 min of growth was only 0.02 nm/min. After 15 min, the growth rate increased to 0.61 nm/min. The slower rate was attributed to deposition of Ge on a Si surface, whereas the faster growth rate was related to the deposition of Ge on a Ge surface. The kinetics of hydrogen adsorption (due to germane decomposition) and desorption on a Si surface were surmised to be faster compared to a Ge surface. This explanation is in agreement with the findings of Surnev et al. who reported a lower activation energy of 34.6 kcal/mole for hydrogen desorption from a Ge surface compared to 59.4 kcal/mole for a Si surface [28].

3.4.3 High temperature Ge growth

Since the growth rate of Ge at 360ºC is very low, in the next step, epitaxial growth was carried out at an elevated temperature. Figure 3.7 shows the growth rate of Ge as a function of inverse temperature at a pressure of 100 Torr. An Arrhenius plot of the growth rates in the temperature range of 500ºC - 700ºC yielded activation energy of 0.25 eV, which is consistent for diffusion limited growth [29]. The low activation energy permits high growth rates of Ge at considerably lower temperatures. This result is also in agreement with the value of 0.29 eV reported by Hartmann et al. [30], for epitaxial growth of Ge carried out at a pressure of 20 Torr. In order to reduce the impact of the boundary layer thickness, the growth rate of Ge was evaluated at a pressure 40 Torr and 700ºC. These parameters yielded a
Ge growth rate of approximately 3.1 Å/s. The thickness of the Ge layer grown in this step varied from 0.5 - 4.0 µm.

Fig. 3.7: Arrhenius plot of Ge growth rate versus inverse temperature using germane.

3.4.4 Dislocation anneal

The as-grown Ge film has a high density of threading dislocations. To reduce TDs in the film, in situ annealing in H₂ was carried out prior to the growth of the n⁺-Ge cap layer. Two kinds of anneals have been reported in literature for Ge [31] as well as GaAs growth on Si [32]: (i) cyclic anneal; and (ii) single-step anneal. It is known that at high temperatures 60⁰ threading segments glide and interact with each other and are annihilated. The anneal temperature and time used for the single-step dislocation anneal in this work was 900°C and 1 h respectively.
3.4.5  \( n^+\)-Ge cap layer

After the completion of the dislocation anneal, the structure was capped with a 1200 Å thick, n-type Ge layer grown at a temperature of 700\(^\circ\)C. N-type doping of the Ge layer was achieved by introducing 0.01% phosphine-hydrogen mixture into the reactor tube. The flow rate of the mixture was adjusted to obtain a carrier concentration of \(4 \times 10^{18}\) cm\(^{-3}\) in the cap layer. The carrier concentration in this layer was determined by Hall measurements [34].

In conclusion, a p-i-n structure was grown using the RPCVD technique, comprising of an intrinsic Ge layer, sandwiched between a p-type Si substrate, and an n-type Ge cap layer. At the end of the growth process, the susceptor was cooled to room temperature in the presence of H\(_2\).

3.5  Material Characterization Techniques

This section reviews the characterization methods used to analyze the films. Thickness and morphology of the films was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The residual strain in the films was determined by high-resolution x-ray diffraction (HRXRD). The chemical composition of the films was obtained using secondary ion mass spectroscopy (SIMS), and the optical property of the films was determined by ultraviolet-visible spectroscopy.

3.5.1  Optical absorption spectroscopy

The intrinsic absorption of photons across the band gap of a semiconductor is the dominant optical absorption process in semiconductor materials. The magnitude of the
absorption is described in terms of an absorption coefficient \( \alpha \), which is a function of the wavelength of light. The absorption coefficient is related to the intensities of the incident \( (I_0) \), transmitted light \( (I_T) \) and the film thickness \( (t) \) by the expression [33]:

\[
I_T = I_0 \exp(\alpha \times t)
\]  

(3)

Transmission measurements were carried out using a Perkin Elmer Lambda 9 spectrophotometer. The instrument is microcomputer-based double beam spectrophotometer covering the wavelength range 185 nm to 3200 nm. Ge epitaxial films on Si were placed in the path of the sample beam \( (I_T) \), and the reference comprising of the substrate used for growth was placed in the path of the reference beam \( (I_0) \). The instrument measures the ratio of the two transmitted intensities \( (I_T/I_0) \), which was used to calculate the absorption coefficient using Eq. 3 [34]. The thickness of the film required for the calculation of the absorption coefficient was measured using XSEM. The transmittance data can be used to determine the band gap of a material [35]. For indirect material \( \alpha^{1/2} \) is plotted against the photon energy \( (h \nu) \); the extrapolated intercept on the \( h \nu \) axes gives the semiconductor band gap, whereas for direct band gap material a plot of \( \alpha^2 \) against \( h \nu \) yields the band gap.

3.5.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is commonly used in semiconductor applications to view surfaces, and perform cross-section analysis to determine dimensions and study interfaces [36]. In this technique, a beam of electrons is scanned across the sample, ejecting secondary and backscattered electrons, which are captured by a detector to produce an image. Contrast in samples comprising of materials with different atomic number is
obtained using backscattered electrons, since backscattering coefficient increases with atomic number. On the other hand, secondary electrons are emitted from the top 10 nm or so of the sample and the main contrast-enchantment feature is sample topography. SEM images reported in this thesis were obtained with secondary electrons. Plan-view SEM was used to study the morphology of the as-grown epitaxial films, whereas cross-sectional SEM (XSEM) was used to determine film thickness.

3.5.3 X-ray diffraction

Double-axes x-ray diffraction is used to measure the strain and composition in epitaxial films [37]. This research made use of a Philips PANalytical X’Pert system for the measurement of the lattice parameter of the as-grown Ge films. The incident Cu K$_\alpha$ radiation with a wavelength of 0.154 nm was conditioned using four Ge 220 symmetric crystals. The X-rays hit the samples at an incident angle $\omega$ and were detected at an angle $2\theta$. The diffractometer allows the rotation of the sample around all three axes and movement it in all three directions. Since strain changes the lattice parameter of a material, an accurate knowledge of strain is important for studying its impact on the optoelectronic properties of Ge films.

3.5.4 Secondary ion mass spectroscopy

Secondary ion mass spectroscopy (SIMS) is widely used for analyzing trace elements in semiconductors thin films. During SIMS analysis, the sample surface is slowly sputtered away, while the emitted secondary ions are continuously analyzed using mass spectrometry.
This produces information on the concentration profile of the various elements as a function of depth, called a depth profile. SIMS was primarily used in this research to determine the interfacial concentration of carbon and oxygen, which has a significant impact on the quality of Ge epitaxial growth, as discussed in the preceding sections.

3.5.5 Atomic force microscopy

Atomic force microscopy (AFM) operates by measuring the forces between a probe and the sample [38]. There are three modes of imaging using AFM: (i) contact mode; (ii) non-contact mode and; (iii) tapping mode. This research employed a tapping mode AFM for topographical imaging of the Ge films. The images were processed to obtain a root-mean-square (RMS) roughness of the surface, which is the standard deviation in the thickness values within a given area.

3.6 Material Characterization Results

The following sections review the characterization results of the buffer layer and the final (thick film) structure. The final structure includes the 0.12 µm thick, n-type Ge cap layer.

3.6.1 Buffer layer characterization by SEM and AFM

Figure 3.8 shows cross-sectional SEM images of the evolution of the buffer layer morphology with growth temperature. Ge grown directly on Si at 700ºC has a 3-D morphology associated with the S-K growth mode (Fig. 3.8a).
**Fig. 3.8:** Tilted cross-sectional SEM micrographs of Ge buffer layer grown at: (a) 700°C, (b) 500°C, and (c) 360°C.

**Fig. 3.9:** 1 µm x 1 µm tapping mode AFM image of the surface of a 55 nm thick Ge buffer layer grown at 360°C, with a RMS roughness of 0.7 nm.
The surface roughness of the film decreases as the growth temperature is lowered from 700°C to 500°C (Fig. 3.8b). However, at a growth temperature of 360°C, Ge exhibits 2-D growth mode (Fig. 3.8c). The transition to 2-D growth mode was confirmed by taking AFM images of the surface of the Ge buffer grown at 360°C (Fig. 3.9). The RMS roughness of the surface was determined to be 0.7 nm, which establishes that the low-temperature buffer layer provides a two-dimensional nucleation layer for the subsequent high temperature epitaxy step.

3.6.2 SEM and AFM characterization of thick films

Figure 3.10a is a plan-view SEM image, showing the surface morphology of a 0.7 µm thick Ge film. Figure 3.10b is a XSEM micrograph of the same film. Figure 3.10c is a XSEM micrograph of a 4.0 µm thick Ge film. The plan-view image of this film did not show any significant surface features. The micrographs confirm the 2-D growth mode of Ge films is retained for film thicknesses up to 4 µm. Both the films were annealed using the process discussed in Section 3.4.4.

Figures 3.11a and b are AFM images of the surface of a 1.7 µm thick Ge film before and after dislocation annealing respectively. The dark contrasts in the images are due to pits corresponding to the surface termination of mixed dislocations [39]. The densities of the pits are approximately 1 x 10^7 cm^-2 and 8 x 10^7 cm^-2 for the annealed and unannealed film respectively. The process of annealing the Ge epitaxial films results in an order of magnitude decrease in the density of threading dislocations. The RMS roughness of the unannealed and annealed films is 1.13 nm and 1.1 nm respectively.
Fig. 3.10: Two-dimensional growth of Ge films grown on Si(001) substrates by the two-step growth technique. (a) plan-view SEM image of a 0.7 µm thick Ge film; (b) XSEM image of a 0.7 µm thick Ge film; (c) XSEM image of a 4.0 µm thick Ge film.

Fig. 3.11: 5 µm x 5 µm tapping mode AFM images of the surface of Ge epitaxial films: (a) unannealed 1.7 µm thick Ge film; and (b) annealed 1.7 um thick Ge film. White arrows denote threading dislocations.
3.6.3 HRXRD characterization of thick films

High-resolution x-ray diffraction was used to measure the residual strain present in the films. Figure 3.12 shows the $2\theta$-ω XRD profiles of the 1.7 µm thick films discussed in the previous section. The most straightforward way to determine strain in the film is to measure the $2\theta$ Bragg ($2\theta_b$) position of the Ge (004) peak and compare it to bulk Ge. Since $2\theta_b$ positions are related to the lattice parameter via Bragg’s law, a shift in position gives the magnitude of the perpendicular strain present in the film.

![HRXRD scans of (004) planes in Ge epitaxial films on Si(001) substrates.](image)

**Fig. 3.12:** $2\theta$-ω HRXRD scans of (004) planes in Ge epitaxial films on Si(001) substrates.

In-plane strain can be readily calculated using the compliance values of bulk Ge (see Eq. 6 in Chapter 2). Note the shift in peak position in both the films, shown in Fig. 3.12, towards larger $2\theta_b$ angles, relative to unstrained Ge, commensurate with the presence of...
compressive strain along the growth direction. Annealing the film at 900°C, results in a noticeable impact on the symmetry of the Ge diffraction peak. It has been hypothesized that this asymmetry is associated with the diffusion profile of Si in Ge during annealing [40]. The asymmetry has been discussed in more detail in Chapter 5.

Table 3.1: Calculated and measured in-plane ($\varepsilon_{||}$) and perpendicular strain ($\varepsilon_\perp$) in Ge thick films.

| Thickness (µm) | $2\theta_B$ (°) | $\sigma_\perp$ (Å) | % $\varepsilon_\perp$ | % $\varepsilon_{||}$ |
|---------------|-----------------|-------------------|-----------------------|----------------------|
| Bulk Ge       | 65.995          | 5.658             | -                     | -                    |
| 0.7 µm unannealed Ge | 66.096       | 5.650             | -0.136                | +0.205               |
| 1.7 µm unannealed Ge | 66.081       | 5.652             | -0.106                | +0.159               |
| 2.2 µm annealed Ge  | 66.084       | 5.651             | -0.120                | +0.178               |
| 3.5 µm annealed Ge  | 66.091       | 5.650             | -0.129                | +0.194               |

Table 3.1 shows the residual strain in the perpendicular and in-plane direction for select Ge films of varying thicknesses. In-plane tensile strain arises due to the differential thermal expansion experienced by the Ge film during cooling from growth temperature to room temperature (calculated using Eq. 6 in Chapter 2, and Poisson ratio 0.25 in Chapter 4, and Ref. 41). For growth carried out at a temperature of 700°C, the theoretically expected strain is approximately +0.24%. The average strains in the perpendicular and in-plane direction for the films grown in this research are -0.11% and +0.17% respectively [standard deviation (SD) 0.03]. Note negative and positive signs denote compressive and tensile strain respectively. This result is in reasonable agreement with MIT researchers [42], who reported
in-plane tensile strain of approximately +0.185% for the same growth temperature. Some possible reasons for the observed discrepancy between the measured and calculated in-plane strain are: (i) presence of residual compressive growth strain; (ii) error associated with the use of bulk elastic constants for calculating in-plane strain in thin films; (iii) strain reduction due to interdiffusion at the Si/Ge interface.

3.6.4 SIMS characterization of thick films

SIMS analysis was carried out on a 3.5 µm thick Ge film to determine the carbon (C), and oxygen (O) concentrations at the interfaces and within the film (Fig. 3.13). SIMS detection limits for C and O are $1 \times 10^{16}$ and $3 \times 10^{17}$ atoms/cm$^3$ respectively. The areal density of the interface contaminants was obtained by integrating the area under the respective peaks at the interface. Figure 3.13 shows the presence of C and O at the interface, but the concentration of these impurities is below the SIMS detection limits within the film. Carbon and oxygen concentration at the interface was determined to be 0.2% of a ML and 20% of a ML respectively. This result indicates that the stability of H passivation is a function of exposure time and humidity in the reactor ambient. It is quite likely that partial pressure of C, and O in the reactor tube is higher due to the absence of a load-lock, thereby providing a source for surface contamination of the hydrogen passivated Si substrate.

Figure 3.13 also shows a smaller O peak (to the left of the larger interfacial peak) located approximately 500 Å above the Si/Ge interface. This location corresponds to the surface of the low temperature Ge buffer layer. Since the flow of GeH$_4$ into the reactor is switched off when the growth temperature is increased from 360ºC to 700ºC, it is quite likely
that O is incorporated from the reactor ambient into the film, during this step. This implies that hydrogen desorbs from the surface of Ge, thus freeing sites that can react with oxygen. This idea is consistent with the lower desorption temperature observed for hydrogen on a Ge(001) surface [28].

![SIMS profile of carbon and oxygen](image)

**Fig. 3.13:** SIMS profiles of carbon and oxygen in a 3.5 µm thick Ge film grown on hydrogen passivated Si (001) substrate.

The concentration of O on the surface of the buffer layer is ~ 0.9% of a ML compared to 20% of a ML at the Si/Ge interface. The amount of O incorporated in the film can be expected to be a function of the concentration of O in the reactor ambient and interruption time during epitaxy. In fact Fig. 3.13 shows O incorporation approximately 0.12 µm below
the surface of the film. This depth corresponds to the high temperature dislocation anneal step. Once again, in this step, the flow of GeH₄ into the reactor is turned off, and O from the reactor ambient can diffuse into the Ge film. Based on the above observations, it can be concluded that the source of C, and O found at the interface is associated with the environment in the reactor tube.

### 3.6.5 Optical characterization of thick films

As mentioned in Chapter 2, in-plane tensile strain causes a decrease in the direct and indirect band gap in Ge. HRXRD measurements, discussed in the previous section, confirmed the existence of in-plane tensile strain in the films. In order to quantify the effect of strain on the direct band gap of Ge, absorption characteristics of the Ge films was measured in the wavelength range of 1.0 to 2.0 µm. Figure 3.14a shows the absorption spectra of the strained Ge films of thicknesses ranging from 1.0 to 3.0 µm. The spectra of bulk Ge is also included for comparison [43]. All the films exhibit identical absorption characteristics, with a shift in the band edge towards longer wavelengths compared to bulk Ge.

The oscillations in the spectrum beyond 1650 nm are associated with Fabry-Perot interference fringes, which can be used to calculate thickness of the film [44]. In Fig. 3.14b, the direct band gap of the 3.5 µm thick film has been extracted by plotting the square of the absorption coefficient against the photon energy. The extrapolated intercept yields a band gap of 0.784 eV for the strained Ge film, which is 16 meV lower than bulk Ge (0.80 eV at 300 K) [43]. The average band gap in the strained films, measured over a series of growth
runs with different film thicknesses was 0.785 eV (SD 0.003), representing a 29 nm red-shift \((\Delta E_g = 16 \text{ meV})\) in the band edge. This result is in good agreement with the band gap shrinkage of 20 meV reported by Hartmann et al. [30], and consistent with the presence of in-plane tensile strain in the film. The mean absorption coefficients of the film at the important wavelength of 1.3 \(\mu\text{m}\) and 1.55 \(\mu\text{m}\) were determined to be 8850 cm\(^{-1}\) and 3500 cm\(^{-1}\) respectively.

**Fig. 3.14:** (a) Optical absorption spectra of epitaxial Ge films of varying thicknesses that were grown on Si. (b) Analysis of the data from the 3.5 \(\mu\text{m}\) thick Ge film for extracting the direct band gap of strained Ge.

The impact of strain on the band gap of Ge can be calculated theoretically using deformation potential theory [45]. The reduction in the direct band gap and the splitting of the valence bands due to in-plane tensile stress can be quantitatively described by [42]:
where $E_g^{\Gamma}(LH)$ and $E_g^{\Gamma}(HH)$ are the band gaps associated with the light hole and heavy hole bands respectively, $a = -9.0 \pm 0.4$ eV and $b = -2.6 \pm 0.2$ eV are the deformation potential constants of Ge at room temperature; $\delta E_{100} = 2b (\varepsilon_\perp - \varepsilon_\parallel)$ and $\Delta_0 = 0.30$ eV for Ge [45]. The results of these calculations are presented in Fig. 3.15.

**Fig. 3.15:** Direct band gap of Ge as function of in-plane tensile strain. The theoretically expected band gap has been shown for comparison. Green dot denotes the theoretically calculated band gap for the theoretically expected in-plane tensile strain of $+0.24\%$ for growth at 700$^\circ$C.
Theory predicts that in-plane tensile strain changes the positions of the $LH$ and $HH$ bands resulting in a decrease in the direct band gap, with the LH band moving above the HH band. The upper and lower limits of the theoretically calculated band gap arises due to the range of error associated with the constants $a$ and $b$. The experimentally determined band gap from the absorption measurements and in-plane strain from HRXRD measurements are shown in Fig. 3.15 along with the standard deviation. The experimental data point is in qualitative agreement with the theoretical prediction of a smaller direct band gap due to in-plane tensile strain. For growth carried out at $700^\circ C$, the theoretically expected strain and band gap are represented by the green dot in the figure. Thus there is a discrepancy between experiment and theory along both axes. In other words, the measured strain is lower than the theoretical strain, and the impact of the measured strain on the direct band gap is also lower than theoretical predictions. In Chapter 5 it will be shown that the lower strain is associated with interdiffusion phenomenon at the Si/Ge interface. The discrepancy between theory and experiment along the $y$-axis is associated with precision in the extraction of the band gap from the absorption measurements. In Chapter 7 it will be seen that photodiodes fabricated with these films exhibit responsivity up to $1.61 \mu m$ ($E_g = 0.770$ eV), which is in better agreement with theoretical prediction of $0.771 - 0.774$ eV, for the measured in-plane strain of $+0.17\%$.

3.7 Summary

Two-dimensional growth of Ge epitaxial films was demonstrated using the two-step growth technique. The thicknesses of the Ge films studied in this research varied from 0.5 to
4.0 µm. AFM analyses indicated that the films have a RMS roughness of approximately 1.1 nm. High-temperature annealing of the films results in an order of magnitude decrease in the density of threading dislocations. The Si/Ge interface shows the presence of contaminants such as C, and O, originating from the reactor ambient. HRXRD measurements indicate the presence of an average in-plane tensile strain of +0.17% in the film. The tensile strain arises due to the thermal mismatch between Si and Ge, on cooling from the growth temperature to room temperature. This strain was found to be lower than the theoretical prediction of +0.24%. Absorption measurements of the films indicate a reduction in the direct band gap of Ge, due to the in-plane tensile strain, by an average of 17 meV. The results were found to be in reasonable agreement with theoretical calculations based on deformation potential theory.
References


CHAPTER 4: POISSON RATIO OF GERMANIUM EPITAXIAL FILMS

4.1. Introduction

Germanium (Ge) epitaxial films grown on silicon (Si) by the two-step technique exhibit a state of in-plane tensile strain, due to the thermal mismatch between the two materials. Since the epitaxial films are thin, in-plane strain cannot be measured directly using techniques such as x-ray diffraction. It is calculated from the readily measurable perpendicular strain component and the elastic constants of bulk Ge. An inherent assumption in this calculation is that the elastic properties of bulk Ge are the same as thin films. Chapter 4 presents experimental evidence to verify this assumption.

4.2. Background

4.2.1. Review of elasticity theory

Elastic behavior of materials can be explained on the basis of Hooke’s law, which states that the applied force \( F \) equals a constant \( k \) times the displacement \( x \) [1].

\[
F = -k \times x \quad (1)
\]

The constant \( k \) is known as the spring constant. If forces and displacements are replaced by stresses and strains, \( k \) gives the elastic modulus of the material. The linear relation in Eq. 1 is valid for small displacements about the equilibrium position and is independent of the sign of the displacement. In other words, \( k \) depends only on the variation in interatomic forces with interatomic distance about the equilibrium position. However, in single crystal materials, the atomic spacing varies along different directions. Hence, the elastic modulus also varies with
direction, causing anisotropy. The generalized expression for Hooke’s law for three-
dimensional stress state for anisotropic materials is given by:

\[ \sigma_{ij} = S_{ijkl} \varepsilon_{kl} \]  \hspace{1cm} (2)

\[ \varepsilon_{ij} = C_{ijkl} \sigma_{kl} \]  \hspace{1cm} (3)

where, \( C_{ijkl} \) is the stiffness modulus, \( S_{ijkl} \) is compliance modulus, \( \sigma_{ij} \) and \( \varepsilon_{ij} \) denote the stress and strain tensor respectively. The above equations show that when a uniform stress is applied to a crystal, the strain is linearly related to each component of the stress tensor through a component of the compliance tensor. Stresses caused by loading forces, and the resultant strain in the material requires the specification of nine components, six of which are independent in an orthogonal coordinate system.

\[
\sigma_{ij} = \begin{pmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{12} & \sigma_{22} & \sigma_{23} \\
\sigma_{13} & \sigma_{23} & \sigma_{33}
\end{pmatrix} \]  \hspace{1cm} (4)

\[
\varepsilon_{ij} = \begin{pmatrix}
\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\
\varepsilon_{12} & \varepsilon_{22} & \varepsilon_{23} \\
\varepsilon_{13} & \varepsilon_{23} & \varepsilon_{33}
\end{pmatrix} \]  \hspace{1cm} (5)

The mixed indices in the above tensors denote shear components. Also, since the body is at equilibrium, \( \sigma_{ij} = \sigma_{ji} \) and \( \varepsilon_{ij} = \varepsilon_{ji} \). Expansion of either of the above equations produces nine equations, each with nine terms, leading to 81 constants. In the case of cubic materials, due to symmetry considerations, and equivalence of the shear conditions, the compliance matrix simplifies to three independent constants: \( S_{11}, S_{12}, \) and \( S_{44} \) [2].
The four subscript notation has been condensed to two, in the above expressions, according to the rules outlined in Table 4.1. The stress and strain tensor in cubic materials can be written as:

\[
S_{ij} = \begin{pmatrix}
S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\
S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\
S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & S_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & S_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & S_{44}
\end{pmatrix}
\]  

(6)

\[
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6
\end{pmatrix} = \begin{pmatrix}
C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{44}
\end{pmatrix} \begin{pmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3 \\
\varepsilon_4 \\
\varepsilon_5 \\
\varepsilon_6
\end{pmatrix}
\]  

(7)

\[
\begin{pmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3 \\
\varepsilon_4 \\
\varepsilon_5 \\
\varepsilon_6
\end{pmatrix} = \begin{pmatrix}
S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\
S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\
S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & S_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & S_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & S_{44}
\end{pmatrix} \begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6
\end{pmatrix}
\]  

(8)

The matrix representation is defined with respect to the unit cube axes, \(<100>\), also known as the crystal axes. Stress and strain relationships can be calculated using either of the above expressions. However, stress-strain relationship in any arbitrary direction is determined using appropriate rotations of the above tensors.
Table 4.1: Condensed notation for cubic materials [3].

<table>
<thead>
<tr>
<th>Tensor notation</th>
<th>Matrix notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>xx or 11</td>
<td>1</td>
</tr>
<tr>
<td>yy or 22</td>
<td>2</td>
</tr>
<tr>
<td>zz or 33</td>
<td>3</td>
</tr>
<tr>
<td>yz, zy or 23, 32</td>
<td>4</td>
</tr>
<tr>
<td>xz, zx or 13, 31</td>
<td>5</td>
</tr>
<tr>
<td>xy, yx or 12, 21</td>
<td>6</td>
</tr>
</tbody>
</table>

The generalized expression for the Young’s modulus of a cubic material is given by:

\[
\frac{1}{E_{100}} = S_{11} - 2 \left( S_{11} - S_{12} - \frac{S_{44}}{2} \right) \left( l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2 \right) 
\]

where, \( l_i \) represents the direction cosines referred to the <100> axes. For a [100] orientation, \( \left( l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2 \right) = 0 \), and \( E = 1/S_{11} \), which is the same for an isotropic material. Stress (\( \sigma \)) and strain (\( \varepsilon \)) in a three-dimensional isotropic system, in biaxial strain, are related by the following basic equations [1]:

\[
\varepsilon_{11} = \frac{1}{E} \left[ \sigma_{11} - \nu \times (\sigma_{22} + \sigma_{33}) \right] \quad (10)
\]

\[
\varepsilon_{22} = \frac{1}{E} \left[ \sigma_{22} - \nu \times (\sigma_{11} + \sigma_{33}) \right] \quad (11)
\]

\[
\varepsilon_{33} = \frac{1}{E} \left[ \sigma_{33} - \nu \times (\sigma_{11} + \sigma_{22}) \right] \quad (12)
\]

where \( \nu \) is the Poisson ratio of the material; an elastic constant that is the ratio of the lateral and axial strain. Since residual stress exists only within the plane of the epitaxial film, but not in the \( z \) direction, \( \sigma_{33} = 0 \). The above expressions can be rewritten as:
\[ \varepsilon_{11} + \varepsilon_{22} = \frac{1 - \nu}{E} [\sigma_{11} + \sigma_{22}] \quad (13) \]
\[ \varepsilon_{33} = \frac{-\nu}{(1 - \nu)} [\varepsilon_{11} + \varepsilon_{22}] \quad (14) \]

Since \( \varepsilon_{11} = \varepsilon_{22} \) for isotropic biaxial strain, we have:
\[ \varepsilon_{33} = \frac{-2\nu}{(1 - \nu)} \varepsilon_{11} \quad (15) \]

Poisson ratio for isotropic materials is related to the elastic compliance and stiffness modulus by [1]:
\[ \nu = \frac{C_{12}}{(C_{11} + C_{12})} = -\frac{S_{12}}{S_{11}} \quad (16) \]

Substituting the values for the elastic constants from Table 4.2 in Eq. 16 yields a value of 0.27 for the Poisson ratio of bulk Ge. Equation 14 can be rewritten in terms of the stiffness modulus as:
\[ \varepsilon_{33} = -\frac{2C_{12}}{C_{11}} \varepsilon_{11} \quad (17) \]

Equations 15 and 17 describe the fundamental relationship between in-plane strain (\( \varepsilon_{11}, \varepsilon_{22} \)) and perpendicular strain (\( \varepsilon_{33} \)) in an isotropic material under biaxial stress in terms of the Poisson ratio and stiffness modulus respectively. Since perpendicular strain (\( \varepsilon_{33} \)) can be easily measured using techniques such as high-resolution x-ray diffraction (HRXRD), knowledge of either the elastic compliance or the Poisson ratio of thin films enables the calculation of in-plane strain.
Table 4.2: Stiffness modulus and Poisson’s ratio of Si and Ge (300 K) [4,5].

<table>
<thead>
<tr>
<th>Material</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$\nu$</th>
<th>$E_{100}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>165.6</td>
<td>63.9</td>
<td>79.0</td>
<td>0.28</td>
<td>130.2</td>
</tr>
<tr>
<td>Ge</td>
<td>128.8</td>
<td>48.3</td>
<td>67.1</td>
<td>0.27</td>
<td>103.7</td>
</tr>
</tbody>
</table>

However, as indicated earlier, elastic constants of thin films are largely unknown. Hence, the values of their bulk counterparts are used instead. Generally, elastic constants of thin films can differ from those of the bulk materials due to: (i) surface effects associated with the relatively larger surface to volume ratio in thin films; (ii) constraints caused by the substrate; (iii) unique microstructure of the thin films; and (iv) presence of defects and impurities [6,7]. Inspection of Eq. 15 shows that the Poisson ratio for epitaxial films under biaxial stress can be easily calculated if the in-plane strain is known. One method to determine in-plane strain using HRXRD is the $\sin^2 \psi$ technique [8].

4.2.2. $\sin^2 \psi$ technique

The analysis of the residual strain using x-ray diffraction is based on the measurement of interplanar spacing in different macroscopic directions. In the case of a rotationally symmetrical biaxial state of the residual stress, the dependence of the elastic lattice deformation on the inclination from the perpendicular direction ($\psi$) can be expressed by the $\sin^2 \psi$ formula, which predicts a linear behavior of the lattice constant with $\sin^2 \psi$. Figure 4.1 shows the orthogonal coordinate system used for the description of the $\sin^2 \psi$ technique. $S_i$ defines the sample coordinate system and $L_i$ defines the laboratory coordinate system, such
that $L_3$ is in the direction of the normal to the family of planes (hkl), whose spacing is measured as function of angles $\phi$ and $\psi$ by HRXRD. Once the lattice spacing for a given (hkl) is obtained, the strain in the laboratory coordinate system is given by:

$$
\varepsilon'_{\phi\psi} = \frac{d_{\phi\psi} - d_0}{d_0} \quad (18)
$$

**Fig. 4.1:** Definition of laboratory ($L_i$) and sample ($S_i$) coordinate system (adapted from Ref. 1).

This strain can be expressed in terms of the strains in the sample coordinate system by a tensor transformation which yields:

$$
\begin{align*}
\varepsilon'_{\phi\psi} &= \frac{d_{\phi\psi} - d_0}{d_0} = [\varepsilon_{11} \cos^2 \phi \sin^2 \psi + \varepsilon_{12} \sin 2\phi \sin^2 \psi + \varepsilon_{22} \sin^2 \phi \sin^2 \psi + \varepsilon_{33} \cos^2 \psi \\
&\quad + \varepsilon_{13} \cos \phi \sin 2\psi + \varepsilon_{23} \sin \phi \sin 2\psi ] \quad (19)
\end{align*}
$$
The strain tensor associated with the laboratory and sample coordinate system has been represented by the primed and unprimed tensor quantities respectively. Equation 19 is the fundamental equation used in the $\sin^2\psi$ technique, and indicates a linear variation of $d_{\phi\psi}$ of a given plane with $\sin^2\psi$. The presence of $\varepsilon_{13}$, $\varepsilon_{23}$ strain components causes a split in the expected $d$ versus $\sin^2\psi$ data. When this split is not observed in the experimental data, $\varepsilon_{13}$, $\varepsilon_{23} = 0$, and Eq. 19 can be simplified as:

$$
\varepsilon'_{\phi\psi} = \frac{d_{\phi\psi} - d_0}{d_0} = [\varepsilon_{11} \cos^2\phi + \varepsilon_{12} \sin 2\phi + \varepsilon_{22} \sin^2\phi - \varepsilon_{33}] \sin^2\psi + \varepsilon_{33} \quad (20)
$$

Equations 19 and 20 represent linear equations that are solved by measuring $d_{\phi\psi}$ over a range of $\psi$ and $\phi$ tilts. For single crystal materials, the angles $\phi$ and $\psi$ are uniquely defined for a given (hkl) and variations in $\psi$ and $\phi$ bring different (hkl) into Bragg condition. The lattice constant ($a_{\text{hkl}}$) in cubic materials is related to the interplanar spacing ($d_{\text{hkl}}$) by the relationship [9]:

$$
a_{\text{hkl}}^2 = d_{\text{hkl}}^2 (h^2 + k^2 + l^2) \quad (21)
$$

Equation 20 can be adapted for single crystal cubic materials as follows:

$$
\varepsilon'_{\phi\psi} = \frac{a_{\phi\psi} - a_0}{a_0} = \left[\varepsilon_{11} \cos^2\phi + \varepsilon_{12} \sin 2\phi + \varepsilon_{22} \sin^2\phi - \varepsilon_{33} \cos^2\phi\right] \sin^2\psi + \varepsilon_{33} \quad (22)
$$

where, $a_0$ is the unstrained lattice parameter of the material. Equation 21 predicts a linear dependence of $a_{\phi\psi}$ with $\sin^2\psi$. Hence, if the lattice parameter is measured in several independent directions as a function of $\psi$, the extrapolated value of $a_{\phi\psi}$ at $\psi = 90^\circ$ yields the in-plane strain present in the film.
4.2.3. Selection of diffracting planes and tilt correction

Figure 4.2 is a standard (001) stereographic projection of a cubic crystal showing the planes that were selected for the $\sin^2 \psi$ analysis.

Fig. 4.2: Standard (001) projection of a cubic crystal showing the planes in the Ge epitaxial film used for the $\sin^2 \psi$ analysis. The dotted line traces the path that was followed in each quadrant by rotation about the $\psi$ and $\phi$ axes [10].

Planes (004), (113), (115), (112), (111) in quadrant 1 (Q1) belong to [-110] zone axis, whereas planes (121) and (151) belong to the [-101] zone axes. The orientation of these planes with respect to the crystal axes varied from 0° for {400} planes to 78.9° for the {511} planes (Table 4.4). Since the poles of planes other than (004) are at an inclination from the
perpendicular direction, appropriate tilts were carried out to bring the pole of the plane parallel to the diffraction vector. Diffraction vector is the vector that bisects the angles of incidence and diffraction and \( \psi \) is the angle of the diffraction plane normal away from the surface normal.

![Diagram of misorientation component](image)

**Fig. 4.3:** Misorientation component (\( \Delta \phi \)) in the experimentally measured \( 2\theta_b \) arising due to the tetragonal deformation (adapted from Ref. 11).

Due to the tetragonal distortion present in Ge, the effect of tilt on strain measurements was corrected by taking by taking two measurements for each \((hkl)\), 180° apart in the direction \( \phi \) [11]. Figure 4.3 shows that in the absence of this correction, the measured \( 2\theta_b \) will be either overestimated or underestimated in by an amount \( \Delta \phi \). An average of two measurements, 180° apart in the direction \( \phi \), eliminates the effect of tilt in the measurements. Figure 4.2 shows that this is equivalent to two measurements made in the quadrants Q1 and Q3 of the stereographic projection, for each \((hkl)\).
4.2.4. Residual strain

Residual strain in thin films consists of three components: (i) lattice misfit strain; (ii) thermal misfit strain (CTE); and (iii) defect strain [12]. Lattice misfit strain is given by \[1- (a_{Ge}/a_{Si})\], where \(a_{Ge}\) (0.56 nm) and \(a_{Si}\) (0.54 nm) are the lattice parameters of Ge and Si respectively. This translates to an in-plane misfit strain of -4.2%. The negative sign indicates compressive strain in the Ge film. Since the critical thickness for pseudomorphic epitaxial growth of Ge on Si is approximately 1 nm [13], the misfit component is expected to be fully relaxed for films grown at elevated temperatures via the formation of dislocations that nucleate at the free surface and glide to the interface. On the other hand, the thermal component of the residual strain is proportional to \(\Delta \alpha \times \Delta T\), where \(\Delta \alpha\) is the difference in coefficients of thermal expansion of Si and Ge in the temperature interval \(\Delta T\). This strain is expected to be on the order of +0.24%, where the positive sign indicates tensile strain in the film. The magnitude of the thermal strain is much smaller and also opposite in sign compared to the misfit strain [14]. The thermal strain is expected to be unrelaxed since the mechanism of relaxation involves the nucleation of dislocations and glide in a relatively thick film. Since the film possesses an inherent strain, it should be possible to compute the Poisson ratio by measuring the in-plane and parallel strain components that exist in the film. Also, since the residual thermal strain is small, the measured strain should be related to the elastic response of the film rather than any plastic yield or inelastic phenomenon. A similar concept, which employed the use of a known residual thermal strain to measure yield stress by HRXRD, has been reported earlier for polycrystalline Pb [15] and Al-2% Cu [16] thin films on Si.
4.3. Experiment

$2\theta$-$\omega$ HR-XRD scans was carried out using a PANalytical X’Pert XRD system. The incident beam optics included a symmetrical 4x Ge crystal coupled with a divergence slit of 0.5 mm and the diffracted beam optics included a 1 mm slit placed in front of the detector. The $2\theta$ step size used during the scan was 0.001°. The $2\theta_B$ peak position was determined by matching the tip of the peak to a Gaussian curve [1], using X’Pert Epitaxy and Smoothfit software. The strained interplanar spacing ($d_{hkl}$) was calculated using Bragg’s law [9].

$$n\lambda = 2d_{hkl} \sin \theta$$

(23)

The strained lattice constant ($a_{hkl}$) was calculated from the interplanar spacing using Eq. 21.

Table 4.3. Characteristics of the Ge films grown on Si $<001>$ substrates for the determination of the Poisson ratio. Samples without dislocation anneal are indicated with an asterisk. Threading dislocation densities were determined using EPD analysis. Perpendicular strain ($\varepsilon_\perp$) was measured using HRXRD, and Poisson ratio of Ge films was calculated using Eq. 15.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thick (µm)</th>
<th>Anneal</th>
<th>Threading dislocation density (cm$^{-2}$)</th>
<th>RMS roughness (nm)</th>
<th>$\varepsilon_\perp$</th>
<th>$\nu$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.7</td>
<td>900°C, 1 h</td>
<td>6.3 ± 0.6 x 10$^6$</td>
<td>1.79</td>
<td>-0.122</td>
<td>0.252</td>
<td>0.9998</td>
</tr>
<tr>
<td>A*</td>
<td>0.7</td>
<td>NA</td>
<td>1.1 ± 0.8 x 10$^7$</td>
<td>1.09</td>
<td>-0.127</td>
<td>0.255</td>
<td>0.9909</td>
</tr>
<tr>
<td>B</td>
<td>1.7</td>
<td>900°C, 1 h</td>
<td>1.4 ± 0.5 x 10$^7$</td>
<td>1.09</td>
<td>-0.106</td>
<td>0.253</td>
<td>0.9925</td>
</tr>
<tr>
<td>B*</td>
<td>1.7</td>
<td>NA</td>
<td>2.1 ± 0.7 x 10$^8$</td>
<td>1.12</td>
<td>-0.118</td>
<td>0.250</td>
<td>0.9997</td>
</tr>
<tr>
<td>C</td>
<td>3.5</td>
<td>900°C, 1 h</td>
<td>6.4 ± 0.5 x 10$^6$</td>
<td>1.43</td>
<td>-0.103</td>
<td>0.249</td>
<td>0.9994</td>
</tr>
</tbody>
</table>

Abbreviations: Thick, thickness; RMS, root-mean-square; NA, not applicable; $R^2$, coefficient of determination.
Three films of thicknesses 0.7 \( \mu m \) (sample A), 1.7 \( \mu m \) (sample B), and 3.5 \( \mu m \) (sample C) were grown for this study (Table 4.3). The samples were annealed in situ at 900\(^\circ\)C for 1 h to reduce the density of threading dislocations (TDs) [17]. The counterparts to samples A and B, grown without in situ anneal were also included for comparison. The motivation behind this selection was to study the sensitivity of the measured Poisson ratio to the defect density and film thickness. Cross-sectional transmission electron microscopy (TEM) was performed on a Hitachi HF 2000 microscope operated at 200 kV. Scanning electron microscopy (SEM) images were acquired using a Hitachi S800 microscope. Lastly, tapping-mode atomic force microscopy (AFM) images were obtained using a Digital Instrument 3100 scanning probe microscope.

### 4.4. Results and Discussion

The surface morphology of the Ge films was characterized using AFM (Fig. 4.4). All the films studied in this research exhibited a RMS roughness of approximately 1 - 2 nm, which confirms the two-dimensional growth of the epitaxial Ge films and the existence of a uniform biaxial stress. The dark contrast seen in the unannealed samples (A*, B*), are pits corresponding to the surface termination of mixed dislocations [18]. The density of the pits is approximately 6 - 8 \( \times 10^7 \) cm\(^2\), which is consistent with values of threading dislocation densities (TDD) found in literature for the as-grown Ge film on Si [19]. The pits are not visible in the annealed samples, indicating a reduction in TDD by high temperature annealing.
Fig. 4.4: 5 μm x 5 μm tapping mode AFM image of the surface of (a) sample A, annealed 0.7 μm thick Ge film with RMS roughness 1.79 nm, (b) sample A* unannealed 0.7 μm Ge thick film with RMS roughness 1.09 nm, (c) sample B, annealed 1.7 μm thick Ge film with RMS roughness 1.09 nm, (d) sample B*, unannealed 1.7 μm Ge thick film with RMS roughness 1.12 nm, (e) sample C, annealed 3.5 μm thick Ge film with RMS roughness 1.43 nm [10].

These results were confirmed by carrying out defect delineation studies on the films (Fig. 4.5). The etchant used for this study was a mixture of acetic acid (67 ml), nitric acid (20 ml), hydrofluoric acid (10 ml), and iodine (30 mg). Figure 4.5 shows SEM micrographs of the etched films that clearly show a drastic reduction in TDD on annealing. For example
TDD in sample B decreases by almost an order of magnitude from \(2 \times 10^8\) cm\(^{-2}\) to \(1.0 \times 10^7\) cm\(^{-2}\) after annealing. The mechanisms associated with the reduction in dislocation density on annealing are explained in detail in Chapter 6.

**Fig. 4.5:** EPD results showing threading dislocation density in the various films. (a) sample A, annealed 0.7 µm thick Ge film with EPD of \(6.3 \times 10^6\) cm\(^{-2}\); (b) sample A* unannealed 0.7 µm Ge thick film with EPD of \(1.1 \times 10^7\) cm\(^{-2}\); (c) sample B, annealed 1.7 µm thick Ge film with EPD of \(1.1 \times 10^7\) cm\(^{-2}\); (d) sample B*, unannealed 1.7 µm Ge thick film with EPD of \(2.0 \times 10^8\) cm\(^{-2}\) [10].
Fig. 4.6: Cross-sectional bright-field TEM images of (a) sample A, annealed 0.7 µm thick Ge film, (b) sample B* unannealed 1.7 µm Ge thick film with EPD of $2.0 \times 10^8$ cm$^{-2}$. The dark contrast in the sample B* along the thickness of the films are threading segments that terminate at the surface of the film [10].

Figure 4.6 shows the cross-sectional TEM micrographs of samples A and B*. TDD in sample B* (unannealed 1.7 µm Ge) was estimated to be $1.28 \times 10^8$ cm$^{-2}$, i.e., very similar to the EPD and AFM analysis. The absence of threading segments in sample A (annealed 0.7 µm Ge), signifies that the overall TDD in this film is less than $2 \times 10^7$ cm$^{-2}$. It has been shown that TD’s in Ge are of 60º glissile type and the reduction in the density on annealing has been postulated to take place by thermal stress induced glide and annihilation [20].

Figure 4.7 shows the measured lattice parameter versus $\sin^2 \psi$ for three samples. The data points were fitted to a best-fit linear regression line. The quality of the fit is given by the $R^2$ value, which is greater than 0.999 for all three samples. This confirms the linear relationship predicted by the $\sin^2 \psi$ method and also the high accuracy of the reported data.
**Fig. 4.7:** Linear plot of lattice parameter as a function of $\sin^2 \psi$ for (hkl) described in Table 4.4. $\psi$ is the angle of the diffraction plane normal away from the surface normal. (a) sample A: 0.7 $\mu$m thick Ge. (b) sample B: 1.7 $\mu$m thick Ge. (c) sample C: 3.5 $\mu$m thick Ge [10].

The in-plane lattice parameter was determined by extrapolation of the best fit line to $\sin^2 \psi = 1$. The calculated lattice parameters for sample B, and the planes used for analysis are listed in Table 4.4. Poisson ratio in all the samples was found to be independent of film thickness as well the defect density (Table 4.3). This is further indication that the measured
strain is associated with the elastic response of the film. The average of the five measurements yielded a value of 0.252 ± 0.002 for the Poisson ratio of Ge epitaxial films.

Table 4.4: Measured lattice parameter for sample A (0.7 µm annealed Ge) as a function of ψ.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>ψ</th>
<th>a (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(400)</td>
<td>0º</td>
<td>5.651</td>
</tr>
<tr>
<td>(113), (-1-13)</td>
<td>15.8º</td>
<td>5.652</td>
</tr>
<tr>
<td>(112), (-1-12)</td>
<td>25.2º</td>
<td>5.654</td>
</tr>
<tr>
<td>(011), (0-11)</td>
<td>35.3º</td>
<td>5.657</td>
</tr>
<tr>
<td>(111), (-111)</td>
<td>45º</td>
<td>5.659</td>
</tr>
<tr>
<td>(044), (0-44)</td>
<td>54.8º</td>
<td>5.662</td>
</tr>
<tr>
<td>(121), (-1-21)</td>
<td>65.9º</td>
<td>5.665</td>
</tr>
<tr>
<td>(151), (-1-51)</td>
<td>78.9º</td>
<td>5.667</td>
</tr>
</tbody>
</table>

Poisson ratio of isotropic materials can be calculated from bulk elastic compliances using the expression, \( \nu = \frac{C_{12}}{C_{11}+C_{12}} \), where \( C_{11} \) (129.2 GPa) and \( C_{12} \) (47.9 GPa) are the elastic compliance of bulk Ge at 300ºK [21]. This gives a value of \( \nu = 0.27 \) for Ge. This study shows that the Poisson ratio of Ge thin films is approximately 7% lower than bulk Ge.

The presence of impurities can be expected to affect the elastic properties of thin film materials. It is known that the elastic constants in Ge are sensitive to the presence of dopants. The addition of 0.05% impurity resulted in a change of 5.5% in the elastic constant, \( C_{44} \) [22]. SIMS analysis of sample C (3.5 µm annealed Ge) was carried out to ascertain the purity of the Ge film (Fig. 6). The elements analyzed included carbon, oxygen, nitrogen, silicon, and boron (B). Carbon and oxygen are typical impurities that are present due to the relatively
higher operating pressure used in RPCVD epitaxy, whereas boron was the dopant in the p-type Si substrates used for growth.

![SIMS profiling graph]

**Fig. 4.8:** SIMS profiling of carbon, oxygen, nitrogen, silicon, and boron in sample C (3.5 µm annealed Ge) [10].

The analysis indicates some out-diffusion of Si atoms from the substrate into the Ge film. However, the concentration of all the elements studied was below the SIMS detection limit in the bulk of the Ge film. The diffusion of these elements can be expected to be substantially lower for samples that did not receive in situ dislocation anneal. This analysis shows that impurities in the film have a negligible impact on the measured Poisson ratio.
Lastly, the impact of using bulk Poisson ratio for strain calculations is considered. The average perpendicular strain measured in the Ge epitaxial films was -0.114%. The calculated in-plane strain using Eq. 15 and Poisson ratio of 0.25 and 0.27 is +0.171% and +0.154% respectively, which yields a difference of 0.02%. Since growth was carried out at 700°C, the theoretically expected thermal misfit strain on cooling to room temperature is +0.24%, which was calculated using:

\[
\epsilon_{//} = \int_{T_{RT}}^{T_{GR}} [(\alpha_{Ge}(T) - \alpha_{Si}(T))]dT \quad (24)
\]

where \(T_{RT}\) and \(T_{GR}\) are the room temperature and growth temperature, respectively, and \(\alpha_{Ge}\), \(\alpha_{Si}\) are the thermal expansion coefficients of Ge and Si [23,24]. Although the magnitude of the residual strain is small, it has a tremendous impact on the optoelectronic properties of epitaxial Ge. It has been shown that in-plane tensile strain on the order of +0.18% decreases the direct band gap of Ge by approximately 20 meV, which corresponds to a 30 nm red-shift in the band edge [25]. Hence, a precise knowledge of the Poisson ratio is essential in studying the impact of strain on the optoelectronic properties of thin films. Clearly, the use of bulk elastic constants results in appreciable error in strain calculation of thin films.

4.5. Conclusion

The Poisson ratio of Ge epitaxial films was determined by analyzing the residual thermal strain present in the film, using HRXRD and the \(\sin^2\psi\) method. The analysis indicated that Poisson ratio in Ge films is 0.25 compared to 0.27 in bulk Ge. The measurement was shown to be independent of the threading dislocation density and film
thickness. The use of a thin film elastic constant gives a more accurate description of the residual strain present in the epitaxial film.
References


CHAPTER 5: STUDY OF THE SILICON-GERMANIUM INTERFACE

5.1. Introduction

The presence of strain in germanium (Ge) epitaxial films has a profound influence on its optoelectronic properties. Experimental work by different research groups has shown that Ge epitaxial films grown on silicon (Si) by the two-step growth technique exhibit residual in-plane tensile strain. This strain arises due to the differential thermal expansion coefficients between Si and Ge and results in the decrease in the direct and indirect band gap of Ge. However, the experimentally determined strain has been found to be lower than the theoretical strain. In the previous chapter, Poisson ratio of the Ge films was experimentally determined to calculate in-plane strain. Although the Poisson ratio was found to be lower than bulk Ge, the magnitude of the change in this elastic constant could not account for the observed discrepancy between theory and experiment. This chapter examines the possibility that interdiffusion at the Si/Ge interface results in a lower than expected in-plane strain.

5.2. Background

Epitaxial growth of Ge on Si substrates has tremendous technological significance in microelectronic and optoelectronic devices desiring compatibility with Si processing technology. However, the 4.2% lattice mismatch associated with Ge/Si(001) heteroepitaxy presents challenging problems in terms of surface roughness and control of threading dislocations. A single step growth carried out at elevated temperatures leads to high surface roughness resulting from the Stransky-Krastanov (S-K) growth mechanism, and a high
density of threading dislocations (TDs) in the Ge epitaxial layer [1]. Since Ge growth on Si(001) switches to two-dimensional (2-D) mechanism at temperatures below 390°C, a two-step growth procedure is employed to minimize surface roughness [2]. In the first step, Ge films thicker than 27 nm [3] are grown typically at a temperature of 360°C, which provides a 2-D template for the second step. In the second step, epitaxial growth is continued on this low-temperature buffer layer at an elevated temperature. Such two-step growth is generally followed by some type of postgrowth annealing to achieve a reduction in threading dislocation density (TDD) [4,5].

It is known that Ge grows coherently on Si up to a critical thickness of ~ 1.0 nm [6]. Beyond this thickness, misfit dislocations form to relieve the strain energy that accumulates in the film [7]. The process of strain relaxation initiates with the nucleation of 60° half-loops at the free surface, followed by glide to the interface [8,9,10]. The 60° dislocations (dislocation with Burgers vectors a/2<110> along {111} slip planes at an angle of 60° with respect to its sense vector in the (001) plane) subsequently react at the interface to form Lomer edge misfit dislocations with their Burgers vector (a/2<110>) lying in the (001) plane. Hence these dislocations are very efficient in relieving misfit strain along the interface. Lattice misfit strain present in the film is expected to be largely relaxed at the end of the postgrowth annealing step. The second source of misfit strain during epitaxy is thermal in origin, arising from the difference in the coefficients of thermal expansion between Si and Ge. Although thermal mismatch strain is an order of magnitude less than the lattice misfit strain, it is an important consideration, especially since thick layers (greater than 1 µm) are usually grown during the second step of epitaxial growth. It is well established that misfit
strain is the principal driving force for nucleation and propagation of dislocation from the free surface, in lattice mismatched structures. However, the thermal misfit strain being relatively smaller, the lower driving force is expected to hinder the nucleation as well as the subsequent glide of the dislocations to the interface. Hence, substantial work needs to be carried out in understanding the mechanism of thermal misfit strain relief associated with the two-step growth technique. This study is especially significant since the high homologous temperatures typically used for growth and anneal of Ge can facilitate interdiffusion at the interface, which is an important mechanism of strain relief in thin films.

5.3. **Experiment**

The Si/Ge interface layer was characterized using high resolution x-ray diffraction, transmission electron microscopy, and secondary ion mass spectrometry. These fundamentals of these techniques were discussed in Chapter 3. This section provides specific information related to the characterization of the interface.

5.3.1. **High resolution x-ray diffraction**

Both symmetric as well as asymmetric HRXRD $2\theta$-$\omega$ scans were acquired at room temperature using a PANalytical X’Pert XRD system. The incident beam optics included a symmetrical 4x Ge crystal coupled with a divergence slit of 0.5 mm, and the diffracted beam optics included a 1 mm slit placed in front of the detector. The $2\theta$ step size used in the scan was $0.002^\circ$. For the acquisition of asymmetric scans, appropriate $\psi$ tilts were carried out to bring the diffracting plane normal parallel to the diffraction vector. Diffraction vector is the
vector that bisects the angles of incidence and diffraction, and $\psi$ is the angle between the plane normal and surface normal. The $2\theta_{h}$ peak position was determined by matching the tip of the peak to a Gaussian curve, using X’Pert Epitaxy and Smoothfit software.

5.4. Results and Discussion

Strain in the epitaxial Ge films along the growth direction ($\varepsilon_{\perp}$) was determined by comparing the Ge(004) peak position in the $2\theta$-ω HRXRD step scans to bulk Ge (Fig. 5.1).

\[
\varepsilon_{\perp} = \frac{d_{f}^{004} - d_{B}^{004}}{d_{B}^{004}}
\]

(1)

where $d_{f}$ and $d_{B}$ are lattice spacing of the (004) planes in the strained film and bulk material respectively. In-plane strain ($\varepsilon_{\parallel}$) can be calculated from $\varepsilon_{\perp}$ and the known elastic constants of the film [11] using

\[
\varepsilon_{\parallel} = -\frac{(1-\nu)}{2\nu}\varepsilon_{\perp} = -\frac{C_{11}}{2C_{12}}\varepsilon_{\perp}
\]

(2)

where $\nu$ is the Poisson ratio, $C_{11}$, and $C_{12}$ are the elastic stiffness constants. The ratio $C_{11}/C_{12}$ is 2.667 [12], and $\nu$ is 0.25 [13] for Ge at 300 K. Commensurate growth in the early stages of epitaxy requires matching of the lattice parameters of Si and Ge along the interface leading to a tetragonal deformation in the film, characterized by the presence of a compressive in-plane strain of $\sim$ -4.0% and a tensile strain (Eq. 2) of +2.7% in the growth direction. Note negative and positive sign denote compressive and tensile strain respectively. As lattice misfit strain in the film is progressively relieved by dislocations, $\varepsilon_{\parallel}$ (and $\varepsilon_{\perp}$) decreases and approaches its unstrained value. The linear thermal expansion coefficient of Ge ($5.9 \times 10^{-6} \text{ K}^{-1}$) [14] is
almost twice that of Si \((2.7 \times 10^{-6} \text{ K}^{-1})\) [15] with a non-linear dependence on temperature. This difference in thermal expansion coefficients also produces an in-plane compressive strain during growth, in addition to the lattice misfit strain present at the interface. However, the magnitude of this strain is much smaller than the lattice misfit strain. If the lattice and thermal misfit strains (both compressive) are completely relaxed at the growth temperature, then on cooling the film to room temperature, thermal mismatch between Si and Ge gives rise to an in-plane tensile strain in the film. The theoretically expected thermal mismatch strain is on the order of +0.11\%, and +0.24\%, for growth carried out at 360\(^\circ\)C and 700\(^\circ\)C, respectively, followed by cooling to room temperature.

\[
\varepsilon_\parallel = \int_{T_1}^{T_2} (\alpha_{Ge}(T) - \alpha_{Si}(T))dT
\]  \hspace{1cm} (3)

where \(T_1, \text{ and } T_2\) represent room temperature and growth temperature, \(\alpha_{Si}\) and \(\alpha_{Ge}\) are the thermal expansion coefficients of Si and Ge respectively. Note the magnitude of in-plane thermal mismatch strain during cooling and heating cycles are equal, but opposite in sign.

The peak position of the as-grown buffer layer (scan A, in Fig. 5.1) is shifted towards lower 2\(\theta\) angles, indicating the presence of tensile strain along the growth direction, and accordingly a compressive strain in the in-plane direction. The magnitude of these strains were determined to be +0.28\% (Eq. 1) and -0.415\% (Eq. 2) respectively. If we take into account the contribution of thermal misfit strain, then the in-plane strain at growth temperature of 360\(^\circ\)C is -0.53\%. The presence of compressive strain implies that lattice misfit strain in the initially pseudomorphic Ge layer is not abruptly relaxed by misfit
dislocations at the equilibrium critical thickness; rather strain relaxation exhibits a thickness-dependence.

**Fig. 5.1:** HRXRD $2\theta$-$\omega$ scans of the (004) planes of epitaxial Ge films grown on Si(001) substrates, after various steps of the two-step growth technique. Peak position and symmetry are strongly influenced by thermal treatment during growth. The vertical dashed line denotes the calculated $2\theta_B$ position for a relaxed Ge film.

Investigation of the residual strain in films with thicknesses ranging from 60 nm to 240 nm showed a logarithmic dependence of strain relaxation with thickness. The lowest strain of -0.082% was recorded for a 240 nm thick film. This behavior has been observed previously [16,17,18], and has been attributed to thermally activated kinetics associated with
nucleation and glide of $60^\circ$ misfit dislocations. Here, the Dodson-Tsao model is generally employed since it provides an elegant explanation for the kinetics of misfit relaxation [19,20]. Annealing the 60 nm thick buffer layer at 700$^\circ$C for 30 min yielded the theoretically expected strain of +0.12%, corresponding to complete relaxation of the lattice and thermal misfit strain at the growth temperature of 360$^\circ$C. The significance of thermal treatment will be evident later in the chapter.

Fig. 5.2: (a) Cross-sectional HRTEM micrograph of a Ge/Si(001) heterostructure. The image was taken along the [011] zone axis. S and F mark the “start” and “finish” of the Burgers circuit used for identifying misfit dislocations. (b) Geometrical relation between Burgers vectors and sense vector of the misfit dislocations along $\{111\}$ planes.
HRTEM was used to examine the morphology of the Ge film and the nature of the misfit dislocation at the interface. Figure 5.2a shows that the film is continuous consistent with the 2-D growth mode, and epitaxial with no sign of misoriented grains. The misfit dislocations identified at the interface have been labeled 1, 2, and 3. The Burgers vector of the dislocations was analyzed by drawing a Burgers circuit in accordance with the right-hand/start-finish convention, with the sense vector pointing into the page ($\xi = 1/\sqrt{2}$[-110], in Fig. 5.2b). Based on this analysis, these misfit dislocations were determined to be of Lomer edge type with their extra half plane in the Si substrate, just below the interface. An edge dislocation can be easily distinguished since it terminates at two {111} planes, compared to a single {111} plane for a 60° dislocation. It is known that Lomer edge misfit dislocations form by the reaction between 60° dislocations at the interface (see, for example, Ref. [21] and references cited therein). Since the Burgers vector of the Lomer edge dislocation is parallel to the heterointerface, it can efficiently relax misfit strain.

Residual elastic strain in the film ($\varepsilon_f$), is related to the equilibrium separation between misfit dislocations ($S$), by $S = |b|/(f - \varepsilon_f)$, where $f$ and $b$ are the misfit strain and Burgers vector respectively. For a Ge film that is fully relaxed by a periodic array of Lomer edge misfit dislocations, $\varepsilon_f$ is zero, and $S$ is expected to be 9.6 nm. The spacing between dislocations 2 and 3 is 10.8 nm, corresponding to a residual compressive strain of ~ -0.5%, at room temperature, whereas the spacing between dislocations 1 and 2 is less than 9.6 nm. Although a conclusion cannot be drawn from a limited examination of the interface, it must be mentioned that the dislocation spacing in Ge/Si(001) heterostructures is known to be
irregular. This has been attributed to an inhomogeneous nucleation in regions with high stress concentration, e.g., at surface steps [22], and surface cusps [23], in the early stages of misfit relaxation. Figure 5.2 also shows the presence of a $60^\circ a/2<110>$ dislocation with a missing plane in Ge, labeled 4, approximately 14 monolayers above the interface. The upward pointing Burgers vector of this dislocation is consistent with the presence of a net compressive strain in the in-plane direction. Had this dislocation nucleated to relieve the tensile strain during cooling, the Burgers vector of this dislocation would have been directed downwards with the extra half plane in the Ge film. This configuration which marks the equilibrium zero-force location for this dislocation clearly shows the problem associated with relieving small misfit strains in the film. As misfit strain is relaxed, the driving force for nucleation and glide is reduced and other forces such as interaction forces between dislocations and line tension of the dislocation become important. The magnitude of the radial component of the interaction force per unit dislocation length between dislocations 3, and 4 can be calculated using [24]

$$\frac{F^r}{L} = \frac{G}{2\pi R} (b_1 \cdot \xi) \cdot (b_2 \cdot \xi) + \frac{G}{2\pi R(1 - \nu)} [(b_1 \times \xi) \cdot (b_2 \times \xi)]$$

(4)

where $G$, is the shear modulus ($5.1 \times 10^{10}$ N/m$^2$), $\nu$ is the Poisson ratio (0.25) of the Ge film, $b_1$, $b_2$, and $\xi$ are the Burgers vector sense vector of the interacting dislocations. Assuming $b_1$ is the Lomer edge misfit dislocation 3, it can be assigned Burgers vector $a/2[110]$ with sense vector $\xi = 1/\sqrt{2}[-110]$ (Fig. 5.2b). Four possible Burgers vectors for dislocation 4 with the same sense vector are shown in this figure. The tangential component of the interaction force
has been neglected by assuming that dislocation 4 is located above dislocation 3 at a distance of \( R = 2.0 \text{ nm} \). Since \((b_1 \cdot \xi) = 0\), for dislocation 3, Eq. 4 can be simplified to

\[
\frac{F^i}{L} = \frac{G}{2\pi R(1-\nu)}[(b_1 \times \xi) \cdot (b_2 \times \xi)]
\]  

(5)

Equation 5 can be solved in a straightforward manner to yield an interaction force per unit length 0.33 N/m. The driving force for glide is governed by the component of stress acting in the slip direction and is given by [24].

\[
\frac{F^g}{L} = \frac{[\eta(b_1 \cdot \xi)\cdot [\xi \times (b_2 \times \xi)]}{(b \times \xi)}
\]

(6)

For the sense vector considered earlier, the 60° dislocations experience a glide force along the \( z \) direction given by

\[
\frac{F^g_{\sigma}}{L} = \frac{Ga(1+\nu)\varepsilon}{\sqrt{3}(1-\nu)}
\]

(7)

where \( a \) is the lattice parameter, and \( \varepsilon = \varepsilon_{xx} = \varepsilon_{yy} \) is the in-plane strain in the film. The magnitude of this force is on the order of 1.2 N/m and 0.14 N/m for strain of 4.0% (coherently strained) and 0.5% respectively. Therefore, it seems reasonable that the glide of a dislocation is strongly influenced by the interaction forces with existing dislocations. The value of the driving force has been overestimated since other forces that contribute to the inefficiency of the glide process such as the line tension of the dislocation and lattice friction force have not been considered. Such interactions between dislocations cause difficulties in generating misfit dislocations and accounts for the sluggish strain relaxation observed experimentally. The attractive-repulsive forces between dislocations can be expected to play
an important role in the relaxation of small misfit strains in thick films as the driving force for dislocation glide in the film is reduced. Lastly, atomistic modeling has shown that the activation energy associated with the nucleation of a 60° dislocation depends on the sign of the misfit strain [25]. Nucleation of a dislocation in a compressively strained film results in the removal of an atomic plane and a decrease in the number of dangling bonds at the surface. The decrease in surface energy helps to overcome the nucleation barrier. On the other hand, nucleation of a 60° dislocation in a tensile strained film results in the introduction of an extra half-plane of atoms and an increase in the surface energy. Thus the activation energy for nucleating a dislocation in a tensile strained film is expected to be relatively higher.

In the second step, growth is carried out at an elevated temperature of 700°C. The increase in growth temperature to 700°C results in an in-plane thermal misfit strain of -0.11%. However, there are some important considerations in the relaxation of this misfit strain. Homogeneous strain relaxation by existing misfit dislocations at the interface would require a thermally activated glide leading to a coordinated rearrangement in the spacing of the existing dislocation network. However, the (100) plane is not a glide plane in diamond cubic semiconductors. Hence, the position of the extra half-plane associated with the Lomer edge misfit dislocation is fixed. With increase in temperature this dislocation can potentially move perpendicular to its slip plane via a climb mechanism, which does not relieve the thermal misfit strain. As we saw in Fig. 5.2, any additional 60° dislocations nucleating at the free surface of the thick films are unlikely to reach the interface to relieve the thermal misfit strain. Hence, the response of the strained film under these conditions is of particular interest.
Fig. 5.3: In-plane strain in Ge films of varying thicknesses grown on Si(001) substrates, as measured by HRXRD. The films were grown by the two-step technique, followed by a 900°C anneal for 1 h. UL and LL denotes upper limit and lower limit respectively (see text).

Figure 5.3 presents the in-plane strain measured in the films as a function of film thickness. The lower limit (LL) in the figure represents the theoretically expected strain due to the differential thermal expansion coefficient in the first growth step (~ +0.12%). The average strain in the films was determined to be +0.17% ± 0.03, quite similar to values reported in literature [26]. As mentioned previously, for a completely relaxed film at the growth temperature of 700°C, the theoretically expected in-plane strain at room temperature is +0.24%. In-plane strain in the thicker films is noticeably closer to the strain obtained in the first growth step, reflecting a tendency of the film to maintain the equilibrium state established in the first growth step. Note the diffraction profiles of the annealed samples.
shows a pronounced asymmetry towards smaller Bragg angles (compare scan B and scan C in Fig. 5.1), indicating the presence of a SiGe peak of unknown composition near the interface.

**Fig. 5.4:** HRXRD scans from 3.5 µm thick Ge films on Si(001) substrates. (a) \(2\theta-\omega\) scans of the (004) planes orthogonal to the interface, showing a shift in peak position to smaller Bragg angles, commensurate with the decrease in residual strain on controlled cooling. (b) \(2\theta-\omega\) scans of the (511) planes oriented at 78.9° with respect to the (004) planes, showing the presence SiGe peaks (A1, A2) at the interface. The scan for the standard film is offset along the vertical axis for clarity. Silicon peaks have been omitted for brevity of the horizontal axis. Dotted lines denote the \(2\theta_h\) position of a relaxed Ge film at room temperature.

To shed light on the mechanism of thermal strain equilibration, the (511) planes oriented at an angle of 78.9° with respect to the (004) planes were analyzed by HRXRD. This
measurement provides an almost direct examination of the strain and composition parallel to the heterointerface. The relatively smaller penetration depth and significantly large area irradiated by the x-ray beam increases the sensitivity of this analysis. The two films of thickness 3.5 µm, shown in Fig. 5.3, with remarkably different strain of +0.192%, and +0.132% were used for this analysis. The film with the higher strain was cooled rapidly (> 50°C/min) to room temperature after growth, whereas the film with lower strain was cooled in a controlled manner (< 30°C/min) to room temperature. Fig. 5.4b shows the presence of a Ge peak and additional peaks, labeled A1, and A2 in the (511) diffraction scan. Note that the intensity of peak A2 is higher than A1 in the sample with a higher residual strain of +0.192%. The existence of these peaks can be explained by the relaxation of thermal misfit strains during growth by the formation of SiGe alloys of specific composition. For example, compressive misfit strain of -0.12% and -0.24% associated with the two growth steps can be relieved by incorporation of approximately 0.5 at. % Si (a = 5.6566 Å) and 6.0 at. % Si (a = 5.6441 Å) in the buffer layer (using Vegard’s law and neglecting the effect of strain on 2θB position). The higher Si content in A2 leads to a relaxation of the cumulative thermal mismatch strains associated with both the growth steps, leading to a larger in-plane strain on cooling to room temperature. The relative intensities of A1 and A2 are reversed in the sample that was cooled gradually to room temperature, resulting in an in-plane strain that is closer to the calculated strain from the first growth step. We consistently obtained diffraction peak A2, located at 2θB position of 90.4° (a = 5.6399 Å), for the strain data presented in Fig. 5.3. Peak
A1 is located at 2θB position of 90.1° (a = 5.6554 Å). The elastic strain energy (E_{el}) stored per unit area of the epitaxial film is given by [27]:

\[ E_{el} = 2G\varepsilon^2 \frac{(1+\nu)}{(1-\nu)}h \]  \hspace{1cm} (8)

where \( h \) is the film thickness and \( \varepsilon \) is the thermal misfit strain. Although the magnitude of the thermal misfit strain is small, it leads to a significant accumulation of strain energy for thick films during growth. Interdiffusion at the SiGe interface results in a decrease in the elastic energy stored in the film. Misfit strain relaxation by interdiffusion has been observed previously in Si/Si_{1-x}Ge_{x}/Si heterostructures (x = 0.24) [28]. As the structure was annealed at higher temperatures, the initially abrupt interface roughened along with a decline in the average Ge content of Ge in the film, resulting in a decrease in misfit strain. The difference noted in this work was the presence of specific compositions associated with the two-step growth technique. The specificity of the Si content arises from thermal misfit strain in each growth step. The theoretical 2θB position associated with 0.5 at. % and 6.0 at. % Si in the (511) scan is 90.08°, and 90.33° respectively, which is close to the observed peak position of alloys A1 and A2, in Fig 5.4b. On the other hand, the 2θB position of A1 and A2 in the (004) symmetrical scan (Fig. 5.4a) is expected to be 66.01°, and 66.17° respectively. These peaks cannot be resolved in the symmetrical scan due to the relatively lower intensity from the thin SiGe layer and the broadening of the Ge diffraction profile due to defects present in the film.

The presence of Si_{0.06}Ge_{0.94} layer at the interface modifies the thermal mismatch strain profile at the interface. First, as previously mentioned, the compressive in-plane misfit strain of -0.24% during growth is minimized to ~ -0.015%, at the SiGe/Ge interface and second, the
residual strain on cooling from the Si/Si$_{0.06}$Ge$_{0.94}$/Ge structure is expected to yield an in-plane strain close to $+0.22\%$ instead of $+0.24\%$, i.e., a reduction of approximately $\sim 6\%$ at each interface. This has been shown as the upper limit (UL) of the biaxial strain data presented in Fig. 5.3. Similarly the presence of composition A1 at the interface leads to an in-plane strain of $+0.12\%$, which is close to the theoretically calculated strain in the first step.

![SIMS analysis of a typical Si diffusion profile in Ge after annealing at 900°C for 1 h.](image)

Fig. 5.5: SIMS analysis of a typical Si diffusion profile in Ge after annealing at 900°C for 1 h.

The diffusion of Si in Ge was investigated by SIMS. Fig. 5.5 shows the presence of two Si diffusion profiles; near the surface and the other at the Si/Ge interface. The profile at
the surface originates from the background concentration of Si in the reactor ambient. Both profiles were fitted with following analytic solution of Fick’s second law [29].

\[ C(x,t) = C_s \text{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) \]  

(9)

where \( D \) is the diffusion coefficient of Si, \( C_s \) is the fixed concentration of the source, \( x \) is the distance, and \( t \) is the time. Assuming that diffusion takes place predominantly on annealing at 900°C, \( t \) is equal to 3600 s, and \( C_s \) equals 3.7 x 10^{18} \text{ cm}^{-3}, and 2.0 x 10^{21} \text{ cm}^{-3} at the surface and interface respectively. Note \( C_s \) in the interface diffusion profile (2.0 x 10^{21} \text{ cm}^{-3}) corresponds to ~4.0 at. % Si. The theoretical fit to the profile is represented by the dotted line in Fig. 5.5, and yielded a diffusion coefficient of 1.0 x 10^{-14} \text{ cm}^{2}/\text{s} for Si diffusion in Ge, at 900°C. This is an order of magnitude lower than the values reported from diffusion experiments on bulk material in literature [30,31].

Part of this discrepancy can be explained by change in the formation energy of vacancies in the presence of compressive stress present during anneal. The concentration of vacancies can be expressed as [32]

\[ N_v = N \exp\left(\frac{-\Delta G_f - \sigma \Omega}{kT}\right) \]  

(10)

where \( N_v \) is the concentration of vacancies and number of atoms per unit volume respectively, \( k \) is the Boltzmann’s constant, \( \sigma \) is the compressive stress, and \( \Omega \) is the atomic volume. Assuming a biaxial compressive strain of approximately -0.2%, and a Young’s modulus of 10.3 x 10^{10} \text{ N/m}^2 for Ge, the quantity \( \sigma \Omega \) is equal to 0.021 eV/atom. The increase in formation energy of vacancy by 0.021 eV/atom results in a decrease of 20% in the
The diffusion coefficient of Si in Ge at 700°C is on the order of $1 - 3 \times 10^{-16}$ cm$^2$/s [33]. Assuming a time of 30 min used for annealing the buffer layer in the first growth step, the diffusion length ($x = \sqrt{4Dt}$) is in the range of 10 - 15 nm, which is about one-third the thickness of the buffer layer. Hence, significant Si diffusion can take place during the second growth step carried out at 700°C. The anneal step at 900°C results in the growth of these alloys, since the thermal misfit strain in this step at the SiGe/Ge interface is elastically accommodated by the increase in surface area of the alloys. This manifests as the asymmetry in the (004) scan and the extra peaks in the (511) scan. Based on these results it can be stated that composition A1 is an integral part of thermal misfit strain relaxation in the first step of Ge/Si(001) heteroepitaxy, and composition A2 is associated with thermal mismatch strain relief from both the growth steps. On cooling, the transition from composition A2 to A1 becomes favorable since thermal misfit strain (tensile strain) in the temperature interval 700°C (second growth step) to 360°C (first growth step) is relieved, enabling the system to return to the equilibrium state established in the first growth step. However, this reaction is expected to be sluggish due to slower interdiffusion during the cooling cycle, resulting in the simultaneous presence of two peaks in the (511) diffraction scan. The difference in cooling rate noted earlier appears to contribute to the kinetics of this reaction. It is likely that the longer dwell time at higher temperature facilitates the transition from composition A2 to A1 by a short-range diffusion mechanism.
Si and Ge form a solid solution over the entire composition range with a lattice constant that deviates only slightly from Vegard’s law [34]. The change in free energy ($\Delta G_m$) in a homogeneous solution with temperature, is given by

$$\Delta G_m = \Delta H_m - T\Delta S_m$$  \hspace{1cm} (11)

where $T$ is the temperature, $\Delta H_m$, and $\Delta S_m$ are the change in enthalpy and entropy of mixing respectively. According to Masalski [35], Ge and Si form a regular solid solution with an interaction coefficient of 0.87 kcal/mole. Based on the regular solution model, the free energy of mixing in SiGe alloys contains a large entropy contribution and a relatively smaller enthalpy contribution (positive). For all SiGe compositions, the free energy of a single-phase is lower than any mixture of two separate phases. In the case of an epitaxial Ge film on a Si substrate, the presence of thermal misfit strain in an initially abrupt interface results in a larger increase in the enthalpy of the film, arising from strained Ge-Ge bonds. The formation of a SiGe alloy near the interface results in a transition from a strained state to an unstrained state in the film. Hence the change in enthalpy of Ge-Ge bonds in this reaction is negative. The change in entropy between these two states can be assumed to be zero. Strictly speaking, the entropy of the relaxed film is expected to be slightly higher relative to the film under compressive strain due to the higher concentration of vacancies (see previous paragraph). Interdiffusion at the interface leading to the formation of SiGe alloys is accompanied by a large increase in the configuration entropy ($\Delta S_m > 0$); hence the change in entropy is positive relative to the initial state that is assumed to be an abrupt interface without intermixing. Lastly, since the alloy compositions noted earlier are closer to Ge, the enthalpy of mixing ($\Delta H_m$, positive term) can be ignored, and the solution can be treated as an ideal solution. Thus
the transition from a strained state to unstrained state via SiGe alloy formation is thermodynamically favored since the change in free energy is negative ($\Delta G < 0$). Based on the preceding discussion, it should be possible to form all possible SiGe compositions depending on the magnitude of the thermal mismatch strain during epitaxy. However, the experiments clearly show the presence of only two compositions at the interface. Hence, it can be stated that thermal mismatch strain modifies the free energy curve resulting in two localized minima (narrow stability gap) at these two compositions. Since this reaction results in the creation of a SiGe/Ge interface (positive energy change), the reaction is likely to occur by nucleation and growth mechanism.

Atomic scale characterization of the interface was carried out using aberration-corrected scanning transmission electron microscopy (STEM) coupled with a high-angle annular dark-field (HAADF) detector. In STEM a beam of electrons is converged onto a narrow spot (approximately 1-10Å) and rastered across the specimen using scanning coils. The incoherent electrons that are elastically scattered at high angles are collected with a high-angle annular dark-field (HAADF) detector to form atomic resolution images [36,37]. The spatial resolution is limited primarily by the probe size. This imaging technique is also called Z-contrast as the cross section for Rutherford elastic scattering is related to $Z^2$ [38] Higher $Z$ regions, scatter more electrons resulting in higher image intensities than regions of low $Z$. Hence, it is possible to distinguish columns of different composition using this technique. The sample was prepared in the [110] orientation by the standard method involving mechanical polishing followed by ion milling in the final stage.
Fig. 5.6: (a), (b) STEM images of the Ge/Si(001) heterointerface taken with a high-angle annular dark-field (HAADF) detector along the [011] zone axis. (c) High magnification image of the interface region with a line scan analysis along the green line (inset).

The images in Fig. 5.6 not only resolve the so-called “dumbbell” spacing of 0.136 nm and 0.141 nm in Si and Ge respectively, but also distinguishes the Si (Z = 14) column from the Ge (Z = 32) column. Further it can be seen that the Si/Ge interface is not atomically sharp, but exhibits pronounced roughness in different regions as expected from interdiffusion at high temperature. Note the presence of two dark contrasts along the interface region.
indicating the presence of a higher Si composition (dark contrast) and lower Si composition respectively (light contrast) at the interface. Moreover, the contrast appears to be inhomogeneous and is not associated with any amorphous phases as noted by the high degree of crystalline perfection in these regions (Fig. 5.6b). To confirm the variation in composition across the interface, a line scan analysis was carried out along the green line shown in Fig. 5.6c. The gradual change in intensity across the interface regions, instead of an abrupt change, confirms that the dark contrast is associated with interdiffusion at the Si/Ge interface.

5.5. Conclusion

HRXRD and HRTEM were used to systematically characterize the lattice and thermal mismatch strain relaxation in Ge/Si(001) heteroepitaxy carried out by the two-step growth technique. Lattice misfit strain is largely relaxed by a heterogeneous network of Lomer misfit dislocations along the interface. However, misfit dislocations are unable to efficiently relieve the relatively smaller thermal and residual lattice mismatch strains during epitaxy. These strains are relaxed by an interdiffusion mechanism at the Si/Ge interface, which activates at higher temperatures. The thermodynamic driving force for interdiffusion increases with temperature, whereas the driving force for misfit relaxation by dislocation nucleation and glide mechanism is reduced for small misfit strains and thick films. HRTEM indicated that the Si/Ge interface is not abrupt but is roughened due to interdiffusion. HRXRD showed the presence of two alloys at the interface with an average composition of approximately 0.5 at. % and 6.0 at. % of Si, associated with the relaxation of thermal misfit strain in the first and
second growth step respectively. The presence of these alloys coupled with roughening at the interface results in the decrease in the theoretically expected in-plane strain. Hence, the assumption of an abrupt Si/Ge interface for calculation of thermal mismatch strain is inaccurate. The highest in plane strain was obtained from films that were quenched to room temperature. These observations successfully address the discrepancy between the theoretical and experimental strain noted in the previous chapters. Interdiffusion is a competing mechanism for relieving small misfit strains at high temperature and is especially significant for thin films.
References


CHAPTER 6: SURVEY OF DEFECTS IN GERMANIUM EPITAXIAL FILMS

6.1. Introduction

Epitaxial growth of germanium on silicon substrates has tremendous technological significance in microelectronic and optoelectronic devices desiring compatibility with Si processing technology. The decrease in the band gap and accompanying shift to longer wavelength detection capability in the presence of in-plane tensile strain makes such applications even more appealing. However, the 4.2% lattice mismatch between Si and Ge presents challenging problems in terms of surface roughness and control of threading dislocations (TDs). The adoption of Ge-based photodetectors in CMOS manufacturing will quite likely depend on the quality of the Ge films grown on Si. The two-step growth technique commonly used in Ge/Si(001) heteroepitaxy was reviewed in Chapter 2. Although several improvements in the electrical properties and reduction in defect density have been reported using this technique, [1,2], substantial work needs to be carried out in understanding the impact of growth parameters on the structure and generation of defects in epitaxial Ge. This chapter reviews the defects delineated in Ge films grown for this research and addresses the above-mentioned issue by studying the dependence of the defect microstructure on thickness of epitaxial Ge films.

6.2. Experiment

Threading dislocations are generally characterized using non-destructive techniques such as transmission electron microscopy (TEM), x-ray topography, and atomic force
microscopy (AFM). Although TEM provides detailed information on the structure of dislocations and other defects such as stacking faults, precipitates, etc., it is expensive and time consuming. A simpler albeit destructive technique that is generally employed is chemical etching. The fundamental phenomenon behind this method is the enhanced dissolution of the strained material associated with defects, relative to the defect-free regions, when exposed to specific etchants. In the case of dislocations, this technique produces pits in the material that mark the intersection of dislocations with the surface, which can be viewed using an optical or scanning electron microscope (SEM). This is commonly referred to as etch pit density (EPD) and gives a good estimation of the various defects present in the material. The etchant used in this research to delineate defects present in the Ge film comprised of a mixture of acetic acid (67 ml), nitric acid (20 ml), hydrofluoric acid (10 ml), and iodine (30 mg) [3]. The etch time was on the order of ten seconds, which yielded pits with diameter of approximately 1 µm. The role of iodine in etching has been discussed in detail in Ref. [4]. The pits were viewed using a Hitachi S800 scanning electron microscope.

The structure of the defects was investigated using conventional cross-sectional transmission electron microscopy (CTEM), along the [011] zone axes of the film. The presence of defects such as dislocation and stacking faults causes bending of the lattice planes in the vicinity of the defect. This bending leads to change in diffracting conditions yielding contrast in the image can be viewed using bright field (direct beam), dark field (diffracted beam) and weak-beam dark field imaging techniques [5]. In diamond and zinc-blende lattices, three types of perfect dislocations with Burgers vector of a/2<110> can exist: edge, screw, and the most probable 60° mixed dislocation. The Burgers vector of these
dislocations are normal, parallel and inclined at 60º degrees respectively to the sense vector. The necessary condition for obtaining maximum contrast from defects is that the diffraction vector be parallel to the displacement field. Conversely, if the two vectors are orthogonal to each other, then the defect is out of contrast. This is also known as the invisibility criterion or the g.b rule for null contrast. In case of mixed or edge dislocations the invisibility criteria is \( g.(b \times u) = 0 \), and \( g.b = 0 \), where \( u \) is the sense vector. For the screw dislocation the invisibility criteria is \( g.b = 0 \). The same rule applies to stacking faults characterized by its fault vector \( R \). Stacking faults are in contrast if \( g. R \neq 0 \). A review of contrast from defects can be found in Ref. [3].

**Table 6.1:** Material characterization results of Ge films grown on Si(001) substrates. Defect densities were determined by chemical etching. In-plane strain was measured using HRXRD and surface roughness by AFM [6].

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>Threading dislocation density ((cm^{-2}))</th>
<th>Line defect density ((cm^{-2}))</th>
<th>rms roughness (nm)</th>
<th>Perpendicular strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>1.2 ± 0.8 x 10^7</td>
<td>NA</td>
<td>3.3</td>
<td>-0.130</td>
</tr>
<tr>
<td>1.2</td>
<td>2.5 ± 0.6 x 10^7</td>
<td>NA</td>
<td>NA</td>
<td>-0.129</td>
</tr>
<tr>
<td>1.7</td>
<td>3.5 ± 0.5 x 10^7</td>
<td>1.3 ± 0.3 x 10^6</td>
<td>NA</td>
<td>-0.108</td>
</tr>
<tr>
<td>2.3</td>
<td>3.5 ± 0.5 x 10^6</td>
<td>1.1 ± 0.2 x 10^5</td>
<td>0.87</td>
<td>-0.119</td>
</tr>
<tr>
<td>3.3</td>
<td>5.2 ± 0.5 x 10^6</td>
<td>1.3 ± 0.2 x 10^5</td>
<td>1.43</td>
<td>-0.128</td>
</tr>
</tbody>
</table>

AFM surface scans of epitaxial films with TDs usually reveals nanometer-scale pits, which appear as black dots since the probe extends to its lower limit at the dislocations. Screw, edge [7], as well as mixed dislocations [8] have been successfully imaged using this
technique. AFM micrographs presented in this chapter were obtained by operating the tool in the tapping mode. The materials characteristics of the samples that were studied are presented in Table 6.1. All the films listed in this table, unless specified otherwise, received an *in situ* dislocation anneal at 900°C for 1 h (see Chapter 3).

6.3. **Results and Discussion**

The films uniformly exhibited a compressive strain of approximately -0.125%, along the growth direction ($\varepsilon_\perp$), arising due to the difference in coefficients of thermal expansion between Si and Ge. For growth carried out at 700°C followed by cooling to room temperature, the theoretically expected in-plane strain ($\varepsilon_\parallel$) strain is on the order of +0.24%. These two trains are related by the equation [9]:

$$\varepsilon_\parallel = \frac{-2\nu}{(1-\nu)} \varepsilon_\perp$$

(1)

The application of Eq. 1 yields a Poisson ratio of 0.21 for epitaxial Ge films, compared to 0.27 that is normally calculated using the elastic compliance of bulk Ge. A similar deviation of the Poisson ratio of Ge films from bulk value was recently reported by Bharathan et al. [10], illustrating that elastic property of thin films can vary significantly from bulk material.

The surfaces of the films were specular with a root-mean-square (RMS) roughness of approximately 1 - 4 nm, determined by AFM (Fig. 6.1). The absence of Ge islands associated with the S-K growth model in these micrographs highlights the importance of the Ge buffer layer, grown by the two-dimensional growth mechanism, which results in the smooth films observed in Fig. 6.1.
**Fig. 6.1:** 5 µm x 5 µm tapping mode AFM image of the surface of (a) 0.7 µm thick Ge film with RMS roughness 3.3 nm, (b) 3.3 µm Ge film with RMS roughness 1.4 nm [6].

Figure 6.2 shows PVSEM micrographs of the defects observed in the 0.7, 1.7, and 3.3 µm films. The pits in the micrographs represent intersection of TDs with the (001) surface. Etch pit density (EPD) in the 3.3 µm film was substantially lower compared to the 0.7 µm and 1.7 µm films. Table 6.1 shows that the average threading dislocation density (TDD) in the 2.3 and 3.3 µm films is approximately 4.0 x 10⁶ cm⁻², which shows a plateau in the defect density for films thicker that 2 µm. An interesting feature observed during etching of the 1.7 µm and 3.3 µm films was the presence of defect lines terminating in etch pits, along both orthogonal <110> directions (Fig. 6.2b, c). Such lines were not seen in the 0.7 µm film, presumably due to the resolution limit of the etching technique. These defects were visible on the as-grown surface under differential contrast microscopy examination.
Fig. 6.2: Plan-view SEM images after preferential etching. (a) 0.7 µm film, with a threading dislocation density (TDD) of $1.2 \times 10^7$ cm$^{-2}$ (b) 1.7 µm film, with a TDD of $3.5 \times 10^7$ cm$^{-2}$ and (c) 3.3 µm film, with a TDD of $5.2 \times 10^6$ cm$^{-2}$. Black and white arrows denote threading dislocations and defect lines associated with stacking faults respectively [6].

Additionally, the etch pits associated with this defect are noticeably smaller compared to the etch pits associated with the 60° TDs. Such features can be formed by planar defects such as stacking faults bounded by partial or stair-rod dislocations. Since the core of a partial dislocation ($b = a/6<211>$) or stair-rod dislocations ($b = a/6<110>$, $a/3<001>$) is smaller than a 60° dislocation ($b = a/2<110>$), etch pits bounding a SF can be expected to be smaller. Note the slope of the sidewall of the etched stacking fault reveals that the lengths of the
defect lines decrease with increasing depth in the film. This defect has been characterized in
detail later in the chapter.

To further understand the nature and interaction of defects present in the relatively
thicker films grown in this research, TEM analysis was carried out on the 1.7 µm film. A
sample that did not receive dislocation anneal was selected due to the higher density of TDs
(2.1 x 10^8 cm^-2) and line defects (6.3 x 10^6 cm^-2) observed during defect delineation,
confirmed by AFM images of the surface of the film (Fig. 6.3b). Figure 6.3a is a bright-field
image of this sample along the [011] zone axes. The dark contrast along inclined <110>
directions is associated with 60° dislocations and has been denoted with an “m” label. The
Burgers vector and sense vector of these dislocations lie along the two inclined <110>
directions associated with a {111} glide plane, for example Burgers vector ±a/2[01T] lying
along the [T01] direction in the (111) slip plane (Fig. 6.3c). Hence, in a TEM specimen
prepared in a <110> orientation these dislocations will be oriented at 54.7° with respect to
the interface. The dark contrast along straight vertical and horizontal directions is due to 90°
perfect edge TDs with Burgers vector ±a/2[110], ±a/2[1T0], and have been represented
with an “e” label. Due to the geometric requirement, the sense vector of this dislocation lies
in one of two possible orthogonal directions, parallel or perpendicular to the interface.
Defects shown at A, B and C clearly show the formation of narrow stacking faults. The
magnified image of the defect at A shows the interaction of two 60° dislocations (m5, m6) on
intersecting {111} planes that react to form the 90° dislocation (e4). Another 60° dislocation
(m7), parallel to m5, dissociates to produce a stacking fault. The defects at B include several
$60^\circ$ threading dislocations that dissociated to produce stacking faults at the interface. The next section describes the mechanism of these interactions.

**Fig. 6.3:** (a) Bright field cross-sectional TEM micrograph of a 1.7 µm thick Ge film along the [011] zone axes, with the SAED pattern (inset). Multibeam imaging conditions were employed to avoid defect invisibility. (b) 10 µm x 10 µm tapping mode AFM image of the surface of the film showing threading dislocations (black arrows) and line defects (white arrows). (c) Possible interactions between $60^\circ$ threading dislocations [6].
Threading dislocations in large mismatch semiconductor heteroepitaxy can interact via three mechanisms [11]: (i) annihilation; (ii) fusion; and (iii) dissociation. In the case of Ge/(001)Si heterostructures, the equilibrium network at the interface comprises of a cross-grid network of perfect 90° edge misfit dislocations lying along two orthogonal <110> directions. The ends of the misfit dislocation form two triple nodes with reacted inclined 60° dislocations with opposite screw components [12]. In the annihilation mechanism, TDs with opposite Burgers vector \( \pm a/2[01\bar{1}] \) on intersecting slip planes, for example (111) and \((\bar{1}11)\), can annihilate upon contact by glide. However, since the 90° edge misfit segments cannot end abruptly in the crystal, this interaction must be accompanied by the reaction between the orthogonal 90° edge misfit segments. A similar consideration applies for TDs associated with separate sources on the same slip plane. In this case, the threading segments on annihilation will lead to the extension of the 90° edge misfit segment. This dependency on the dislocation morphology at the interface would limit this mechanism to short range interactions between 60° TDs on orthogonally intersecting, or on the same \{111\} planes. In the second mechanism, a perfect 90° threading dislocation can be formed by the reaction between two glissile 60° dislocations with opposite screw components, at intersecting glide planes by the reaction:

\[
\frac{a}{2}[\bar{1}01](\bar{1}11) + \frac{a}{2}[01\bar{1}](\bar{1}11) \rightarrow \frac{a}{2}[\bar{1}10] , \ b_1^2 + b_2^2 > b_3^2
\]

\[
m_5 + m_6 \rightarrow e_4
\]
Such a reaction is energetically favored due to the reduction in the total energy of dislocations. The total energy of a dislocation comprises of two components; (i) an elastic component associated with the strained bonds, and (ii) core energy of the dislocation. The elastic component is proportional to $b^2$, where $b$ is the magnitude of Burgers vector. The above reaction leads to a 50\% reduction in the elastic component of the total energy (Franks rule). Since the core energy of a $60^0$ and $90^0$ dislocation is about 1.0 eV/Å and 0.5 eV/Å respectively [13,14], there is a relatively larger reduction in the core energy accompanying the above reaction. Hence, the reaction between $m_5$ and $m_6$ to form $e_4$, in Fig. 6.3a, can be explained by the above reaction. The above interaction mechanism is analogous to the reaction that occurs at the interface to relieve lattice misfit strain between Si and Ge [15,16] in the early stages of epitaxy, with the exception that in the latter case the $90^0$ misfit dislocation lies along the interface. Note that this mechanism permits relatively long-range interactions between $60^0$ threading dislocations. With increasing thickness, as more of the $60^0$ TDs react via this mechanism to form $90^0$ dislocations, this leads to a concomitant decrease in the threading dislocation density at the surface. The saturation observed during defect delineation shows that beyond a certain thickness, this reaction is limited by the availability of TDs of the opposite screw component. Lastly, with respect to the dissociation mechanism, it has been shown that the interaction of $60^0$ dislocations pairs with parallel screw components, for example $a/2[10\bar{1}]$, $a/2[01\bar{1}]$on intersecting glide planes ($\langle\bar{1}11\rangle$, ($\bar{1}11$) respectively, leads to the formation of stacking faults [17]. One of the $60^0$ dislocations splits according to the reaction:
\[
\frac{a}{2}[10\bar{1}][\bar{1}11] \rightarrow \frac{a}{6}[1\bar{1}2]+\frac{a}{6}[21\bar{1}], \quad b_1^2 > b_2^2 + b_3^2
\]

\[m_7 \rightarrow \text{partials}\]

Although this reaction is also energetically favorable based on Frank’s rule, it does not lead to a decrease in TDD in the film. Referring back to Fig. 6.3a, the 60° dislocations \(m_7\) with screw component parallel to \(m_6\), dissociates to form a stacking fault.

The geometry of the SFs in Fig. 6.3a cannot explain the presence of the defect lines on chemical etching, chiefly because of the small width (< 40 nm) of these faults. Such narrow SFs cannot be resolved during defect delineation and would most likely be interpreted as a 60° etch pit. Planar defects such as SFs and microtwins can be generated by two possible mechanisms: (i) stress-induced splitting of perfect 60° dislocations into Shockley partials (see previous paragraph); and (ii) growth-related stacking errors due to the presence of surface contaminants [18]. Figure 6.4a is a TEM micrograph on another location of the 1.7 \(\mu\)m film, which shows a different configuration of a SF originating at the surface of the buffer layer. Note the increase in size of the fault with film thickness. The intersection of the segment A–A’ and B–B’ of the fault with the free surface would produce the defect lines seen in Fig. 6.4b. The fault is only partially visible since the \{111\} plane on which it lies intersects the plane of the foil. Assuming the outer bounds of the fault lie along the <110> directions of two intersecting \{111\} planes, the length of the line defect \(x\), can be related to the film thickness \(t\) through a geometric relationship, \(x=1.414 \times t\) [19]. This explains the thickness correlation of the length of defect lines to the film thickness. Note the presence of
relative lower density of L-shaped faults and one square fault represented by L₁, L₂, and S respectively, in Fig. 6.4b.

**Fig. 6.4:** (a) Bright field cross-sectional TEM micrograph of a 1.7 µm film showing a stacking fault polyhedron that gives rise to defect lines. (b) SEM image of the etched film taken from an area of the film with relative higher density of L-shaped defects [6].

It is known from Si(111) homoepitaxy that defect lines could be traces of either a simple stacking fault bounded by Shockley partials (Fig. 6.5c), lying in any of the octahedral planes [20,21], or it could contain two closely spaced parallel faults (Fig. 6.5d) with stair-rod dislocations at each bend [22,19]. A close inspection of the defect in Fig. 6.4 shows additional SF contrast probably from the inclined \{111\} planes bordering the major fault. This implies that the line defects are most likely associated with the configuration in Fig.
6.5d rather than Fig. 6.5c. The shape of the defects can be explained by considering the mismatched boundary at the interface in the form of a distorted square. If only two sides of these squares propagated as SFs on inclined \{111\} planes, it would yield an L-shaped defect (Fig. 6.5b). On the other hand if the two sides lie on parallel \{111\} planes, then a defect line would result. Faults on all four inclined \{111\} planes would yield an inverted square pyramid.

**Fig. 6.5:** Shape of the mismatch boundary that can cause: (a) line defects, (b) L-shaped defects. Line defects caused by: (c) a simple stacking fault bounded by Shockley partials, (d) two closely spaced parallel faults (adapted from Ref. 22) [6].

The initiation of such defects during epitaxy is thought to be due to the presence of contaminants at the interface [21]. In the case of growth carried out in a RPCVD reactor, the concentration of impurities such as carbon (C) and oxygen (O) is typically higher [23,24],
relative to ultra-high vacuum platforms. Both these contaminants are known to generate stacking faults during epitaxy [18]. It is conceivable that contamination of the film takes place when growth temperature is increased, due to the increase in partial pressure of these impurities in the reactor ambient.

Fig. 6.6: (a) SIMS profile of carbon and oxygen concentration at the Ge/Si interface. (b) Diamond crystal lattice of Ge with the characteristic hexaring pattern [6].

Carbon and oxygen concentrations at the Ge/Si interface were determined by SIMS analysis (Fig. 6.6a). Note the presence of two O peaks in the vicinity of the Si/Ge interface. Carbon and oxygen concentration at the interface was found to be 0.2% of a monolayer (ML) and 20% of a ML respectively. The smaller O peak at the surface of the buffer layer to the left of the larger interfacial peak corresponds to a concentration of ~1.0% of a ML. The
location of the O peak from the SIMS analysis is consistent with the TEM micrograph (see Fig. 6.4a), which showed that this defect originates at the surface of the buffer layer. Hence, based on these results, it can be stated that the defect lines in the films are associated with the incorporation of O during epitaxy, when the growth temperature is increased from 360°C to 700°C.

Next, a mechanism is proposed for O incorporation leading to stacking fault formation during Ge epitaxy. Figure 6.6b depicts the diamond lattice structure of Ge comprising of a three-dimensional array of the characteristic hexaring pattern, represented by atoms 1, 2, 3, 4, 5, and 6. In the perfect case, growth in the [001] direction is achieved by incorporation of three-atom nuclei (4, 3, 7; 4, 5, 8), which satisfies the requirement for three-dimensional periodicity of the hexaring pattern. Each atom in this three-atom nucleus is covalently bonded to 2 atoms above and below the {111} plane on which it resides. The presence of O during epitaxy can result in the formation of a Ge–O–Ge molecule in the hexaring, which interrupts the stacking sequence of the {111} planes, since O can form only two bonds with the underlying Ge atoms in the lattice. This disruption in the {111} stacking sequence yields stacking faults, that subsequently propagate along the growth direction producing the configurations shown in Fig. 6.5. This mechanism is in agreement with the experimental findings in the solid-phase epitaxial growth of Si in Ref. [18]. The presence of SFs is detrimental to device performance since they give rise to dark currents analogous to the behavior of threading dislocations [25].
6.4. Conclusion

The microstructural characteristics of epitaxial Ge films grown on Si(001) substrates were studied by x-ray diffraction, atomic force microscopy and transmission electron microscopy. The films were grown using two-step technique by reduced chemical vapor deposition, where the first step promotes two-dimensional growth at a lower substrate temperature. A decrease in TDD was observed with increasing film thickness, which was shown to occur by the reaction of $60^\circ$ threading dislocations to form $90^\circ$ threading dislocations. Germanium films with a thickness of 3.5 $\mu$m exhibited a TDD of $5 \times 10^6$ cm$^{-2}$. The presence of large stacking faults was also observed in the films, which was shown to originate at the surface of the low temperature Ge buffer layer, due to the presence of oxygen in the reactor ambient. The density of these defects ($5 \times 10^5$ cm$^{-2}$) was an order of magnitude lower than the threading dislocation density. Stacking faults represent another important defect that would need consideration for achieving low dark current for Ge-on-Si growths carried out using the two-step growth technique in RPCVD systems.
References

CHAPTER 7: PHOTODIODE FABRICATION AND CHARACTERIZATION

7.1. Introduction

The optoelectronic properties of epitaxial Ge films were evaluated by fabricating normal-incidence p-i-n (p-type Si/intrinsic Ge/n-type Ge) photodiodes. The materials characterization data presented in Chapter 3 indicated strain-induced shrinkage of the direct band gap of Ge, and the presence of a high density of threading dislocations in the films. Chapter 6 showed a decrease in defect density with increasing film thickness. The objective of this chapter is to present a correlation between the electrical performances of devices fabricated using these films to the materials characterization results.

7.2. Background

Photodiodes are semiconductor devices that convert optical signals into electrical current. They contain a p-n junction and often an intrinsic layer between the n and p layers. When the structure includes an intrinsic layer, then it is called a p-i-n photodiode. The p-i-n photodiode is a commonly fabricated photodetector, because it enables the optimization of the frequency response as well as quantum efficiency by varying the thickness of the intrinsic layer. When light is incident on the surface of the photodiode, electron-hole pairs are generated by band-to-band transitions, which are separated by the depletion region, giving rise to an electric current. The important performance metrics desired from a normal-incidence photodiode are high responsivity, low dark current density, and high bandwidth [1]. Spectral responsivity (SR) of a detector is defined as the ratio of the photocurrent to the
incident optical power and is related to the quantum efficiency. Two types of quantum efficiencies are often considered, internal quantum efficiency (IQE) and external quantum efficiency (EQE). External quantum efficiency of a detector includes the effect of optical losses such as transmission and reflection. Internal quantum efficiency refers to the efficiency with which photons that are not reflected or transmitted out of the detector generate collectable carriers.

\[
SR = \frac{Output \ current}{Input \ power} \tag{1}
\]

\[
EQE = \frac{SR \times h\nu}{q} \tag{2}
\]

\[
IQE = \frac{SR \times h\nu}{q \times (1 - R) \times [1 - \exp(-\alpha \times d)]} \tag{3}
\]

where \( h \) is the Planck’s constant, \( \nu \) is the frequency of the incident radiation, \( R \) is the Fresnel reflectance of the Ge surface (approximately 0.36), \( \alpha \) is the absorption coefficient at a given wavelength, and \( d \) is the thickness of the film. The term \([1 - \exp(-\alpha \times d)]\) is known as the absorption efficiency of the film, which is calculated from optical absorption measurements.

Ge photodetectors based on p-i-n structures exhibit a significant built-in electric field of several kV/cm inside the intrinsic Ge layer. Hence, carrier collection depends on carrier drift rather than diffusion [2]. Since the epitaxial films has a high density of defects, a dependence on carrier diffusion would result in relatively long transit times and significant carrier recombination at these defects, thereby reducing the QE of the detector. Dark current is the current generated in the detector in the absence of any radiation. This current gives rise to noise, which reduces the fidelity of the photogenerated electrical signal. Noise in
photodiodes is generally characterized by the dynamic resistance, $R_0$. The current-voltage characteristics of an ideal photodiode are given by the Shockley equation [3]:

$$I = I_s \left[ \exp\left(\frac{q V}{\eta k T}\right) - 1 \right]$$

(4)

where $I_s$ is the saturation current, $q$ is the electron charge, $V$ is the applied voltage, $\eta$ is the ideality factor, $T$ is the temperature and $K$ is the Boltzmann’s constant. $R_0$ of a diode is defined as slope of the voltage versus current plot measured at zero volts, and is given by [4]:

$$R_0 = \left(\frac{dI}{dV}\right)_{0V}^{-1}$$

(5)

Differentiating Eq. 5 with respect to voltage and using the relationship in Eq. 4 yields:

$$R_0 = \frac{kT}{qI_s}$$

(6)

Since the saturation current depends on the diode area, the resistance-area product ($R_0A$) is usually calculated to characterize noise. For commercial applications in integrated circuits, detectors are required to have high $R_0A$ at small device dimensions. The total dynamic resistance of a photodiode comprises of contributions from the bulk as well as the surface of the diode. As a first approximation, the zero-bias dynamic resistance of a photodiode can be expressed as [5]:

$$\frac{1}{R_0 A} = \left(\frac{1}{(R_0 A)_{\text{bulk}}} + \frac{1}{r_{\text{surface}} A}\right)^{-1}$$

(7)

where $(R_0 A)_{\text{bulk}}$ ($\Omega$ cm$^2$) is the bulk $R_0A$ contribution, $r_{\text{surface}}$ ($\Omega$ cm) is the surface resistivity, $P$ is the perimeter of the diode, and $A$ is the area of the diode. A plot of $1/R_0A$ versus $P/A$
yields the bulk $R_0A$ value (intercept at $P/A = 0$) and the surface resistivity of the diode (slope of the line). Surface leakage occurs primarily due to the discontinuity in the periodic crystal structure caused by mesa delineation, which is a necessary step for the fabrication of photodiodes. The abrupt termination in the crystal is thought to promote the formation of leakage pathways [6,7]. Bulk leakage is associated with the presence of defects in the material, which in the case of Ge-on-Si photodetectors is predominantly due to the high density of threading dislocations.

There are three kinds of noise that influence detector performance [4]: thermal, shot, and dark current noise. Thermal noise, also known as Johnson noise, is the electronic noise generated in all resistors due to the thermal agitation of charge carriers. Shot noise arises due to the statistical nature of the carriers injected into the photovoltaic junction. Dark current noise is sometimes also considered as another type of shot noise. The main mechanisms of dark current generation in Ge-on-Si p-i-n photodetectors are (i) generation-recombination associated with SRH process in the depletion region; (ii) field-assisted tunneling; and (iii) surface leakage [8,9]. Generation-recombination arises due to the random transitions of free carriers between energy bands, for example transitions between defect states and the conduction band or the transition between the conduction and valence band. Crystal defects play an important role in this mechanism as they serve as traps for the carriers. The statistics of generation and recombination governing these transitions was introduced in 1952, and is known as Shockley-Read-Hall (SRH) mechanism [10]. The processes can be visualized as a two-step transition between the conduction and valence band leading to the generation or
recombination of an electron-hole pair. The simplified expression for the generation rate \( G \) and recombination rate \( U \) is given by [3]:

\[
G_{SRH} = -U_{SRH} = \frac{(v_{th} \sigma_o N_i) n_i}{2 \cosh \left( \frac{E_i - E_i}{kT} \right)} = \frac{n_i}{\tau_g} \tag{8}
\]

where \( v_{th} \), \( \sigma_o \), \( N_i \), \( n_i \), \( E_i \), \( \tau_g \), and \( T \) are the thermal velocity of the carriers, capture cross section, trap density, energy level of the trap, generation lifetime, and temperature respectively.

### 7.3. Device Structure and Fabrication

The schematic cross section of the Ge p-i-n photodiode fabricated in this research is shown in Fig. 7.1a. The thickness of the intrinsic Ge layer within the p-i-n structure varied from 0.5 \( \mu \)m to 4.0 \( \mu \)m, whereas the thickness of the \( n^+ \)-Ge cap layer was constant at 0.12 \( \mu \)m. The carrier concentration of the cap layer was \( \sim 3.5 \times 10^{18} \) cm\(^{-3} \), determined separately using Hall measurements.

Contacts to \( n^+ \)-Ge were defined using standard photolithography technique, followed by evaporation of titanium (50 nm) and gold (500 nm) by electron-beam evaporation. Two different patterns were used to define the contact metal: a circular geometry was used for I-V measurements to minimize sheet resistance; and an annular geometry was used for spectral response measurements to allow light into the photodiode (Fig. 7.1b). In the next step mesa structures were defined using a second photolithography step in conjunction with reactive ion etching in a fluorine-based chemistry [11]. The etch time was adjusted to ensure that the
mesas extended into the Si substrate. The diameters of the mesas fabricated were 550 µm, 450 µm, 350 µm, 300 µm, and 250 µm. The last step of the process involved the blanket metallization of platinum and gold contacts on the Si substrate. No antireflection coating or passivation was deposited on the devices.

Fig. 7.1: Schematic representation of the device structure: (a) cross-section view of the device and (b) plan-view showing the two geometries used for the Ti/Au contact to $n^+$-Ge.

7.4. Characterization Methods

The photodiodes were studied using current-voltage and spectral response measurements. This section reviews the instrumentation used to characterize the photodiodes.
7.4.1. Current-voltage measurement

Current-voltage (I-V) measurement of the photodiodes was carried out in the dark using an HP4140B semiconductor parameter analyzer. The purpose of these measurements was to determine the ideality factor ($\eta$) and leakage current in the photodiodes. The presence of defects strongly influences the carrier generation lifetime, which is an important parameter affecting the leakage current of a p-n junction device [12]. Dark I-V characteristics presented in this chapter are from diodes with diameter of 550 $\mu$m. The smaller diodes were used for the $1/R_oA$ analysis.

7.4.2. Spectral response measurement

Spectral responsivity (SR) of the photodiodes was measured using a Horiba iHR320 imaging spectrometer. The setup consists of a tungsten lamp, a computer controlled monochromator, an optical chopper, and a lock-in amplifier (Fig. 7.2).

Fig. 7.2: Schematic representation of the spectral response measurement system.
Measurement was made in a synchronous detection scheme with the sample uniformly illuminated from the epitaxial film side. Light from a tungsten lamp was chopped and passed through a bifurcated NIR-visible optical fiber, after exiting the monochromator. Light from one of the branches was focused on the surface of the photodiode, whereas the other branch was coupled to a calibrated Ge detector to determine the incident optical power. Separate measurements established the relative power splitting as a function of wavelength between the two fibers. This enables the determination of the optical power incident on the device using the power measured in the Ge reference channel, thereby permitting the direct calculation of responsivity or QE at each wavelength. Using this technique, only the current component that varies synchronously with the chopped light is detected, and the effects of constant leakage current or ambient lighting are eliminated. Devices with annular contacts and mesa diameter of 550 µm were used for this measurement. Care was taken to ensure that the incident light was focused within the annulus.

7.5. Review

The large lattice mismatch of 4.2% between Si and Ge gives rise to a high density of threading dislocations in the Ge epitaxial films grown directly on Si using the two-step growth technique. It is well known that the threading dislocations (TDs) serve as generation centers that contribute to the leakage current in photodiodes [13]. Samavedam et al. [14] used SiGe graded buffer layers to reduce the TDD’s to less than 2 x 10^6 cm^-2 (see Chapter 2). Using this approach they demonstrated devices with a dark current density of 0.15 mA/cm² at a reverse bias of -1 V. Colace et al. used heavily doped, low temperature Ge buffer layers to
prevent the depletion region from extending into the defective interface layer. Annealing was also carried out at a high temperature to improve the material quality, prior to the growth of $i$-Ge. This approach resulted in a decrease in the dark current density to approximately 1-2 mA/cm$^2$ [20]. Growth was carried out in reduced pressure chemical vapor deposition system, at a pressure of 100 Torr.

**Table 7.1:** Performance comparison for normal incidence Ge photodiodes [1].

<table>
<thead>
<tr>
<th>Responsivity at 1,550 nm (A/W)</th>
<th>Dark current density (mA/cm$^2$)</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13 at 1.3µm, 0V</td>
<td>0.2</td>
<td>1998</td>
<td>[14]</td>
</tr>
<tr>
<td>0.75</td>
<td>15</td>
<td>2002</td>
<td>[15]</td>
</tr>
<tr>
<td>0.035*</td>
<td>100</td>
<td>2005</td>
<td>[16]</td>
</tr>
<tr>
<td>0.56</td>
<td>10</td>
<td>2005</td>
<td>[2]</td>
</tr>
<tr>
<td>-</td>
<td>1 x 10$^6$</td>
<td>2006</td>
<td>[17]</td>
</tr>
<tr>
<td>-</td>
<td>375*</td>
<td>2006</td>
<td>[18]</td>
</tr>
<tr>
<td>0.28</td>
<td>180*</td>
<td>2007</td>
<td>[9]</td>
</tr>
<tr>
<td>0.037</td>
<td>27</td>
<td>2007</td>
<td>[19]</td>
</tr>
<tr>
<td>0.18*</td>
<td>1.5*</td>
<td>2007</td>
<td>[20]</td>
</tr>
</tbody>
</table>

All performance data taken at -1 V reverse bias, unless stated otherwise. * Data calculated using the referenced material.

Recently, a dark current density of 4 x 10$^{-2}$ mA/cm$^2$ at a bias voltage of -1 V was demonstrated by growing Ge using plasma-enhanced chemical vapor deposition. It is believed that this may be due to defect passivation by plasma-introduced atomic hydrogen [21]. The above-mentioned approaches are rapidly approaching the theoretically expected
dark current limit of approximately $10^{-2} \text{ mA/cm}^2$, based on thermionic emission process [22].

Table 7.1 summarizes the results using the different approaches.

7.6. **Results**

7.6.1. **Impact of dislocation anneal**

The importance of carrying out the dislocation anneal step, on device performance, was evaluated by studying the I-V characteristics of diodes fabricated from films grown with and without this anneal. Table 7.2 describes the samples that were used for this analysis. Samples B, C, and D received dislocation anneal of $900^\circ \text{C}$ for 1 h, whereas sample E did not receive any anneal.

**Table 7.2:** Electrical characteristics of samples B through E with total film thickness of 1.7 µm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dislocation anneal</th>
<th>TDD (cm$^{-2}$)</th>
<th>Ideality Factor</th>
<th>$J_{-1\text{V}}$ (mA/cm$^2$)</th>
<th>$(R_0A)_{\text{Bulk}}$ (Ω cm$^2$)</th>
<th>$r_{\text{surface}}$ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>900$^\circ$C for 1 h</td>
<td>$2.2 \times 10^7$</td>
<td>1.28</td>
<td>$64.5 \pm 22.5$</td>
<td>6.3</td>
<td>$1.1 \times 10^3$</td>
</tr>
<tr>
<td>C</td>
<td>900$^\circ$C for 1 h</td>
<td>$2.5 \times 10^7$</td>
<td>1.36</td>
<td>$76.2 \pm 10.7$</td>
<td>2.7</td>
<td>$2.4 \times 10^3$</td>
</tr>
<tr>
<td>D</td>
<td>900$^\circ$C for 1 h</td>
<td>$1.9 \times 10^7$</td>
<td>1.20</td>
<td>$55.6 \pm 2.9$</td>
<td>3.2</td>
<td>$1.3 \times 10^3$</td>
</tr>
<tr>
<td>E</td>
<td>NA</td>
<td>$2.2 \times 10^8$</td>
<td>-</td>
<td>$1897.5 \pm 28.9$</td>
<td>0.42</td>
<td>-</td>
</tr>
</tbody>
</table>

Abbreviations: TDD, threading dislocation density; $J_{-1\text{V}} =$ dark current density at -1 V; NA, not applicable.

I-V characteristics of photodiodes fabricated with these samples are presented in Fig. 7.3. Sample E has the highest dark current density, and from Table 7.2, also the highest
threading dislocation density (TDD) compared to the other samples from this set that received dislocation anneal. The relatively lower \((R_0/\lambda)_{\text{Bulk}}\) in sample E confirms the degradation in device performance is due to the higher TDD present in the film. Hence, the dislocation anneal step is critical in obtaining low dark current in devices since it enables the reduction in threading dislocation density. The mechanisms of TD reduction were reviewed in the previous chapter.

Fig. 7.3: Current-voltage characteristics of samples B, C, D, and E.

7.6.2. Impact of intrinsic Ge layer thickness

Figure 7.4 shows the I-V characteristics of the Ge p-i-n photodiodes as a function of the intrinsic Ge (i-Ge) thickness, increasing from sample A to sample H. All the samples
received a single-step dislocation anneal at 900°C for 1 h. Table 7.3 summarizes the electrical performance of the photodiodes.

**Table 7.3:** Electrical characteristics of samples A, B, F, G, and H with varying thickness of the intrinsic Ge layer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>i-Ge thick (µm)</th>
<th>TDD (cm⁻²)</th>
<th>Ideality Factor</th>
<th>J₁V (mA/cm²)</th>
<th>(R₀A)bulk (Ω cm²)</th>
<th>r_surface (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>1.5 x 10⁷</td>
<td>1.18</td>
<td>170.9 ± 19.6</td>
<td>4.97 ± 1.9</td>
<td>7.74 x 10³</td>
</tr>
<tr>
<td>B</td>
<td>1.6</td>
<td>2.2 x 10⁷</td>
<td>1.28</td>
<td>64.5 ±22.5</td>
<td>6.26 ± 0.89</td>
<td>1.05 ± 0.4 x 10³</td>
</tr>
<tr>
<td>F</td>
<td>2.2</td>
<td>3.5 x 10⁶</td>
<td>1.23</td>
<td>4.86 ± 0.7</td>
<td>29.4 ± 3.6</td>
<td>2.7 ± 0.1 x 10⁴</td>
</tr>
<tr>
<td>G</td>
<td>2.5</td>
<td>4.9 x 10⁶</td>
<td>1.22</td>
<td>4.01 ± 0.4</td>
<td>26.2 ± 3.2</td>
<td>1.7 ± 0.2 x 10⁴</td>
</tr>
<tr>
<td>H</td>
<td>3.2</td>
<td>5.2 x 10⁶</td>
<td>1.17</td>
<td>4.76 ± 0.2</td>
<td>30.0 ± 4.4</td>
<td>1.18 ± 0.1 x 10³</td>
</tr>
</tbody>
</table>

Abbreviations: thick, thickness; TDD, threading dislocation density; J₁V = dark current density at -1 V.

**Fig. 7.4:** Current-voltage characteristics of samples A, B, F, G, and H. Thickness of the intrinsic Ge layer increases from sample A to sample H [23].
The ideality factors ($\eta$) of the diodes lie between 1.1 and 1.3. When recombination current dominates, $\eta$ is expected to be closer to 2.0 [3]. A lower $\eta$ suggests that diffusion current dominates the forward I-V characteristics. The dark current density decreases with increasing film thickness and exhibits a saturation behavior for the thicker films, consistent with the trend in TDD observed in these films. The ($R_{\text{0}}A$)$_{\text{Bulk}}$ displays a similar trend with the thicker films yielding the highest $R_{\text{0}}A$ values of 30.0 $\Omega$ cm$^2$. These measurements not only confirm the improvement in electrical properties of the film with increasing film thickness, but also the strong correlation between the material and electrical properties of the epitaxial Ge films. Note that TDD of $\sim 5.0 \times 10^6$ cm$^{-2}$ in the above samples matches the TDD reported in Ge films grown using graded SiGe buffer layers [14]. The goal in composition grading is to keep the strain rate low and temperature high enough, to enable relaxation of the growing film by the glide of some minimum number of dislocations. In contrast, TDD in the direct growth of Ge on Si is initially at a maximum due to the large lattice mismatch, but appears to reduce to the same density as compositional grading technique via the interaction of TDs in the growing film.

Figure 7.5 shows the zero-bias resistance-area product ($1/R_{\text{0}}A$) as a function of the perimeter to area ratio (at 300 K) for samples A, B, G, and H. $1/R_{\text{0}}A$ increases with increasing perimeter to area ratio, which shows bulk as well as surface contributions to the measured dark current. Surface phenomenon plays an important part in determining detector performance. Surfaces can have large density of interface states that can increase the diffusion as well as depletion region generated currents. Figure 7.5 shows this analysis for
samples A, B, G, and H with data points fitted to a best-fit linear regression line along with the $R^2$ value, a measure of the quality of fit.

![Graph showing $1/R_0A$ as a function of $P/A$ for samples A, B, G, and H at 300 K. The error bars for the thicker films are not visible since they are the same size as the markers [23].]

Samples G and H showed a higher bulk $R_0A$ compared to sample B (see Table 7.3). The larger variance in the data for sample A indicates the existence of inhomogeneous dislocation morphology, associated with the dislocation interactions discussed earlier. Such interactions will have a larger impact on the electrical and structural properties of the thinner films. With increasing film thickness contributions from this region to the overall properties of the epitaxial film is reduced. EPD analysis of sample A ($TDD = 1.5 \times 10^7 \text{ cm}^{-2}$) and sample B ($TDD = 2.2 \times 10^7 \text{ cm}^{-2}$) appears to contradict the trend in dark current presented
earlier. This may be due to the fast etch rate during defect delineation, which limits the depth resolution obtainable by this technique. Hence, TDs close to each other and also those that interact, for example via the fusion mechanism, cannot be resolved, and would give rise to a single etch pit, thereby leading to an underestimation in the dislocation density. Such interactions are expected to strongly influence the microstructure of thinner films. This limitation can also result in the observation of a dramatic change in TDD with increasing film thickness, compared to a gradual change observed in the XRD analysis. Nonetheless, this method gives an approximate upper bound and an accurate lower bound of the TDD present in the film. The surface resistivity of the unpassivated photodiodes was found to be in the range of $1 \times 10^3 - 2 \times 10^4 \, \Omega \, \text{cm}$. The higher surface resistivity in some of samples, signaling a weaker dependence of diode I-V characteristics on the surface effects, may be due to the sidewall passivation during RIE etching.

Fig. 7.6: Measured dark current density as a function of threading dislocation density.
The above experiments demonstrate a relationship between the measured dark current to the TDD present in the films. The dark current density under reverse bias can be approximated by the sum of the ideal diffusion current and the generation current from traps as [3]:

\[
J_R = q \sqrt{\frac{D_n}{\tau_n}} \frac{n_i^2}{N_A} + J_{SRH}
\]

(9)

\[
J_{SRH} = \frac{qn_i w}{\tau_g}
\]

(10)

where \(J_R\) is the saturation current density under reverse bias, \(J_{SRH}\) is the generation current density associated with traps in the depletion region, \(\tau_n\) is the lifetime of electrons in p-type Ge, \(N_A\) is the density of acceptors, \(D_n\) is the diffusion coefficient of electrons, \(n_i\) is the intrinsic carrier concentration (\(2 \times 10^{13}\) cm\(^{-3}\) at 300 K), \(w\) is the depletion width. The dependence of the generation lifetime on the trap density is given by [3]:

\[
\tau_g = \frac{2 \cosh \left[ \frac{E_t - E_i}{kT} \right]}{v_\infty \sigma_0 N_t}
\]

(11)

where \(E_t\) and \(E_i\) are the energy level of the trap and intrinsic Fermi level in Ge respectively, \(v_\infty\) is the carrier thermal velocity (1.17 \(\times 10^7\) cm/s at 300 K), \(\sigma_0\) is the effective capture cross section of defect states related to threading dislocations, and \(N_t\) is trap density. A carrier capture cross section of \(4 \times 10^{-12}\) cm\(^2\) obtained from SiGe alloys was used in this study [24]. Since it is well known that the energy level of the defect states in Ge is close to the center of the band gap [8], the above equations can be rewritten to yield the following dependency of the dark current density on the trap density:
Patel et al. studied the electrical activity of dislocations in SiGe alloys using deep level transient spectroscopy [25]. They demonstrated a linear relationship between the trap density and TDD, which is given by:

\[ N_i = N_{TD} \times N_D \]  

(13)

where \( N_{TD} \) is the threading dislocation density and \( N_D \) is the number of traps per unit length of the dislocation. Their experiments showed that \( N_D \) was about \( 10^6 \) cm\(^{-1}\). Hence, assuming that this linear relationship applies to Ge epitaxial films, Eq. 12 can be modified to correlate the dark current density directly to the TDD as follows.

\[ J_{SRH} = \frac{q n_{ths} \sigma_s N_i}{2} N_{TD} N_D \]  

(14)

A plot of \( J_{SRH} \) versus \( N_{TD} \) should yield \( N_D \) (slope of the line), and once \( N_D \) is known, it is straightforward to calculate the effective carrier lifetime and trap density. Figure 7.6 shows this plot using the I-V data of samples B to H, at a reverse bias of -0.5 V. A depletion width of 0.35 \( \mu \)m was used in this analysis, which was obtained from capacitance-voltage measurements of sample H. The slope of the line yielded a value of \( 7.17 \times 10^5 \) cm\(^{-1}\) for \( N_D \). Giovane et al. [13] reported an \( N_D \) of \( 1.0 \times 10^6 \) cm\(^{-1}\) for p-i-n diodes fabricated with Si\(_{0.75}\)Ge\(_{0.25}\) epitaxial films grown on Si(001) substrates. The similarity in the results is not surprising given that the sources of the traps in both the cases are the 60\(^\circ\) TDs present the film.
Table 7.4: Summary of threading dislocation density, trap density, and carrier lifetime in samples B to H.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Threading dislocation density (cm$^{-2}$)</th>
<th>Trap density (cm$^{-3}$)</th>
<th>Generation lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2.2 x 10$^7$</td>
<td>2.12 x 10$^{13}$</td>
<td>3.0</td>
</tr>
<tr>
<td>E</td>
<td>2.2 x 10$^8$</td>
<td>4.23 x 10$^{14}$</td>
<td>0.1</td>
</tr>
<tr>
<td>F</td>
<td>3.5 x 10$^6$</td>
<td>2.51 x 10$^{12}$</td>
<td>17.0</td>
</tr>
<tr>
<td>G</td>
<td>4.9 x 10$^6$</td>
<td>3.51 x 10$^{12}$</td>
<td>12.2</td>
</tr>
<tr>
<td>H</td>
<td>5.2 x 10$^6$</td>
<td>3.73 x 10$^{12}$</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Table 7.4 summarizes the calculated trap density and the carrier lifetime of the samples. The minority carrier lifetimes are three to four orders of magnitude smaller than electronic grade bulk Ge, illustrating the impact of TDs on the electrical properties of Ge. The data is in reasonable agreement with values reported in literature [26]. Note the measured lifetimes are effective lifetimes consisting of bulk as well as surface components. The reliable separation of both these components in thin films is not straightforward.

7.6.3. Spectral response measurement

Figure 7.7a shows the zero bias spectral response (SR) of the photodiodes (at 1.55 μm) as a function of the epitaxial film thickness. The increase in SR with film thickness is due to the increase in absorption efficiency of the film. The plateau in the SR data corresponds to the optical absorption length in Ge at a wavelength of 1.55 μm, which is roughly 3.0 μm. Sample H, exhibited the highest SR of 0.26 A/W at 1.55 μm. This corresponds to an EQE and IQE of 21.0% and 48.0% respectively.
Fig. 7.7: (a) Zero bias responsivity as a function of film thickness. (b) Zero bias responsivity spectra of the samples in (a), showing SR up to 1.61 µm.

The red dot in Fig. 7.7a represents the SR from sample E. This sample did not receive a dislocation anneal and had the highest TDD of 2.2 x 10^8 cm^-2. The SR, EQE, and IQE, at 1.55 µm, in this sample were 0.03 A/W, 2.0%, and 7.0% respectively. This result highlights the impact of defects and the dislocation anneal step on the performance of the photodiodes. In the absence of the anneal step, a comparatively higher defect density leads to a decrease in the recombination lifetime, and consequently a weaker SR in the photodiode. A significant quantity of the photogenerated carriers recombine at the traps prior to being extracted from the device.

Figure 7.7b shows the zero bias SR spectra of the samples. All the samples exhibit SR up to 1.61 µm, which corresponds to an approximately 60 nm shift in the band edge, compared to bulk Ge (1.55 µm). The decrease in the direct band gap of Ge by 30 meV is due
to the existence of in-plane tensile strain in the film. This result is in reasonable agreement with the reduction of 17 meV that was measured by optical absorption spectroscopy of the epitaxial films (Chapter 3).

**Fig. 7.8:** Zero bias internal quantum efficiency of Ge p-i-n photodiodes as a function of Ge film thickness at: (a) at 1.3 µm, and (b) 1.55 µm. Blue dot denotes the shift in IQE for the 3.3 µm thick film (sample H) at a reverse bias of -0.5 V.

Figure 7.8 shows the zero bias IQE and EQE of the films, at the two important telecommunication wavelengths of 1.3 µm and 1.55 µm respectively. The solid line represents the absorption efficiency, which was calculated using the absorption coefficient of the films (Eq. 3). Absorption efficiency increases with film thickness, since more of the incident photons are absorbed instead of being transmitted from the film. The thickness of the film required to maximize the absorption is lower at a wavelength of 1.3 µm compared to 1.55 µm, since the absorption coefficient of Ge increases for wavelengths smaller than the
band gap. The graphs show that the QE of the devices increases with increasing film thickness, but is less than 50%, implying that a large fraction of the photogenerated carriers are lost due to recombination at defects. The blue dot shows the IQE of sample H under a reverse bias of -0.5 V. The shift of the position of the dot to 100% IQE indicates saturation of the photoresponse in sample H, i.e., complete collection of the photogenerated carriers. The presence of an electric field overcomes the recombination effects at the traps and the devices approach 100% IQE. The SR of sample H at 1.3 µm and 1.55 µm, at a reverse bias of -0.5 V, is 0.69 A/W and 0.54 A/W respectively. These results are amongst the highest reported in literature (see Table 7.1), and underscores the importance of achieving low defect density in the Ge epitaxial films.

7.7. Conclusion

The electrical performance of Ge epitaxial films was studied by fabricating p-i-n photodiodes. Annealing the film to reduce the density of threading dislocation density had a tremendous impact on the dark current characteristics. Sample without any anneal yielded devices with an order of magnitude higher leakage current compared to devices fabricated from annealed films. The dark current density was found to be dependent on the film thickness, with the lowest dark current of 4.0 mA/cm² recorded from films greater than 2.0 µm in thickness. $1/R_0A$ analysis of the photodiodes indicated that bulk and surface resistivity of the unpassivated photodiodes lies in the range of 5-30 Ω cm², and $1 \times 10^3$ - $1 \times 10^4$ Ω cm respectively. The thicker films displayed the highest bulk resistivity, consistent with the reduction in defect density in the material. Further improvements in surface leakage can be
achieved by suitable passivation techniques. The dark current measured in the photodiodes was shown to be a combination of surface leakage, and generation current associated with TD-related traps present in the film. All devices showed spectral response up to 1.61 µm, confirming a strain-induced shrinkage of the direct band gap by approximately 30 meV (E_g = 0.770 eV). This is in reasonable agreement with the 17 meV reduction in the band gap that was measured by optical absorption spectroscopy. The highest spectral responsivity (0.26 A/W at 1.55 µm), at zero bias, was obtained from a 3.3 µm thick film. With the application of a small reverse bias the responsivity improved to 0.54 A/W at 1.55 µm, which corresponds to 100% internal quantum efficiency.
References


SUMMARY

Two-dimensional growth of Ge films on Si (001) substrates was obtained using a two-step growth technique in a reduced-pressure chemical vapor deposition system. A Ge buffer layer was first grown at a low growth temperature of 360°C, which kinetically suppresses the formation of Ge islands. This layer served as a 2-D nucleation layer for the subsequent high temperature epitaxy carried out at 700°C, resulting in the smooth films with root-mean-square roughness of approximately 1 nm to 4 nm. High temperature annealing carried out at 900°C for 1 h did not cause any degradation in the surface morphology of the films demonstrating the stability of the buffer layer. 2-D growth of Ge films up to 3.5 µm thickness was demonstrated. High-resolution x-ray diffraction measurements showed a plateau in the broadening profile for thicker films, signifying an improvement in the structural quality of the films and the existence of a steady state density of defects. The predominant defects in the films were identified to be threading dislocations and large stacking faults. Stacking fault formation was correlated to the presence of interfacial oxygen on the surface of the low-temperature buffer layer. Germanium films with a thickness of 3.5 µm exhibited the lowest threading dislocation densities of 5 x 10^6 cm^2. The mechanisms of interactions between threading dislocations has been discussed with the aid of transmission electron microscopy to explain the reduction in the observed threading dislocation density.

The Poisson ratio of Ge epitaxial films was determined by analyzing the residual thermal strain present in the film, using HRXRD and the sin^2ψ method. The analysis indicated that Poisson ratio in Ge films is 0.25 compared to 0.27 in bulk Ge. The
measurement was shown to be independent of the threading dislocation density as well as film thickness.

HRXRD and HRTEM was used to systematically characterize the lattice and thermal mismatch strain relaxation in Ge/Si(001) heteroepitaxy carried out by the two-step growth technique. Lattice misfit strain relaxation is relieved by heterogeneous network of Lomer misfit dislocation along the interface. However, this mechanism is unable to relieve the relatively smaller thermal mismatch strain during epitaxy due to the lower driving force for nucleation and glide of misfit dislocations. This strain is relieved by an interdiffusion phenomenon at the interface. HRTEM indicated that the Si/Ge interface is not abrupt but is roughened due to interdiffusion. HRXRD showed that the interface has an average composition of approximately 0.5 at. % and 6.0 at. % of Si associated with the relaxation of the thermal misfit strain in the first and second growth step respectively. The in-plane strain at room temperature was found to be lower than the theoretically expected strain due to the presence of these alloys at the interface.

The electrical performance of Ge epitaxial films was studied by fabricating p-i-n photodiodes. Annealing the film to reduce the density of threading dislocation density had a tremendous impact on the dark current characteristics. Sample without any anneal yielded devices with an order of magnitude higher leakage current compared to devices fabricated from annealed films. A strong correlation was obtained between electrical performance of the devices and defect density. Thicker films with the lowest threading dislocation density of $5 \times 10^6$ cm$^{-2}$ also yielded devices with the lowest dark current density of $\sim 5$ mA/cm$^2$ (1 V reverse bias). $1/R_0A$ analysis of the photodiodes indicated that bulk and surface resistivity of
the unpassivated photodiodes lies in the range of 5-30 $\Omega$ cm$^2$, and $1 \times 10^3 - 1 \times 10^4$ $\Omega$ cm respectively. Further improvements in the surface leakage can be achieved by suitable passivation techniques. The dark current measured in the photodiodes was shown to be a combination of surface leakage, and generation current associated with the TD-related traps present in the film. All the devices showed spectral response up to 1.61 $\mu$m, which is in agreement with the strain-induced shrinkage of the direct band gap observed by optical absorption spectroscopy. The highest spectral responsivity (0.26 A/W at 1.55 $\mu$m), at zero bias, was obtained from a 3.5 $\mu$m thick film. With the application of a small reverse bias the responsivity improved to 0.54 A/W at 1.55 $\mu$m, which corresponds to 100% internal quantum efficiency.