OBSERVATION OF DEFECTS EVOLUTION IN ELECTRONIC MATERIALS

By

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To my parents, Heeja and Dr. Craciun
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<tr>
<td>ε</td>
<td>strain</td>
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<tr>
<td>D</td>
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<tr>
<td>ω</td>
<td>omega</td>
</tr>
<tr>
<td>𝜃</td>
<td>theta</td>
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<tr>
<td>ψ</td>
<td>psi</td>
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<td>φ</td>
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<tr>
<td>ω/2θ</td>
<td>omega/2theta</td>
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<tr>
<td>λ</td>
<td>x-ray wave length</td>
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<td>α</td>
<td>thermal expansion coefficient</td>
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<tr>
<td>χ</td>
<td>inclination angle</td>
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<td>t3D</td>
<td>3D growth mode time</td>
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<td>GIXD</td>
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<tr>
<td>LT</td>
<td>low temperature</td>
</tr>
<tr>
<td>HT</td>
<td>high temperature</td>
</tr>
<tr>
<td>NL</td>
<td>nucleation layer</td>
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<td>XRR</td>
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<td>RSM</td>
<td>reciprocal space map</td>
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<tr>
<td>RLP</td>
<td>reciprocal lattice point</td>
</tr>
<tr>
<td>g</td>
<td>diffraction vector</td>
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<tr>
<td>GRL</td>
<td>germanium rich layer</td>
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<tr>
<td>GDL</td>
<td>germanium deficient layer</td>
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OBSERVATION OF DEFECTS EVOLUTIONS IN ELECTRONIC MATERIALS

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Advanced characterization techniques have been used to obtain a better understanding of the microstructure of electronic materials. The structural evolution, especially defects, has been investigated during the film growth and post-growth processes. Obtaining the relation between the defect evolution and growth/post-growth parameters is very important to obtain highly crystalline films. In this work, the growth and post-growth related defects in GaN, ZnO, strained-Si/SiGe films have been studied using several advanced characterization techniques.

First of all, the growth of related defects in GaN and p-type ZnO films have been studied. The effect of growth parameters, such as growth temperature, gas flow rate, dopants used during the deposition, on the crystalline quality of the GaN and ZnO layers was investigated by high resolution X-ray diffraction (HRXRD) and transmission electron microscopy (TEM). In GaN films, it was found that the edge and mixed type threading dislocations were the dominant defects so that the only relevant figure of merit (FOM) for the crystalline quality should be the FWHM value of ω-RC of the surface perpendicular plane which could be determined by a grazing incidence x-ray diffraction (GIXD) technique as shown in this work. The understanding of the relationship between the defect evolution and growth parameters allowed for the growth of high crystalline GaN films. For ZnO films, it was found that the degree of texture and crystalline
quality of P-doped ZnO films decreased with increasing the phosphorus atomic percent. In
addition, the result from the x-ray diffraction line profile analysis showed that the 0.5 at % P-
doped ZnO film showed much higher microstrain than the 1.0 at % P-doped ZnO film, which
indicated that the phosphorus atoms were segregated with increasing P atomic percentage.

Finally, post-growth related defects in strained-Si/SiGe films were investigated. Post-
growth processes used in this work included high temperature N₂ annealing, ion-implantation,
and thermal oxidation. Advanced characterization techniques have been used to obtain
information about strain, relaxation, layer thickness, elemental composition, defects,
surface/interface morphology changes and so on. Based on the understanding of defects behavior
during the strain relaxation after post thermal processes, a new manufacturing process to obtain
highly-relaxed and thin Si₁₋ₓGeₓ layers, which could be used as virtual substrates for strained-Si
applications, was found.
CHAPTER 1
INTRODUCTION

Motivation

Many of the available technology are exploiting the special physical and chemical properties of the materials, such as thickness, elemental composition, interface roughness, structural defects and so on. These device properties of the bulk materials can be controlled or engineered by reducing the device dimensions. Obtaining desirable material properties is one of the fundamental researches in the MSE field. For example, dislocations play a key role in the strain hardening of the materials in which the dislocation motion will be impeded by the repulsive force between the dislocations [1]. In addition, the yield strength of most crystalline solids increases with decreasing grain size, which is well described by the Hall-Petch relationship [2,3]. It seems intuitively correct that fine grain solids should have high yield strengths because the grain boundary can act as an obstacle to dislocation motion. Therefore, accurate characterization techniques for the microstructure analysis are necessary for the desired materials performance. Many analytical methods are now available; transmission electron microscopy (TEM), x-ray diffraction (XRD), atomic force microscopy (AFM), ellipsometry, photoluminescence and so on. These analytical techniques play a specific role in the determination of the structural details and have been continuously developed because of the continuous challenges resulting from the development of new materials and scaling of the material dimension. This dissertation will endeavor to encompass the advances in the analysis of a wide spectrum of the electronic materials by using advanced characterization techniques.

Objective

In this work, advanced x-ray based techniques have been employed to observe and understand the structural evolutions in thin films. The structural modifications occurred during
the film growth as well as post-growth processes. When the films are grown, the understanding of the effect of the growth parameters, such as growth temperature and ambient pressure, gas flow rate, and dopants, on the microstructural evolutions is extremely important for the growth optimization process to obtain high crystalline films. After the growth stage, the film will undergo various post-growth processes, such as high temperature annealing, ion implantation and thermal oxidation. During these post-growth processes, other types of the structural evolutions are generated. Therefore, observation and understanding of these microstructural evolutions induced during the film growth and post-growth processes are necessary to obtain the desired material performances.

**Dissertation Organization**

The contents of this work are categorized into six chapters. Chapter 1 outlines the motivation and objectives as well as the introduction of the electronic materials used in this work. Chapter 2 provides the experimental methods, including the materials processing and the advanced characterization methods. Chapter 3 and 4 introduce the defects evolution during film growth in GaN and ZnO films, respectively. In chapter 3, the influence of a p-type dopant, phosphorous, on the microstructure of ZnO films is investigated. In chapter 4, the effects of the growth parameters on the microstructure of GaN films as well as the case of advanced characterization techniques to assess their quality are presented. Chapter 5 discusses the microstructural evolution in the strained-Si/SiGe layers during the post-growth processes, such as high temperature nitrogen annealing, ion-implantation, and thermal oxidation. In addition, a new route for the fabrication of highly relaxed Si_{1-x}Ge_{x} layers is presented. Finally, chapter 6 summarizes the obtained results.
Background and Literature Review

Strained-Si/SiGe

Strain technology: A strained-layer is one in which the lattice dimensions are stretched or compressed beyond their equilibrium interatomic distance. This is accomplished by epitaxially growing the layer over another material with a larger or smaller lattice parameter. The best known example is strained-Si grown on SiGe layer. Because the lattice parameter of germanium (Ge) is just 4% larger than that of silicon (Si) and both have the same lattice type, SiGe layers are a useful substrate for implementing the idea of strained silicon technology. Since Intel announced that strained silicon can speed up the flow of electrons through transistors increasing their performance and decreasing power consumption, the strained-silicon technology has been intensively studied [4]. Basically, the carrier mobility is given by [5],

\[ \mu = \frac{q \cdot \tau}{m^*} \]  \hspace{1cm} (1-1)

where, \( \mu \) is the carrier mobility, \( m^* \) the effective mass of charge carrier, \( \tau \) the carrier life time and \( q \) the carrier charge, respectively. Fig. 1 shows a strained-Si grown on SiGe layer. In bulk-Si at room temperature the conduction band is comprised of six degenerate valleys, as shown in Fig. 1-1 (a). These valleys are of equal energy, as indicated by \( \Delta 6 \) in Fig. 1-1 (a) and (c). Since the effective mass for any direction is the reciprocal value of the curvature of the electron energy function in that direction and the effective mass of each ellipsoid is anisotropic, the total electron conductivity mass, \( m^* \), is obtained by adding the contributions of the six degenerate valleys and is given by [6],

\[ m^* = \left[ \frac{1}{6} \left( \frac{2}{m_i} \right) + \left( \frac{4}{m_i} \right) \right]^{-1} \]  \hspace{1cm} (1-2)
where, $m_l$ and $m_t$ are longitudinal and transverse mass, respectively. On the other hand, the strain removes the degeneracy between the four in-plane valleys ($\Delta 4$) and the two out-plane valleys ($\Delta 2$) by splitting them, as shown in Fig. 1-1 (c). The lower energy of the $\Delta 2$ valleys means that they are preferentially occupied by electrons. The electron mobility partially improves via a reduced in-plane and increased out-of-plane $m^*$ due to the favorable mass of the $\Delta 2$ valleys, which results in more electrons with an in-plane transverse effective mass ($m_t=0.19m_0$) and out-of-plane longitudinal mass ($m_l=0.98m_0$). In addition, the electron scattering is reduced due to the conduction valleys splitting into two different energy levels, which lowers the rate of intervalley phonon scattering between the $\Delta 2$ and $\Delta 4$ valleys. Hence, a strain enhances the mobility by decreasing the effective mass and intervalley scattering of charge carriers [6]. Using strained silicon, one can achieve a higher device performance without shrinking the size of the transistors.

**Strain relaxation and defects**: there are several ways to induce a strain into silicon for higher electron mobility. One of these is an Epitaxial Strain-Inducing Template (ESIT) in which the silicon can be pseudomorphically grown on a relaxed $\text{Si}_{1-x}\text{Ge}_x$ buffer layer, resulting in the biaxial tensile strain, as shown in Fig. 1-1. This is the most used approach in HBTs (hetero-bipolar transistors). In addition, the compressive strain in the MOS (metal-oxide semiconductor) channel can be induced by introducing a $\text{Si}_{1-x}\text{Ge}_x$ layer into source and drain regions [7,8]. During the production of strained-Si/SiGe or post-growth processes, the strain begins to relax by generating misfit defects. The presence of these defects, such as misfit/threading dislocations and stacking faults, has an undesirable influence on the device performance, such as increased leakage current in MOSFETs [9]. Therefore, it is important to determine the ideal thickness of
the strained layer in order to avoid strain relaxation, which could begin once the thickness reaches a critical value.

**High Crystalline GaN**

**GaN**: wide bandgap semiconductors are extremely attractive for devices that work under harsh conditions, such as high temperature. GaN is the most promising material because of its intrinsic properties: wide bandgap energy, high saturation velocity, and high breakdown electric field. As summarized in Table 1-1, GaN is suitable for device operation in high frequency and temperature regions [10]. In order to maintain high transconductance in FETs, the channel conductivity must be as high as possible. Basically, the conductivity can be increased by increasing the doping in the channel. However, the increased doping also causes increased scattering by the ionized impurities, which leads to a degradation of mobility. What is needed is a way of creating a high electron concentration in the channel of a MESFET by other means than doping. An ingenious approach to achieve this requirement is to use dissimilar heterostructure materials with different bandgaps [11]. This can be achieved when the donor energy level in the wider-bandgap material lies above the conduction-band edge of the lower bandgap material, resulting in the occurrence of the band bending and presence of discontinuities in the conduction and valence bands. The discontinuity in the conduction band creates a triangular quantum well in which electrons are trapped, forming a so called 2-Dimensional Electron Gas (2-DEG), as shown in Fig. 1-2. Since the narrower bandgap semiconductor is usually undoped, the electrons trapped in this region could move without the ionized impurity scattering. Therefore, the electron mobility at lower temperatures, where the impurity scattering is dominant, is significantly enhanced over the usual values measured in epitaxial layers of equivalent doping density. While it is possible to get a high charge density in the interfacial region by high doping of wide bandgap semiconductor in conventional III-V based HEMT, AlGaN/GaN heterostructure can
have higher charge carrier density at the interface without intentionally doping. GaN has a wurtzite crystal structure in which the unit cell is asymmetric along the c-axis, as shown in Fig. 1-3 (a). This asymmetric arrangement of atoms in GaN can induce a spontaneous polarization, which could have a great influence on the device performance, as shown by several studied [12,13]. Also, the in-plane lattice constant of AlN (a=3.111Å and c=4.978Å) is smaller than that of GaN (a=3.189Å and c=5.185Å) so that AlGaN epitaxial layer experiences an in-plane biaxial-tensile strain, resulting in a piezoelectric polarization. Therefore, the net polarization in AlGaN/GaN heterojunction is the sum of the spontaneous polarization of GaN and the piezoelectric polarization of strained-AlGaN, which results in the formation of a positive polarization in the heterointerface, as shown in Fig. 1-3 (b) [14]. The electrons are attracted by this positive charge, and then they accumulate at the interface. This results in a higher charge density as well as a higher carrier mobility, even without intentionally doping.

**Growth and defects of GaN:** sapphire and SiC substrates are commonly used in GaN film growth due to the lack of GaN bulk single crystal. The growth of GaN on these substrates generates many misfit defects because of a large mismatch of both in-plane lattice constants and thermal expansion coefficients between GaN and substrate. Fig. 1-4 displays the lattice mismatch and thermal expansion coefficient of several materials with respect to those of GaN [15]. To minimize the dislocation density and obtain a smooth surface, a two-step growth method has been proposed, where the first layer is grown at low temperature (500–600°C), known as low temperature (LT) layer or nucleation layer (NL), and then the second layer is grown at higher temperatures (over 1000°C), being known as high temperature (HT) layer [16-18]. GaN nucleation layer grown at low temperature contains several types of defects, such as dislocations, point defects, and stacking faults because a 3-dimensional island growth mode (3-D Volmer-
Weber mode) is active here [19,20]. These defects have a significant effect on the GaN based device performance. Fig. 1-5 shows that there are several scattering factors that affect the electron mobility [21,22]. The carrier transport mechanism at low temperatures is affected by scattering due to the background unintentional donor (Ns), the alloy disorder of AlGaN barrier, the interface roughness at the AlGaN/GaN heterojunction, and the threading dislocations. The acoustic and optical phonon scattering can be ignored because their effects on the carrier mobility are not significant at low temperatures. The scattering effect of the threading dislocations on the electron transport is considered by the coulombic interaction from a charged core as well as the deformation potential interaction from the strain field surrounding dislocations. In Fig. 1-5, it is clear that the threading dislocation density is the most important scattering factor limiting mobility. In addition to the mobility limiting factor, the threading dislocations act as a leakage current path. It was reported that the leakage current increased with increasing the dislocation density in GaN based light emitting diodes (LEDs) [23]. As these structural defects in GaN have a great influence on the device performance, they need to be studied in depth.

**P-type ZnO**

ZnO: ZnO has attracted a great deal of attention for many years as the most promising material for optoelectronics device applications due to its wide bandgap energy (3.37 eV) and large exciton binding energy (60 meV) [24-26]. Also, bulk ZnO substrates are readily available, as compared to GaN. However, the key issue is to produce p-type ZnO films because of the deep level location of the candidate acceptors from ZnO valence band and their self-compensation by native point defects [27,28]. Therefore, it is critical to be able to produce reliable and reproducible p-type ZnO films.
**Microstructure of p-type ZnO:** ZnO has a wurzite crystal structure, as shown in Fig. 1-6. In fact, there are three kinds of possible crystal structure for ZnO: wurzite, zinc blend, and rock salt structures [29]. The wurzite crystal structure is the most thermodynamically stable phase.

It has been reported that high quality ZnO films could be grown on a number of substrates, such as silicon, sapphire, GaN, AlN, and GaAs [30-33]. In order to reduce strain and dislocation density of films, the lattice mismatch and thermal expansion coefficient between the substrate and film should be small. The lattice parameter and thermal expansion coefficient of several possible substrates are shown in Table. 1-2 [29]. A widely used substrate for high quality ZnO films is the sapphire due to its transparency and relatively low cost. However, the films grown on sapphire substrate show mosaicity, residual carrier concentration, and low mobility because the in-plane lattice mismatch is 18 % even for a 30 ° in-plane rotation of the film lattice with respect to the substrate. In this study, the effect of phosphorus atoms as a p-type dopant on the microstructure and defects evolution during film growth is investigated in detail.
Table 1-1. Material properties of common semiconductors [10].

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Si</th>
<th>GaAs</th>
<th>SiC</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Gap (eV)</td>
<td>1.11</td>
<td>1.43</td>
<td>3.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Breakdown E-Field (V/cm)</td>
<td>6.0·10^5</td>
<td>6.5·10^5</td>
<td>3.5·10^6</td>
<td>3.5·10^6</td>
</tr>
<tr>
<td>Saturation Velocity (cm/s)</td>
<td>1.0·10^7</td>
<td>2.0·10^7</td>
<td>2.0·10^7</td>
<td>2.5·10^7</td>
</tr>
<tr>
<td>Electron Mobility (cm^2/V-s)</td>
<td>1350</td>
<td>6000</td>
<td>800</td>
<td>1600</td>
</tr>
<tr>
<td>Thermal Conductivity (W/cm-K)</td>
<td>1.5</td>
<td>0.46</td>
<td>3.5</td>
<td>1.7</td>
</tr>
<tr>
<td>BFOM Ratio*</td>
<td>1.0</td>
<td>9.6</td>
<td>3.1</td>
<td>24.6</td>
</tr>
<tr>
<td>JFOM Ratio*</td>
<td>1.0</td>
<td>3.5</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>Heterostructures</td>
<td>SiGe/Si</td>
<td>AlGaAs/GaAs</td>
<td>InGaP/GaAs</td>
<td>None</td>
</tr>
</tbody>
</table>

*BFOM: Baliga’s figure of merit for power transistor performance which is function of thermal conductivity and carrier mobility

*JFOM: Johnson’s figure of merit for power transistor performance which is function of breakdown field and carrier saturated velocity
Table 1-2. Lattice parameter and thermal expansion coefficient of substrates for ZnO crystalline films [29].

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal Structure</th>
<th>Lattice parameter</th>
<th>In-plane lattice mismatch</th>
<th>Thermal expansion coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>α (K⁻¹)</td>
</tr>
<tr>
<td>ZnO</td>
<td>Hexagonal</td>
<td>3.252</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.213</td>
<td></td>
<td>4.75</td>
</tr>
<tr>
<td>GaN</td>
<td>Hexagonal</td>
<td>3.189</td>
<td>1.8</td>
<td>5.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.185</td>
<td></td>
<td>4.55</td>
</tr>
<tr>
<td>AlN</td>
<td>Hexagonal</td>
<td>3.112</td>
<td>4.5</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.980</td>
<td></td>
<td>4.2</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>Hexagonal</td>
<td>4.757</td>
<td>(18.4 % after 30° in-plane rotation)</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.983</td>
<td></td>
<td>8.1</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>Hexagonal</td>
<td>3.080</td>
<td>3.5</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.117</td>
<td></td>
<td>4.68</td>
</tr>
<tr>
<td>Si</td>
<td>Cubic</td>
<td>5.430</td>
<td>40.1</td>
<td>3.59</td>
</tr>
<tr>
<td>ScAlMgO₄</td>
<td>Hexagonal</td>
<td>3.246</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.195</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>GaAs</td>
<td>Cubic</td>
<td>5.652</td>
<td>42.4</td>
<td>6.0</td>
</tr>
</tbody>
</table>
Figure 1-1. The lattice and ellipsoids of constant energy in reciprocal space. (a) the equilibrium and (b) strained silicon (not to scale). (c) is the energy level at the bottom of the six conduction band valleys [6].

Figure 1-2. Energy band diagram for wide (Semiconductor 2) and narrow (Semiconductor 1) bandgap semiconductors [11].
Figure 1-3. Crystal structure of GaN and polarization of AlGaN/GaN. (a) crystal structure of Ga-face GaN (b) net positive charge at the AlGaN/GaN interface caused by the sum of the net spontaneous and piezoelectric polarizations between AlGaN/GaN [10].

Figure 1-4. The mismatch lattice parameter and expansion thermal coefficient for alternative substrates with respect to GaN layer [10,15]. Most used substrates for GaN growth are sapphire and SiC.
Figure 1-5. Low temperature scattering processes limiting electron mobility in AlGaN/GaN 2DEG system with three different dislocation densities [21].

Figure 1-6. ZnO crystal structure (Wurtzite).
CHAPTER 2
EXPERIMENTAL METHODS

Materials Processing

Molecular Beam Epitaxy (MBE)

Cho and Arthur, the pioneers of molecular beam epitaxy (MBE) technique, described that MBE was the epitaxial growth of semiconducting films by the reaction between the molecular beams of its constituents and a crystalline surface held at a certain temperature under ultra-high vacuum (UHV) conditions [34]. Fig. 2-1 shows a schematic diagram of conventional molecular beam epitaxy system. The molecular beam of some constituents, such as Ga, Al, and As, are generated from the heated Knudsen effusion cells and the flux of each source can be rapidly controlled by a shutter that blocks the beam from hitting the substrate. The molecular beams generated from the effusion cells impinge on a rotating substrate mounted on a heated Mo block. The cell was fabricated from pyrolytic boron nitride (PBN) or high-purity graphite because of their chemical inertness and endurance to a high temperature.

The flux density emanating from the effusion cell is given by [35]

\[ J = \frac{A \cdot p \cdot \cos \theta}{\pi \cdot L^2 \cdot (2 \cdot \pi \cdot m \cdot k_B \cdot T)^{1/2}} \]  

(2-1)

where \( A \) is the area of the aperture, \( p \) is the equilibrium vapor pressure in the cell, \( L \) is the distance between the cell and the substrate, \( m \) is the mass of the effusing species, \( k_B \) is the Boltzmann constant, and \( T \) is the cell temperature. Note that the above equation is only valid when the cell aperture size is smaller than the mean free path of vapor molecules within the cell.

After the species impinge on the substrate, they experience adsorption and migration on to the surface until they combine to form the films. This whole process can be described by a
“sticking coefficient, \( S \)”, which is defined as the fraction of the total number of impinging atoms or molecules that stick to the surface to that which are incorporated into the film.

The growth step for the desired film by MBE can be monitored by reflection high-energy electron diffraction (RHEED) which allows for the arrangement of the top few monolayers and crystal structure to be observed.

As elemental sources in MBE growth technique, gas or metal-organic sources, such as \( \text{PH}_3 \) and \( \text{AsH}_3 \), can be used due to easy control of the vapor pressure [36].

**Chemical Vapor Deposition (CVD)**

The chemical vapor deposition (CVD), which is sometimes also called by vapor phase epitaxy (VPE), is a technique in which the species for the growth of epitaxial film are transported as vapors to the substrate using a carrier gas. As the substrate is kept at a high temperature, the species experience surface diffusion and then combine with each other or other species to form the crystalline films. Typically, the following steps are common to CVD/VPE processes [37]:

1) Transport of the species to the substrate located in reaction chamber by the carrier gas
2) Adsorption of the species on the substrate surface
3) Reaction between the adsorbed species to form an epitaxial film
4) Desorption of reaction products from the substrate surface
5) Transport of the by-products away from the reaction chamber

Most of silicon and silicon-germanium films have been grown by the CVD technique because they have many available gas sources. Four sources of silicon have been widely used for epitaxial film: silicon tetrachloride (\( \text{SiCl}_4 \)), trichlorosilane (\( \text{SiHCl}_3 \)), dichlorosilane (\( \text{SiH}_2\text{Cl}_2 \)), and silane (\( \text{SiH}_4 \)). At a given temperature, the vapor pressure of silane is greater than other sources and that of silicon tetrachloride is the lowest of them, as shown in Fig. 2-2. This indicates that the silicon tetrachloride is the most stable silicon source, in turn the growth
temperature (1100 °C~1250 °C) using by SiCl₄ gas is the highest for the epitaxial film. On the other hand, the growth temperature when using the silane and/or dichlorosilane is around 500 °C~600 °C because they pyrolyze easily. In this study, the dichlorosilane as a silicon source was used because lower growth temperature was required for the strained epitaxial films.

**Metal Organic Chemical Vapor Deposition (MOCVD)**

Metal-organic chemical vapor deposition (MOCVD) is a variant of CVD technique. The only difference is the use of metal-organic materials as sources. For example, the mixture of trimethylgallium ((CH₃)₃Ga) and arsine under the presence of hydrogen can be pyrolized at 600 °C to deposit layers of GaAs.

There are two major advantages in MOCVD technique. First of all, the metal alkyls, which serve as sources of group III elements, are volatile liquids at room temperature so that they can be transported easily using a carrier gas. Second, the pyrolysis temperature of metal alkyls is lower than that of the metal halides, resulting in lower growth temperature [35].

The MOCVD technique is widely used for a variety of materials, such as GaAs, GaAlAs, InGaAsP, GaAsSb, InAsN, GaInP, ZnSe, ZnTe, AlN, GaN and so on [38-46]. In addition, the superlattices and quantum-well laser heterostructure can be easily deposited. In this study, MOCVD technique has been used for high crystalline GaN films.

**Pulsed Laser Deposition (PLD)**

Pulsed laser deposition (PLD) is one of the most famous techniques in research laboratories due to its wide application to almost any materials, in particular for compounds that are difficult or impossible to produce in thin film form by other techniques. In addition, PLD has the ability to closely maintain the target composition in the deposited thin films because of the very short duration and high energy of the laser pulse. On the other hand, there are some
disadvantages. The ablation plume cross section is generally small due to a limited laser spot size. In turn, this limits the sample size that can be prepared by PLD. Also, the plume of ablated material is highly forward directed, which causes poor conformal step coverage. Because of these disadvantages, PLD is mainly used for the investigation of new materials in a research environment. A schematic diagram of the basic PLD configuration is shown in Fig. 2-3 [47]. Lasers that are commonly used are ArF, KrF excimer layers, and Nd:YAG laser. It is generally recognized that the shorter the wave length, the more effective the ablation process is [48]. In this study, a KrF excimer laser was used as the ablation source and p-type ZnO films were grown by PLD. A focused laser pulse (pulse duration, 10~30 ns) strikes a target of the desired composition in a vacuum chamber. This incident high power pulsed laser beam (typically 2~5 J/cm²) heats up the target materials well beyond the evaporation temperature and produces an ejected plasma or plume of atoms, ions, and molecules. The materials dissociated from the target surface are deposited (velocities typically ~10⁶ cm/s in vacuum) as a thin film on a substrate. The growth process is strongly dependent on several parameters, such as the laser fluence and wavelength, the structural and chemical composition of the target materials, the chamber pressure and the chemical composition of the background gas, and the substrate temperature and the distance between the target and the substrate. These variables have to be optimized to achieve high quality epitaxial films.
Materials Characterization

X-ray Diffraction (XRD)

Instrument: X’Pert system for PANalytical

X-ray source: The ceramic filament with Cu target is used as the x-ray source in X’Pert system. The wavelengths of the characteristic X-ray lines for Cu target are $k_{\alpha 1} = 1.54056 \text{ Å}$, $k_{\alpha 2} = 1.54439 \text{ Å}$, and $k_{\beta} = 1.396 \text{ Å}$.

Goniometer: The goniometer for the X’Pert system has four-axis for rotation: omega ($\omega$), 2theta ($2\theta$), psi ($\Psi$) and phi ($\Phi$), as shown in Fig. 2-4. $\theta$ is an angle between the diffracted x-ray beam and the incident beam, $\omega$ is an angle between incident x-ray beam and sample surface, $\Psi$ is the tilt angle, and $\Phi$ is an in-plane rotation angle.

Primary optics (Incident x-ray beam): Two kinds of primary optics have been used: x-ray mirror and hybrid mirror which are shown in Fig. 2-5. First, the x-ray mirror gives a dichromatic beam of $k_{\alpha 1}$ and $k_{\alpha 2}$, eliminating $k_{\beta}$. The incident x-ray beam is 1.2 mm wide and 20 mm high without a mask or divergence slit and quasi-parallel to the samples surface with a horizontal divergence of $0.05^\circ$. The x-ray mirror is primarily used for 2theta-theta ($2\theta/\theta$), x-ray reflectivity (XRR), and grazing incidence x-ray diffraction (GIXD) scans. Second, the hybrid mirror gives the best resolution due to its monochromatic x-ray line in which $k_{\alpha 1}$ is only used.

Secondary optics (diffraction beam): there are two kinds as the secondary optics: parallel plate collimator over detector and triple axis optics which are shown in Fig. 2-6. The parallel plate collimator is used for x-ray reflectivity (XRR), 2theta-theta ($2\theta/\theta$), grazing incidence x-ray diffraction (GIXD) scans and its divergence is $0.27^\circ$. The triple axis optics has a double-arm attachment for high resolution applications. One arm is the rocking curve attachment and detector with a 6 mm aperture, which is corresponding to an acceptance angle of around 1
Another arm is a germanium crystal channel cut analyzer in which the diffracted beam from the sample experiences (022) reflections before entering the detector. The acceptance angle of this analyzer is 12 arc secs which is the highest resolution for all optic systems.

**Measurement method**

X-ray diffraction line profile analysis (microstrain and crystallite size): One of many characterization techniques for microstructure analysis is x-ray diffraction line profile analysis (LPA) in which the finite crystallite size and microstrain can be estimated by using the broadening of the diffraction peak. In 1918, Scherrer devised a famous formula explaining how the width of a Bragg reflection is affected by finite crystallite size [49].

\[
D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta_B}
\]  
(2-2)

where D is a size parameter, \( \theta_B \) Bragg angle, \( \beta \) a full width half maximum (FWHM), \( \lambda \) a wavelength and \( K \) a constant which is near unit. The diffraction peak broadening is also affected by other microstructural features, such as microstrain, dislocation, twin planes and stacking faults. Especially, the strain field in the vicinity of the dislocations makes d-spacing variable, resulting in the line broadening. The relationship between the strain and line broadening can be obtained by differentiating the Bragg equation.

\[
\frac{\Delta d}{\Delta(2\theta)} = \frac{\lambda \cdot \cos \theta}{4 \cdot \sin^2 \theta} = \frac{d_B \cdot \cot \theta}{2}
\]  
(2-3)

\[
\beta_D = 2K_D \varepsilon_{rms} \tan \theta
\]  
(2-4)

where \( \beta_D \) is the integral breadth, \( \varepsilon_{rms} \) root mean square strain and \( K_D \) a scaling factor.

Fig. 2-7 shows powder X-ray diffraction patterns from high temperature annealed and ball-milled Mo powder [50]. Annealed Mo has very sharp peaks which indicate free-strain and very large grain size. However, the width of the diffraction peak obtained from ball milled Mo (120
hr) is very broad which means that this sample has both finite grain size and microstrain. Since these two effects are generally mixed, they should be separated in order to estimate strain and size. The total peak broadening can be expressed with the combination of Eq. (2-2) and (2-4),

$$\beta_{2\theta} = \frac{K_S \cdot \lambda}{D_V \cdot \cos \theta} + 2K_D \varepsilon_{rms} \tan \theta$$  \hspace{1cm} (2-5)

The first and second terms in the right side relate to the finite size and microstrain, respectively. It is possible to separate these two effects using their different angle dependence. Multiplying both sides of above equation by $\frac{\cos \theta}{\lambda}$, we get:

$$\beta_{2\theta} \frac{\cos \theta}{\lambda} = \frac{K_S}{D_V} + K_D \varepsilon_{rms} \frac{2 \sin \theta}{\lambda}$$  \hspace{1cm} (2-6)

The plot of $\beta \frac{\cos \theta}{\lambda}$ vs $\frac{2 \sin \theta}{\lambda}$, which is called Williamson-Hall plot [51], should be a line, from which the average crystallite size and root mean square (RMS) strain can be determined from the intercept and slope, respectively. In addition, the separation of the effects of crystallite size and microstrain on the line broadening is possible by using the Warren-Averbach method, which makes use of the Fourier coefficients of the diffraction lines [52]. In this method, the Fourier coefficient ($A_L$) is the product of the size coefficient ($A_L^S$) and the strain coefficient ($A_L^D$) [53],

$$A_L = A_L^S \cdot A_L^D$$  \hspace{1cm} (2-7)

Warren has also shown that the Fourier coefficients can be written as following,

$$\ln A(L) = \ln A^S(L) - 2\pi^2 L^2 h^2 \langle \varepsilon^2 \rangle / a^2$$  \hspace{1cm} (2-8)

where $L$ is the Fourier length and $a$ the lattice parameter. If the $\ln A(L)$ values are plotted versus the square of reflection order, $h^2$, the slope and intercept of the curves could be
determined which are corresponding to the average microstrain and size coefficient, respectively. In addition to the line broadening by the finite size and microstrain, another broadening source is the instrumental broadening which is dependent on the used slit system and X-ray, imperfect focusing and so on. In order to perform line profile analysis, the Bragg diffraction peak needs to be fitted by mathematical functions. Since LPA is strongly dependent on the used fitting function, this needs to be carefully selected. In general, the measured diffraction profile is not well fitted by pure Gaussian or Cauchy (or Lorentzian) functions so that several other mathematical functions, such as Pearson VII, Voigt and Pseudo-Voigt functions [54-56], are suggested for an accurate Line Profile Analysis. Their shape is shown in Fig. 2-8.

X-ray reflectivity (thickness, density, and roughness of the thin films): X-ray reflectivity (XRR) curves give us useful information about the thin film, such as the thickness, roughness, and density. The X-ray reflectivity curve obtained from a strained-Si$_{1-x}$Ge$_x$/Si layer and its simulation are shown in Fig. 2-9. First of all, we can see the appearances of thickness fringe which are so called Kiessig fringes [57]. Using the periodic of the oscillations from the XRR curve, we can estimate the thickness of the layer. The electron density of the material can be also determined by measuring the critical angle at which the total reflection occurs. In addition, XRR curve can be affected by free surface and interfacial roughness. The kinematical and dynamical theories for the reflectivity allow us to determine the roughness. In Fig. 2-9, the layer model, which consists of interfacial layer, Si$_{1-x}$Ge$_x$, and free surface, was applied for the best simulation. The result of the simulation for the strained-Si$_{1-x}$Ge$_x$ sample is also shown in Fig. 2-9.

Omega-2theta rocking curve (thickness, strain, lattice mismatch, alloy composition): In an omega-2theta rocking curve (ω-2θ RC) of pseudomorphically grown strained-Si$_{1-x}$Ge$_x$, or Al$_{1-x}$Ga$_x$N, Ge and Al compositions can be estimated by a separation of different Bragg peaks of
substrate and strained-layer. In the case of symmetric diffraction, an angular separation \( \Delta \eta_i \) is given by [58]

\[
\Delta \eta_i = \Delta \theta_0 + \Delta \theta_B
\]  
(Eq.2-9)

where \( \Delta \theta_0 \) is the angular separation due to the different amount of the refraction of the X-ray beam at the air-layer and layer-substrate interface, and \( \Delta \theta_B \) is the Bragg angle difference between the layer and substrate. Fig. 2-10 shows a rocking curve recorded around (004) Bragg angle of strained-Si\(_{1-x}\)Ge\(_x\) and its simulation using Philips Epitaxy Program. The different angular position of the diffraction peaks from strained layer and substrate depends on Ge composition and strain-relaxation in the epitaxial layer. It was also found that the thickness oscillation occurred around the Bragg peak. The oscillations can be understood by the multiple scattering of diffracted waves along Q\(_z\)-axis due to the different boundaries. This is similar to X-ray Reflectivity. But, while XRR is independent of the crystal form, the reflection near Bragg angle in the rocking curve is dependent on the lattice periodicity. For asymmetric Bragg diffraction, the inclination angle, which is an angle of the plane with respect to the sample surface, should be considered in an angular separation \( \Delta \eta_i \). If it is assumed that the strained layer will be tetragonally distorted, the inclination angle of the substrate and strained layer at given diffraction plane has a different value. If the refraction is independent of the diffraction geometry, the separation of Bragg and inclination angles can be determined by using two complementary geometries, which are the so called \( \phi_+ \) and \( \phi_- \). Fig. 2-11 shows the two different geometries for asymmetric Bragg diffraction and \( \omega-2\theta \) RC recorded around for (115) plane of strained Si\(_{1-x}\)Ge\(_x\) layer, respectively. These different geometries for asymmetric Bragg diffraction allow us to separate \( \Delta \theta_B \) and \( \Delta \phi \).
\[
\begin{align*}
\Delta \theta_+ &= \Delta \theta_b + \Delta \theta \\
\Delta \eta_+ &= \Delta \theta_b - \Delta \theta
\end{align*}
\Rightarrow
\begin{align*}
\Delta \theta_b &= \frac{1}{2} (\Delta \eta_+ + \Delta \eta_-) \\
\Delta \theta &= \frac{1}{2} (\Delta \eta_+ - \Delta \eta_-)
\end{align*}
\tag{2-10}
\]

If the separation of Bragg diffraction and inclination between the substrate and top layer is given, it gives rise to the lattice mismatch components [58].

\[
\begin{align*}
\delta_{L\perp} &= \Delta \phi \tan \phi - \Delta \theta_b \cot \theta_b \\
\delta_{L//} &= -\Delta \phi \cot \phi - \Delta \theta_b \cot \theta_b
\end{align*}
\tag{2-11}
\]

where \( \delta_{L\perp} \) and \( \delta_{L//} \) are perpendicular and parallel mismatch, respectively. The cubic lattice mismatch \( \delta_{L\perp} \) is given by

\[
\delta_{L\perp} = \frac{a_{L\perp} - a_s}{a_s} = \frac{\delta_{L\perp} \cdot c_{11} + 2 \cdot \delta_{L//} \cdot c_{12}}{c_{11} + 2 \cdot c_{12}}
\tag{2-13}
\]

where \( c_{11} \) and \( c_{12} \) are the elastic constants at each crystallographic direction and \( a_{L\perp} \) is a cubic lattice parameter at certain Ge composition [59,60].

Reciprocal space map (relaxation, strain, lattice mismatch, alloy composition): The reciprocal space map (RSM) represents an intensity distribution of the diffracted x-rays along \( Q_z \) and \( Q_X \) at which \( Q_z \)-axis is parallel to the normal of the sample surface in outward direction and \( Q_X \)-axis is parallel to the sample surface. Fig. 2-12 (a) shows the position of two reciprocal lattice points belonging to the substrate and the layer for symmetric and asymmetric geometry. In the case of symmetric geometry, the perpendicular mismatch between the substrate and layer can be measured from reciprocal space map, while there is no information about the parallel mismatch due to same inclination angle. Since the asymmetric space map could reveal the parallel mismatch as well as the perpendicular mismatch, it is more helpful to provide more
information about the strained layer. In Fig. 2-12 (a), if the reciprocal lattice positions of the substrate and layer are \( Q(X_S, Z_S) \) and \( Q(X_L, Z_L) \), the lattice mismatch can be given by

\[
\delta_z = \frac{Z_L - Z_S}{Z_L} \\
\delta_x = \frac{X_L - X_S}{X_L}
\]

As the perpendicular and parallel mismatches are determined, it is possible to estimate Ge composition of the strained layer. In Fig. 2-12 (b), a reciprocal space map recorded around (115) diffraction point of strained-Si\(_{1-x}\)Ge\(_x\) is shown. The reciprocal lattice points of silicon substrate and strained Si\(_{1-x}\)Ge\(_x\) layer are located to above and below region, respectively. It was found that the parallel and perpendicular lattice mismatches were 116 ppm and 10350 ppm and the estimated Ge content was 15.70%. This small parallel mismatch indicates that the strained-Si\(_{1-x}\)Ge\(_x\) layer is pseudomorphically grown on silicon substrate. In other way, the shape and position of each reciprocal lattice point also contain microstructural information. Around the reciprocal lattice point of Si substrate, the coherent crystal truncation rod and analyzer streak appeared. In contrast to Si substrate, it is shown that the reciprocal lattice point of the strained layer is relatively broadening along \( Q_Z \)-axis because it has a finite vertical thickness compared to the infinite thickness of the silicon substrate. Another information obtained from this reciprocal space map is the presence of a tetragonal distortion of the strained Si\(_{1-x}\)Ge\(_x\) layer which is confirmed because the different inclination angle between two crystals can be expressed by the angle difference between two reciprocal lattice directions.

Mosaicity (tilt, twist, and lateral & vertical coherence length): The lattice parameter, thermal expansion coefficient, and crystal structure of the epitaxial layer with respect to the substrate should be considered for high quality film growth due to the lack of bulk substrate.
These mismatches during the film growth generate the mosaic structure, which means that the films have sub-grain slightly misoriented with respect to each other and the underlying substrate. Fig. 2-13 represents a reciprocal space map (RSM). Fig. 2-13 (a) shows how the RSM is recorded around a given lattice point by omega-2theta scans with different offset omega values. Fig. 2-13 (b) represents a comparison between reciprocal and real lattices. If it is assumed that the substrate has a perfect crystal structure, there is not any broadening effect in the reciprocal lattice point of the substrate. However, the epitaxial layer should have some structural defects which are a source of the broadening of the reciprocal lattice point. In general, since the thickness of the epitaxial layer is much thinner compared to the substrate, the reciprocal lattice point is vertically broadened. In this study, the recorded reciprocal lattice points due to heteroepitaxial mosaicity were broadened in both the lateral and the vertical directions. Generally, the mosaic structure can be described by four parameters; tilt, twist, lateral and vertical coherence lengths [61]. Fig. 2-14 (a) shows a mosaic structure. The tilt and twist are out-of-plane and in-plane misorientation, respectively.

The coherence length can be defined as an average size extension of the crystal lattice regions which scatter coherently and are defects free. These mosaic domains cause reciprocal lattice point broadening, which in turn means that they are related to crystal structural defects. Fig. 2-14 (b) represents the reciprocal lattice point broadening due to the mosaic spread. The finite vertical coherence length broadens the reciprocal lattice point along QZ axis, whereas the finite lateral coherence length broadens it along QX or QY axis. These coherence lengths give information on average crystallite size in a mismatched epitaxial layer. In addition, the mosaic tilt & twist broaden the reciprocal lattice point along the lattice tilt direction. In general, since these mosaic parameters are mixed, they need to be separated. Since the separation of these
effects is still very complex using x-ray diffraction, it is an active research topic. The most interesting result in this study is that these mosaic parameters are strongly dependent of the specific type of the dislocations. This will be presented in chapter four.

**Transmission Electron Microscopy (TEM)**

To obtain highly magnified images of the samples structure, transmission electron microscopy (TEM) technique has been widely used. Basically, TEM is very similar to the optical microscopy (OM) because both have a series of lenses systems to magnify an image. However, TEM has a great strength in the resolution issue, approaching around 0.08 nm. The following is a resolution equation,

\[ s = \frac{0.61 \cdot \lambda}{N \cdot A} \]  

(2-16)

where \( s \) is the resolution (the minimum distance between points or parts of an object), \( \lambda \) is the beam wavelength, \( N \cdot A \) is the numerical aperture (resolving power of the lens and the brightness of the image). In the optical microscopy, NA is around 1 and \( \lambda = 500 \text{ nm} \), giving \( s = 300 \text{ nm} \). In TEM, while NA is around 0.01 due to large imperfection of the electro-magnetic lens system, the electron wavelength conventionally used in TEM under 100 kV is around 0.004 nm, giving \( s = 0.25 \text{ nm} \) which is much better than OM.

A schematic of a TEM instrument is shown Fig. 2-15 [62]. The high energy electron beam with 100 to 400 kV voltages are generated and accelerated from the electron gun. There are two kinds of the electron gun: thermal and field emission electron gun. The electron beam can be focused on the thin sample (around 50~200 nm thick) by the electro-magnetic condenser lenses. The transmitted and scattered electron beams from the thin sample give diffraction pattern and magnified image in the back focal and image planes of the objective lens, respectively. There are
several imaging methods using TEM: bright-field, centered beam dark-field, weak beam dark-field and high resolution lattice imaging techniques.

In this study, both the TEM 200 CX and TEM 2010F instruments located in MAIC, University of Florida, were used.

**X-ray Photoelectron Spectroscopy (XPS)**

X-ray photoelectron spectroscopy (XPS), which is sometime also known as electron spectroscopy for chemical analysis (ESCA), is a technique using the photoelectric effect. This technique is used for identifying chemical elements and bonding information for all elements except hydrogen and helium atoms. Mg Kα (1253.6 eV), Al Kα (1486.6 eV), or monochromatic Al Kα (1486.7 eV) x-rays are usually used [63]. XPS is a surface sensitive technique because only e⁻ generated in the upper 0.5-5 nm depth of the sample could exit the material without losing energy. Fig. 2-16 shows a schematic of a XPS instrument and its electron excitation process [62]. A high energy x-ray beam is incident into the sample, and then the electrons are emitted from specific orbitals when x-ray energy exceeds their binding energy. The conservation of energy for the ejected electrons taking into account the binding energy can be described as following,

$$E_b = h\nu - E_{detect} - q\phi$$  \hspace{1cm} (2-17)

where $E_b$ is a binding energy, $h\nu$ is the incident x-ray energy, $E_{detect}$ is the measured energy in the electron detector, and $\phi$ is the work function. The binding energy may be regarded as the energy difference between the initial and final states after the photoelectron has left the atom. Note that since the binding energy is dependent on the incident x-ray energy, it should be monochromatic. Each element has a specific binding energy and it is possible to identify the element information using tabulated values and other references. In addition, since the electron
binding energy is dependent of the chemical ambience, XPS allows for understanding of the chemical bonding state.

**Atomic Force Microscopy (AFM)**

Atomic force microscopy (AFM) or scanning probe microscopy (SPM) is a high resolution surface imaging technique. The AFM consists of a microscale cantilever with a sharp probe, laser source, photodiode and detector & feedback electronics, as shown in Fig. 2-17 [64]. The principle of AFM is based on the effect of interaction force between the sharp tip and the sample surface that bends the cantilever. When the tip is brought to the sample surface, the cantilever bends by responding to the interaction force according to the topography of the surface, resulting in the dependent position of the incident laser beam on the detector. Finally, the photodiode, which is sensitive to the cantilever deflection, generates topographic data.

There are two different imaging methods in AFM: tapping and contact modes. In the tapping mode, the image can be produced by imaging the interaction force of the oscillating contacts of the tip with the sample surface. However, in the contact mode, the cantilever drags directly across the sample surface at constant force, resulting in possible surface damage.

**Hall Measurements**

Hall effects allow us to determine the carrier type, carrier density, carrier mobility and film resistivity. When the magnetic field is applied normal to the sample surface, the electric field is set up across the sample due to the charge separation. This potential difference by the induced electric field is so called Hall voltage. Hall theory gives the Hall coefficient \( R_H \) as following [62],

\[
R_H = \frac{r(p - b^2 n)}{q(p + bn)^2} = \frac{r}{qp} (p - \text{type}) = -\frac{r}{qp} (n - \text{type})
\]  

(2-18)
where \( R_H \) is the Hall coefficient, \( r \) is the scattering factor, \( p \) is the hole density, \( n \) is the electron density, and \( b = \frac{\mu_n \text{(electron - mobility)}}{\mu_p \text{(hole - mobility)}} \). Typically, it is assumed that \( r \) is of the order of unit. The Hall coefficient allows us to determine the carrier type as well as the carrier concentration.
Figure 2-1. A schematic of a conventional MBE system [35].

Figure 2-2. Vapor pressure dependence with temperature for different silicon sources used in epitaxy [37].
Figure 2-3. The schematic diagram of a pulsed laser deposition (PLD) system [47].

Figure 2-4. PANalytical X’Pert system. (a) schematic of X’Pert system and (b) four-axis variables.
Figure 2-5. Mirrors used in primary optics. (a) x-ray mirror and (b) hybrid mirror.

Figure 2-6. Secondary optics. (a) parallel plate collimator and (b) triple axis optics.
Figure 2-7. Powder x-ray diffraction pattern of Mo powder. (a) high temperature annealed Mo powder and (b) ball milled (120hr) Mo powder [50].

Figure 2-8. (102) reflection of the GaN grown on sapphire substrate and curve fitting using Gauss, Cauchy, Pearson, and Pseudo-Voigt functions.
Figure 2-9. Experimental and fitted X-ray reflectivity curves of a strained Si$_{1-x}$Ge$_x$ on silicon substrate. The simulation was performed by using Wingixa software from PANalytical.

Figure 2-10. Experimental (004) omega-2theta rocking curve and simulation curve. The simulation was carried out by using Epitaxy software from PANalytical.
Figure 2-11. Omega-2theta rocking curve of asymmetric diffraction plane. (a) $\Phi_-$ and $\Phi_+$
geometry and (b) omega-2theta rocking curve obtained from $\Phi_-$ and $\Phi_+$ geometry in
strained Si$_{1-x}$Ge$_x$ on silicon substrate [58].

Figure 2-12. Reciprocal space map (RSM). (a) reciprocal lattice points of substrate and layer in
symmetric and asymmetric Bragg diffraction and (b) reciprocal space map recorded
around (115) plane.
Figure 2-13. Reciprocal space map and real crystal lattice. (a) reciprocal space map and (b) comparison between reciprocal lattice point and real space lattice.

Figure 2-14. Mosaicity. (a) mosaic structure of epitaxial layer and (b) reciprocal lattice point of (002) and (102) [61].
Figure 2-15. A schematic of a transmission electron microscope (TEM) [62].

Figure 2-16. A schematic of a XPS instrument and its electron excitation process [62].
Figure 2-17. A schematic of an AFM instrument and its operation [64].
CHAPTER 3
DEFECTS EVOLUTION IN P-TYPE ZNO

Phosphorus Doped ZnO Thin Films Grown on Sapphire Substrates

Experimental Design

The ZnO:P layers were grown on c-plane sapphire substrates by the pulsed laser deposition (PLD) technique at 700 °C in an oxygen partial pressure of 150 mTorr. Prior to ZnO:P deposition, an undoped ZnO buffer layer was deposited on the sapphire at 400 °C in 20 mTorr. The buffer layer was annealed at 650 °C in an oxygen ambient prior to ZnO:P deposition. This served as a nucleation layer for ZnO:P growth, greatly improving surface morphology and reproducibility in the transport properties. Phosphorus-doped ZnO targets were fabricated using high-purity ZnO powder (99.9995 %) mixed with P₂O₅ (99.998 %) powder as the doping agent and sintered at 1000 °C for 12 h in air. The phosphorus doping levels chosen for this study were 0.5 and 1 at. %. The target was ablated by a KrF excimer laser with a laser frequency of 1 Hz and energy density of approximately 1.5 J/cm². The film thickness was approximately 400 nm for the ZnO:P layer and 100 nm for the undoped ZnO buffer layer. The microstructure of ZnO:P was examined by Philips MRD X'Pert system for 2theta/theta (2θ/θ) scan and omega rocking curves (ω-RCs). The room temperature electrical properties were investigated by Hall effect measurements using the four-point van der Pauw geometry with a commercial LakeShore Hall measurement system. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical bonding state of atoms in ZnO:P films with a Perkin-Elmer PHI 5100 ESCA System. In XPS analysis, the position of the adventitious C 1s peak was considered as a standard reference with a binding energy at 284.6 eV.
Results and Discussion

**Microstructure of phosphorus doped ZnO films:** high quality ZnO films have been grown on several substrates, such as sapphire (Al₂O₃), silicon carbide (SiC), gallium nitride (GaN), silicon (Si), and so forth [30-33]. Of these substrates, c-plane sapphire substrates are commonly used for ZnO film growth due to its hexagonal crystal structure, transparency and relatively low cost. However, the large mismatch of the in-plane lattice parameter and rather different thermal expansion coefficient between the sapphire (a₂₃=4.757Å, $\alpha_a = 7.3 \times 10^{-6}/K$) and zinc oxide (a₂₃=3.252 Å, $\alpha_a = 2.9 \times 10^{-6}/K$) are a challenge for the high quality film growth [29]. Fig. 3-1 (a) shows the $\{11\bar{1}0\}$ pole figure of as-grown, 0.5, and 1.0 at. % P-doped ZnO films grown on the c-plane sapphire substrate. It is shown that the ZnO films are textured along the c-axis and the degree of texture is degraded with increasing phosphorus atomic percent in ZnO. Interestingly, it is also found from the pole figure that there are two columnar structures with different in-plane orientations in hexagonal crystal structure in which one possesses higher crystallinity than the other. In order to identify the crystal orientation, the $\{10\bar{1}1\}$ and $\{10\bar{1}4\}$ phi ($\phi$)-scans of ZnO film and sapphire substrate, respectively, were performed, as shown in Fig. 3-1 (b). While the broad periodic peaks are exactly matched to the sapphire peaks, the sharp ones are deviated from the substrate peaks. The measured deviation angle between the sharp and broad peaks was exactly 30°. The growth of ZnO films on c-plane sapphire substrate resulted in the in-plane epitaxial relationship of $ZnO[10\bar{1}0] // Al_2O_3[11\bar{2}0]$ and $ZnO[10\bar{1}0] // Al_2O_3[10\bar{1}0]$ for two columnar structures with sharp and broad peaks, respectively. The reason for smaller peak width of ZnO films with 30° in-plane rotation with respect to the sapphire substrate is a decrease in the lattice mismatch from 31.6 % to 18.4 %. Conventionally, the two step growth method has been used for high quality
ZnO films in which the nucleation layer was grown at low temperature or low oxygen pressure, followed by subsequent growth of the main ZnO at high temperature and/or high oxygen pressure [65,66]. In our study, the growth temperature used during the deposition of the nucleation layer was 400 °C, which is lower than that conventionally used for high crystalline quality n-type ZnO film growth. Relatively lower nucleation temperature causes a reduction of adatom surface mobility/diffusion length during the film growth, leading to poorer crystalline quality.

Omega rocking curves (ω-RCs) were recorded in order to investigate the crystalline quality, as shown Fig. 3-2. (0002) and (10 T 1) ω-RCs were measured in symmetric and asymmetric geometries. For all samples the (0002) ω-RCs showed higher intensity and smaller full width at half maximum (FWHM) values than the (10 T 1) ω-RCs, which indicates that the in-plane columnar domains are twisted with a certain angle due to the presence of threading dislocations, resulting in the formation of the low angle grain boundary. It was reported that the low angle grain boundary was due to the edge type dislocations generated from the high defective initial nucleation layer [67]. Hence, the ZnO samples consisted of highly textured columnar grains along c-axis with certain width. This width can be described by the lateral coherence length, which can be defined by the average extension of the crystal lattice regions which scatter coherently. [61,68]. The lateral coherence length calculated from (0002) ω-RC gives under-estimated value because an influence of the edge type dislocations in the low angle boundary on the change in the d-spacing of out-of-plane is very slight. Therefore, the coherence length should be measured from the FWHM of the ω-RC of the diffraction plane with high inclination angle (χ), which is the angle between sample surface normal direction and diffraction plane normal direction. From the Scherrer equation and FWHM values of (10 T 1) ω-RC (χ=60°)
the calculated lateral coherence length is 67 Å, 40 Å, and 15 Å for as-grown, 0.5, and 1.0 at % P-doped ZnO films, respectively. It is clear from Fig. 3-2 that the crystalline quality degrades and the columnar grain width decreases with increasing phosphorus atomic percent in ZnO films.

**Line profile analysis of phosphorus doped ZnO:** for further analysis of the microstructure of P-doped ZnO films, an x-ray diffraction line profile analysis (LPA) was performed. The width of Bragg reflections is caused by the microstructural features, in which the finite crystallite size and microstrain play a key role in the diffraction line broadening. Several {0001} diffraction planes were recorded in $\theta/2\theta$ scan mode. Using a Williamson-Hall plot, the strain and size broadening effects can be separated, as shown in Fig. 3-3 [51]. The plot of $\beta \cdot \frac{\cos \theta}{\lambda}$ versus $\frac{2 \sin \theta}{\lambda}$, in which $\beta$ is the integral breadth, $\theta$ is the Bragg angle, and $\lambda$ is the x-ray wavelength, gives a straight line which allows for the determination of average crystallite size ($<D>_V$) and the r.m.s. strain ($\varepsilon_{\text{rms}}$) from the intercept and slope, respectively. It is clearly shown from the Williamson-Hall plot that while the crystallite size is almost identical at around 500~600 Å in all ZnO samples, the 0.5 at % P-doped ZnO film shows the highest microstrain of around 0.119%. For an accurate separation of these two contributions, the data were analyzed by the Warren-Averbach method which makes use of the Fourier coefficients from at least two harmonic reflections [53]. In this study, the Warren-Averbach method was performed by Philips Line Profile Analysis program using the (0002) and (0004) diffraction planes. The result is shown in Fig. 3-4 and table 3-1. Although two methods give different strain values about ZnO films, the 0.5 at % P-doped ZnO film shows the highest strain by both methods. The behavior of the P atoms in ZnO films is still under debate. It was reported that the P atoms are substitutionally incorporated on the oxygen sites, resulting in the formation of a deep level acceptor from the valence band of ZnO [69]. Another report showed that the phosphorus doping
in ZnO formed the antisite complex (P_{Zn}-2V_{Zn}) due to the large mismatch between the phosphorus and oxygen ionic radii [70]. Regardless of the different behavior of the phosphorus as mentioned above, we believe that its incorporation into the ZnO films must generate an internal strain. From the x-ray diffraction line profile analysis, the phosphorus in 0.5 at % P-doped ZnO was effectively incorporated into ZnO films, resulting in the highest strain. From the Hall measurement, the 1.0 at % P-doped ZnO film (1.8 × 10^{17} cm^{-3}) showed lower carrier density than the 0.5 at % P-doped ZnO film (6.2 × 10^{17} cm^{-3}) which is consistent with lower substitutional incorporation confirming the results of the x-ray diffraction line profile analysis.

Phosphorous segregation: for the chemical analysis of the films, x-ray photoelectron spectroscopy (XPS) investigations were performed. Fig. 3-5 shows high resolution scans of the P 2p_{3/2} region for the 0.5 and 1.0 at % P-doped ZnO films. The acquired spectra can be deconvoluted into two different peaks centered at binding energies of 130.0 and 133.5 eV [71]. The lower binding energy, denoted by P1, corresponds to P-P bonding state, while the higher binding energy could be regarded as P-O bonding state. Hence, P incorporated into ZnO films exists as P-P and P_{Zn}. In Fig. 3-5, the ratio of A_{P1}/A_{P2} was determined, indicating that P in 0.5 at % P-doped ZnO film has been effectively incorporated into Zn site while P in 1.0 at % P-doped ZnO film tended to segregate. From the analysis of XRD and XPS results, it appears that 0.5 at % P-doped ZnO film shows higher strain due to the occupancy of P into Zn site while 1.0 at % P-doped ZnO film relaxed a strain with the P segregation, resulting in the degradation of the crystalline quality and electrical properties.

Conclusion

The microstructure of P-doped ZnO films with different phosphorus atomic percent was investigated. From XRD and XPS data, a significant fraction of phosphorus atoms in 1.0 at % P-
doped ZnO film are segregated while in 0.5 at % P-doped ZnO film they are effectively incorporated into ZnO film, resulting in high internal strain. The degree of texture and crystalline quality of ZnO films degraded with increasing phosphorus atomic percent.
Table 3-1. Comparison of results from Williamson-Hall plot and Warren-Averbach method applied to as-grown and phosphorus doped ZnO films.

<table>
<thead>
<tr>
<th></th>
<th>Williamson-Hall plot</th>
<th></th>
<th>Warren-Averbach method</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Strain (%)</td>
<td>Crystallite size (Å)</td>
<td>Strain (%)</td>
<td>Crystallite size (Å)</td>
</tr>
<tr>
<td>As-grown</td>
<td>0.002</td>
<td>540</td>
<td>0.038</td>
<td>550</td>
</tr>
<tr>
<td>0.5 at. % P-doped</td>
<td>0.119</td>
<td>680</td>
<td>0.072</td>
<td>618</td>
</tr>
<tr>
<td>1.0 at. % P-doped</td>
<td>0.035</td>
<td>558</td>
<td>0.059</td>
<td>535</td>
</tr>
</tbody>
</table>
Figure 3-1. Crystal orientation of ZnO films. (a) pole figures of as-grown, 0.5 and 1.0 at % P-doped ZnO films and (b) phi scans of \{10\overline{1}4\} sapphire substrate and \{10\overline{1}1\} ZnO film.

Figure 3-2. Omega rocking curves of symmetric and asymmetric diffraction planes of as-grown, 0.5, and 1.0 at % P-doped ZnO films.
Figure 3-3. Williamson-Hall plot of as-grown, 0.5, and 1.0 at % P-doped ZnO films.
Figure 3-4. Microstrain of as-grown, 0.5, and 1.0 at % P-doped ZnO films obtained from the Williamson-Hall plot and Warren-Averbach method.

Figure 3-5. XPS spectra acquired from 0.5 and 1.0 at % P-doped ZnO films. P 2p$^{3/2}$ of (a) and 0.5 (b) 1.0 at % P-doped ZnO films.
CHAPTER 4
DEFECTS EVOLUTION IN GaN EPITAXIAL LAYERS

GaN Grown on Sapphire Substrate

Experimental Design

The GaN films were grown on c-plane sapphire substrates using a Veeco P75 vertical MOCVD reactor via a conventional two-step growth method [16,18]. Trimethylgallium (TMGa), ammonia (NH₃), and hydrogen (H₂) were used as the Ga and N precursors, and carrier gas, respectively. The growth process was monitored by the reflectance transient method [72]. A 20 nm thick GaN nucleation layer (NL) was grown initially at 532~550 °C. Then, the temperature was ramped up to 1028~1096 °C for high temperature three-dimensional (3D) islands growth. The growth conditions for the high temperature islands and low temperature nucleation layer, which are shown in table 4-1, were controlled by changing TMGa flow rate with the same V/III ratio and growth temperature. Finally, about 2 μm thick main GaN layers were deposited with a growth rate of 1.8 μm/h in 100 Torr. A PANanalytical MRD X'Pert system was used for ω-RCs and φ-scans in skew and grazing incidence geometries. For the cross sectional TEM imaging of the GaN layers, a JEOL TEM 200CX was used and the sample preparation was carried out by using the focused ion beam (FIB) technique.

Results and Discussion

Grazing incidence x-ray diffraction (GIXD) technique: many investigations have been performed using high resolution x-ray diffraction (HRXRD) for the estimation of threading dislocation density of high quality GaN films because of their specific dislocation structure in which the line direction and Burgers vectors are $l = [0001]$, $\vec{b}_{\text{screw}} = [0001]$, $\vec{b}_{\text{edge}} = \frac{1}{3}[11ar{2}0]$. 

64
respectively [73,74]. The structural defects of GaN with a high dislocation density can be described by mosaic parameters: tilt, twist, lateral and vertical coherence lengths [61,68]. Tilt and twist are out-of-(polar spread) and in-plane (azimuthal spread) misorientations, respectively, and the lateral and vertical coherence lengths are an average crystallite size that is free of defects. The reciprocal lattice points are broadened along specific directions by these mosaic parameters. The strain fields near the screw and edge dislocations, which distort the d-spacing of the planes parallel and perpendicular to the surface, respectively, are associated with the polar and azimuthal spreads [75]. If the widths of the omega rocking curves (ω-RCs) measured from parallel and perpendicular planes are obtained, then the screw and edge dislocation densities can be estimated. Measurement of the polar spread is very straightforward and directly obtained by a symmetric high resolution X-ray diffraction setting. The determination of the azimuthal spread requires diffraction from planes normal to the surface and it can be achieved by transmission or edge geometry diffraction methods as shown in Fig. 4-1 [76,77]. However, the diffracted beam from the film is too heavily attenuated by the thick substrate for the transmission geometry and a micro-focusing X-ray beam is required for the edge geometry [78]. On the other hand, Srikant et al. indirectly estimated the twist angle by using the plot of the full width at half maximum (FWHM) values of the ω-RCs vs the inclination angles ($\chi$) and Heinke et al. reported that FWHM of the ω-RC of (3032) plane with a large inclination angle ($\chi = 72^\circ$) could be used as a figure of merit (FOM) for the edge dislocation density [79,80]. Also, the theoretical model for the determination of the mosaic parameters developed by Lee et al. showed much-improved agreement between the XRD and TEM results [81]. Here, this study presents the results of the grazing incidence phi (ϕ)-scans to directly obtain the twist parameter without any complicated computation.
If the ω-RCs of on-axis reflections, such as (0002), (0004), and (0006), are measured, the tilt angle can be estimated by using the Williamson-Hall plot in which the slope and y-axis interception correspond to the tilt angle and lateral coherence length, respectively [73]. On the other hand, when diffraction from the surface normal planes (χ = 90°), such as (10 Č 0) or (11 Č 0), is required for the determination of the twist angle, the grazing incidence φ-scan is performed. In this study, the broadening of the RCs due to the finite vertical and lateral coherence length is neglected because its effect is minor. Other broadening effects, such as X-ray extinction, film curvature, and instrumental limits, are also negligible because they contribute to only a few arcsec [82]. Therefore, FWHM values of the ω-RCs of (0002) and φ-scan of (10 Č 0) are considered as a FOM for screw and edge type dislocation densities, respectively. Fig. 4-2 (a) shows a φ-scan of the {10 Č 0} plane recorded by grazing incidence XRD technique. The six diffraction peaks are well defined, which represent the six-fold symmetry of the wurtzite GaN. Since the ω-axis is co-axial with the φ-axis for χ = 90°, the diffraction profile of the (10 Č 0) ω-RC measured under grazing incidence angle is shown in Fig. 4-2 (b). In this study, ‘ω’ can be defined as the angle between the X-ray incident beam and the diffraction plane parallel direction and ‘χ’ as an angle between the diffraction plane and sample surface normal directions. The in-plane resolution of ω-RC is 0.0001°, which is much finer than φ-scan because the maximum resolution step of the φ-axis in our X’Pert system is just 0.01°. Therefore, all grazing incidence φ-scans acquired during this study were performed by the ω-RC technique measured in χ~90°. In addition, the line profiles were fitted by using a Pseudo-Voigt function, because a pure Gaussian function was not suitable due to the broadening near the tail region of the diffraction profiles [56].
The measured FWHM values of the in-plane, asymmetric plane and out-of-plane ω-RCs of the GaN films used in this study are shown in Table 4-2. In this study, the instrumental broadening was neglected because it contributed to only a few arc sec. The tilt and twist angles of the high defective GaN layers are associated with the screw and edge type dislocations \((l = [0001], \ b_{\text{screw}} = [0001], \ b_{\text{edge}} = \frac{1}{3}[1\overline{1}20])\), respectively \([73,74]\). Heying et al. reported that FWHM of \((10\overline{1}2)\) ω-RC could be a relevant figure of merit (FOM) for the crystal quality because this can be broadened by both type dislocations \([83]\). As shown in Table 4-2, the FWHM values of the ω-RC of the surface normal plane are much larger than one of the surface parallel plane, which is indicative that the edge type threading dislocations are dominant. Therefore, the crystalline quality of GaN layer should be determined only by the edge dislocation density.

Typical bright field images from sample ‘A’ and ‘E’ in Table 4-1 are shown in Fig. 4-3. Under \(\bar{g} = 0002\), the type of the threading dislocations that can be observed are pure screw or mixed \((l = [0001], \ b_{\text{mixed}} = \frac{1}{3}[1\overline{1}23])\), while the edge or mixed dislocations are visible under \(\bar{g} = 11\overline{2}0\). By analyzing Fig. 4-3, it was found that the edge and mixed type dislocations were the dominant defects in the GaN films, which is consistent with XRD data mentioned above. Heinke et al. suggested that the FWHM of \((30\overline{3}2)\) ω-RC could be a figure of merit for the edge dislocation density because this plane has a high inclination angle (~71°) with respect to the surface plane. They reported that the twist angle was \(1.14 \pm 0.04\) times the FWHM value of the \((30\overline{3}2)\) ω-RC \([84]\). In our case, the sample ‘D’ shows the minimum FWHM value of the \((30\overline{3}2)\) ω-RC, but the sample ‘E’ shows the minimum FWHM value of the \((10\overline{1}0)\) ω-RC and the best crystalline quality of all GaN films. This discrepancy might be due to the dependent distribution of the tilt and twist angles. Srikant et al. used a mathematical formulation to obtain a relationship between
the tilt and twist distributions [79]. Therefore, a FOM for the crystalline quality should be determined by the FWHM value of the \( \omega \)-RC of the surface perpendicular plane. In this aspect, the grazing incidence X-ray diffraction is a more suitable technique than above mentioned theoretical method for the study of the growth optimization since it requires only one omega rocking curve and the twist angle can be directly measured without any theoretical computation.

**Relationship between growth conditions and defects:** Fig. 4-4 shows a plot of the FWHMs of the \( \omega \)-RC of sample ‘A’ \( (t_{3D}=10.0 \text{ min}) \) and ‘B’ \( (t_{3D}=16.7 \text{ min}) \) and inclination angles \( (\chi) \). One can see that FWHM values of the \( \omega \)-RC increase with increasing the inclination angle. While Zheng et al. determined the mean twist angle by taking the average values of FWHM values of the \( \omega \)-RC and \( \phi \)-scan of \( (12\overline{3}1) \) plane with the inclination angle \( 78.6^\circ \), this study uses a FWHM value of \( (10\overline{1}0) \) \( \omega \)-RC as a twist angle, which is directly obtained from the grazing incidence geometry [85]. Now, the screw- and edge-type dislocation densities can be estimated by introducing the FWHMs measured from \( (0002) \) \( \omega \)-RC and \( (10\overline{1}0) \) \( \phi \)-scan into the following equations,

\[
D_{\text{screw}} = \frac{\text{FWHM}^2_{0002}}{9 \cdot \vec{b}_{\text{screw}}^2}
\]

\[
D_{\text{edge}} = \frac{\text{FWHM}^2_{10\overline{1}0}}{9 \cdot \vec{b}_{\text{edge}}^2}
\]

where \( \vec{b}_{\text{screw}} (=0.5185\text{nm}) \) and \( \vec{b}_{\text{edge}} (=0.3189\text{nm}) \) are Burgers vectors [86]. The dislocation density of GaN layers grown using different 3D growth mode times is shown in Fig. 4-5. The 3D growth mode time during the HT island growth increases with decreasing growth temperature and TMGa flow rate, as shown in Table 4-1. All GaN layers grown under same growth condition for the nucleation layer possessed almost the same screw dislocation densities, around
7 \times 10^7 \sim 8 \times 10^7 / \text{cm}^2$, which was independent of the 3D HT island growth. However, the edge threading dislocations decreased with increasing 3D growth mode time, as shown in Fig. 4-5. Mixed type dislocations with $\vec{b}_{\text{mixed}} = \frac{1}{3}[11\overline{2}3]$ contributed to the broadening of the RCs of both parallel and perpendicular surface planes. However, since the FWHM values of (0002) rocking curves of all samples used in this study were almost the same, it could be inferred that the defects generated during the 3D HT island growth are pure edge-type dislocations.

For further investigation of the defects structure of GaN films, TEM investigations were performed. Typical bright field images obtained from sample ‘D’ ($t_{3D}=21 \text{ min}$) are shown in Fig. 4-6. The Burgers vector of dislocations in GaN films was determined using the method, known as the ‘$g \cdot b=0$ invisibility criterion’ [87]. Bright field images were taken near the [0011] zone axis (Fig. 4-6 (a)) using a two-beam condition. The results, displayed in Fig. 4-6 (b) and (c), were obtained using different diffraction vectors in order to figure out the type of the threading dislocations. Under $g = 0002$, the types of the threading dislocations that can be observed are pure screw or mixed, while the edge or mixed dislocations are present under $g = 11\overline{2}0$. It was found from TEM results that the threading dislocations of the GaN layers are either pure edge or mixed types. Very few pure screw dislocations were found in these GaN samples. An increase of the number of defects in the interfacial region could be seen, which corresponds to the initial nucleation layer.

The data shown above provides us several information including the generation and reduction of the threading dislocations of GaN films. It is clear from the TEM images that the threading dislocations are mixed- and pure edge-types in these GaN films. Therefore, the XRD data indicates that the broadening of (0002) and (10\overline{1}0) $\omega$-RCs is due to mixed- and pure edge-
types threading dislocations, respectively. For sample ‘A’ and ‘B’ the ramping rate and HT island growth temperature were the same, only the TMGa flow rate was varied, resulting in different lateral growth rate ($t_{3D}(A)$: 10 min, $t_{3D}(B)$: 16.7 min). A low island growth temperature in sample ‘C’ gives a reduced number of HT island density and slow the lateral growth rate ($t_{3D}(A)$: 18.5 min), compared to sample ‘A’ and ‘B’. For longer 3D growth mode time with respect to other samples, sample ‘D’ ($t_{3D}(A)$: 21 min) was grown at a relatively low temperature and TMGa flow rate. The mixed-type threading dislocation density of ‘A’, ‘B’, ‘C’, and ‘D’ samples described in this study is almost the same, as shown in Fig. 4-5. Hence, the mixed-type dislocations are independent of the HT island density and lateral growth rate. The edge-type dislocation density decreased with decreasing the lateral growth rate as well as the HT island density. The reason is that the longer the 3D growth mode time was, the more likely it was for the edge-type dislocations to annihilate each other. It is clearly seen in Fig. 4-6 (c) that edge dislocations near the interfacial region between GaN film and sapphire substrate are bent, which indicates concrete evidence for the dislocation annihilation by their interaction.

Next, the nucleation layer would be thought as another source of defects generation because it acts as a template for high temperature main GaN films growth. As shown above, since the mixed threading dislocation density was not changed even though using different growth conditions used during the high temperature island growth, we believe that the mixed dislocations could be controlled by changing the growth condition for the nucleation layer. In addition, the initial GaN layers grown at low temperature were found to have a zinc blend crystal structure with high density of stacking faults in one set of {111} planes, and then they were transformed into the wurtzite crystal structure by introducing Shockley partial dislocations during the high temperature ramping [19,88]. In this time, the edge type dislocation can be also
generated from the reaction between the sub-boundary dislocations and these Shockley partial dislocations. Since this large stacking disorder of nucleation layers was caused by a low growth temperature, it has been thought that the growth temperature must be an important parameter, having a great influence on the crystalline quality of the main GaN layers. Samples ‘E’ and ‘F’ have a nucleation layer grown at a relatively lower temperature than samples ‘A’, ‘B’, ‘C’, and ‘D’, as shown in Table 4-1. Sample ‘F’, which have the nucleation layer grown at 542 °C and the 3D growth mode time of 19.3 min showed the highest crystalline quality among our samples.

**Conclusion**

The growth optimization study was performed by using the values of ω-RC measured by grazing incidence X-ray diffraction. The threading dislocation density could be controlled by using different growth conditions during the deposition of the nucleation layer and high temperature islands growth. The results from XRD and TEM investigations showed that the pure edge and mixed type dislocations were the dominant defects in our GaN films. Therefore, the relevant figure of merit (FOM) for the crystalline quality should be determined by the FWHM values of ω-RC of the surface perpendicular planes. In our study, a GaN film grown at 542 °C for the nucleation layer and with the 3D growth mode time of 19.3 min showed the best crystalline quality so far.
### Table 4-1. The growth conditions used during the deposition of GaN nucleation layer and 3D islands.

<table>
<thead>
<tr>
<th>Growth conditions</th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>Nucleation layer</td>
<td>Temperature (°C)</td>
<td>550</td>
<td>550</td>
<td>550</td>
<td>550</td>
<td>532</td>
</tr>
<tr>
<td></td>
<td>V/III</td>
<td>19880</td>
<td>19880</td>
<td>19880</td>
<td>19880</td>
<td>19880</td>
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<tr>
<td>3D island growth</td>
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<td>1095</td>
<td>1028</td>
<td>1062</td>
<td>1085</td>
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<tr>
<td></td>
<td>TMGa (sccm)</td>
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<td>8</td>
<td>10</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>V/III</td>
<td>5964</td>
<td>6088</td>
<td>5964</td>
<td>6012</td>
<td>6012</td>
</tr>
<tr>
<td></td>
<td>Time (min)</td>
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<td>16.7</td>
<td>18.5</td>
<td>21.0</td>
<td>16.6</td>
</tr>
</tbody>
</table>

### Table 4-2. FWHM values (arc sec) of in-, asymmetric and out-of-planes ω-RCs. The FWHM values of the (10T0) ω-RC are much higher than one of the (0002) ω-RC.

<table>
<thead>
<tr>
<th>Plane</th>
<th>χ</th>
<th>Samples</th>
<th>Si reference samples</th>
<th>Samples</th>
<th>Si reference samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0002)</td>
<td>0.0°</td>
<td>A</td>
<td>195</td>
<td>B</td>
<td>199</td>
</tr>
<tr>
<td>(10T2)</td>
<td>42.9°</td>
<td>C</td>
<td>346</td>
<td>D</td>
<td>330</td>
</tr>
<tr>
<td>(30T2)</td>
<td>70.2°</td>
<td>E</td>
<td>399</td>
<td>F</td>
<td>367</td>
</tr>
<tr>
<td>(10T0)</td>
<td>90.0°</td>
<td>χ</td>
<td>537</td>
<td>FWHM</td>
<td>490</td>
</tr>
</tbody>
</table>

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Figure 4-1. Transmission and edge geometries for the determination of the azimuthal spread.

Figure 4-2. Grazing incidence x-ray diffraction (GIXD). (a) grazing incidence \{10 \bar{1} 0\} 360° Φ-scan (b) (10-10) ω-RC of sample ‘A’ (t_{3D}=10 min). The acquired phi scan corresponds to the six-fold symmetry of wurtzite structure of GaN.
Figure 4-3. Cross sectional bright field TEM images of GaN films. (a, b) and (c, d) were taken from sample “A” and “E”, respectively.

Figure 4-4. FWHM of ω-RCs measured from different diffraction planes of sample ‘A’ (t_{3D}=10 min) and ‘B’ (t_{3D}=16.7 min).
Figure 4-5. The screw- and edge-type dislocation density of GaN films grown using various 3D growth mode times.

Figure 4-6. Cross sectional bright field images of sample ‘D’. The images were taken near (a) [1\,\overline{1}00] zone axis using two-beam condition ((b) \, \vec{g} = 0002 and (c) \, \vec{g} = 11\overline{2}0). The edge- and mixed-type dislocations are marked as ‘e’ and ‘m’, respectively.
 CHAPTER 5
DEFECTS EVOLUTION IN STRAINED LAYERS DURING STRAIN RELAXATION

Strained-Si Layer Grown on Graded SiGe Substrate

Experimental Design

A compositionally graded layer to confine threading dislocations was grown by gradually accommodating the lattice mismatch between Si$_{1-x}$Ge$_x$ layers [89,90] on (100) silicon substrate via Molecular Beam Epitaxy (MBE) technique. The growth conditions were shown in references [91,92]. A 630 nm thick layer of the fully relaxed Si$_{0.7}$Ge$_{0.3}$ was grown on top of the graded layer, followed by a 50 nm strained Si capping layer. After growth, some of the strained samples were annealed at 800°C for 30 min in a furnace under N$_2$ atmosphere to study how temperature affects the microstructure of the strained layer. A PANanalytical MRD X’Pert system equipped with a mirror and a Ge (220) monochromator on the primary optics and a Ge (220) analyzer on the secondary optics was used to collect high resolution X-ray diffraction rocking curves (RCs) and reciprocal space maps (RSM). For X-ray reflectivity (XRR) spectra, X-ray mirror and parallel plate collimator were used as the primary and secondary optics, respectively. The scan conditions for all the samples were 0.002° step size and 10 seconds time per step for the ω-RCs and 0.005° and 3 seconds for XRR. In order to confirm the strain relaxation, the presence of misfit dislocations and investigate the surface morphology of the strained silicon layer, transmission electron microscopy (TEM) and atomic force microscopy (AFM) investigations were carried out with the aid of a JEOL TEM 200CX and a Digital Instruments Nanoscope AFM set up under tapping mode, respectively.

Results and Discussion

Strain relaxation during thermal annealing: Fig. 5-1 shows a typical high resolution reciprocal space map (RSM) recorded around the asymmetric (113) reflection from an annealed
strained-Si/Si$_{0.7}$Ge$_{0.3}$/Si$_{1-x}$Ge$_x$/Si-substrate sample. This diffraction pattern is displayed as a function of scattering vector $Q_x$ parallel and $Q_y$ perpendicular to the surface. From this RSM, several information regarding the sample structure can be extracted. First of all, it is found that the Si$_{0.7}$Ge$_{0.3}$ buffer layer is fully relaxed. If a buffer layer is relaxed and the thickness of strained silicon is less than the critical thickness [93,94], there is a small driving force for the movement of the dislocations from the interface between strained layer and relaxed buffer layer to the surface layer which indicates that misfit dislocations are not present. As suggested by Loo et al. [95], although the thickness of the strained silicon layer is below the critical thickness, thermal treatment can result in the formation of misfit dislocation originating at the heteroepitaxial interface between strained and buffer layers if the latter is not fully relaxed. The presence of the graded layer (Si$_{1-x}$Ge$_x$, with x from 0 to 0.3) between the Si-substrate and Si$_{0.7}$Ge$_{0.3}$ in which Ge was incorporated at a rate of 10 at.% per micrometer up to a composition of 30 at.%Ge is clearly seen in Fig. 5-1. This continuous graded layer was employed for an effective reduction of threading dislocations density. Since the misfit dislocations in the graded layer are distributed homogeneously, the movement of the rather mobile threading dislocations will be blocked [96]. Finally, the topmost strained silicon peak appears to the upper left region of the silicon substrate peak. Since the peak width of the strained layer is very broad compared to Si-substrate or fully relaxed Si$_{0.7}$Ge$_{0.3}$, it can be expected that this broadening is due to defects, such as dislocations, and finite crystallite size. Also, the measured parallel and perpendicular mismatches between strained silicon and relaxed buffer layers are $1.01 \times 10^{-3}$% and 2.25 %, respectively. The horizontal shift of the strained silicon with respect to the relaxed buffer layer is very small, suggesting that there are two possibilities for the shift of this magnitude: (I) small strain relaxation due to post-growth annealing process and (II) presence of surface steps due to a small
wafer misorientation [97]. Therefore, it is difficult to make an assertion whether the observed peak shift of the strained silicon layer with respect to the SiGe buffer layer is due to strain relaxation.

Fig. 5-2 displays the x-ray reflectivity (XRR) curves acquired from as-grown and annealed strained samples. Since x-ray reflectivity curves were obtained using the symmetric θ/2θ configuration with very small angles, this technique is suitable for the investigation and characterization of thin films. The film density was determined by the critical angle (θc), which is affected by an experimental deviation of around ±3% in our study. The non-specular diffuse scattering as well as the specular scattering was considered in order to obtain the surface and interfacial roughness values. Fig. 5-2 shows different reflectivity curves for the as-grown and annealed strained Si deposited on a SiGe buffer layer, resulting from the changes of the strained layer’s roughness and interfacial layer’s density. Using the Wingixa® software from PANanalytical to simulate the XRR curves, one can get layer roughness, density, and thickness values, which are listed in Table 5-1. In the simulation of XRR curves, a multi-layer model, which consists of the Si1-xGex buffer, interfacial, strained silicon and surface layers, was used to obtain the best simulation. Estimated Ge composition of relaxed SiGe buffer layer was about 31–32% [59]. It is found in Table 5-1 that the density of the interfacial layer and roughness of the strained layer in the annealed sample are higher than those in the as-grown sample. It appears that Ge atoms in the relaxed Si0.7Ge0.3 layer slightly diffused into the strained silicon layer and strain was relaxed during the post-growth annealing process [98]. The Ge interdiffusion near the interfacial layer between strained-Si and fully-relaxed SiGe buffer layer was also confirmed by using Raman spectroscopy, as shown in Fig. 5-3. The curve shown in Fig. 5-3 (a) was fitted using a Lorentzian function in order to determine the peak position and intensity of the Raman
scattered light arising from the Si-Si vibrational modes in the SiGe buffer layer, strained-Si, and Si substrate, respectively. Fig. 5-3 (b) shows Si-Si vibrational modes in the strained-Si of as-grown and annealed samples, in which the intensity of the strained-Si peak for the annealed sample is smaller than that recorded from the as-grown sample, probably due to the thinning of the strained Si layer. Therefore, this decrease of strained-Si peak intensity of annealed sample in Raman spectroscopy is attributed to interdiffusion at the Si/SiGe interface.

**Calculation of dislocation density from FWHM of omega rocking curves:** The broadening of an omega rocking curve (ω-RC) acquired from a sample results from several factors: (I) finite crystallite size, (II) film curvature, (III) strain of the specimen, and (IV) instrumental limit [82]. Of these effects, the size and strain effects are the two main causes of line broadening. The former depends on the size of the coherent domain, which is limited by planar defects, such as stacking faults, twin faults and subgrain boundaries, while the latter is caused by dislocations and point defects. Analyzing these line broadening effects, one can estimate the dislocation density and coherence length. In the line profile analysis (LPA) of x-ray diffraction peaks, the primarily used fitting functions for ω-RCs are Gaussian, Lorentzian, Voigt and Pseudo-Voigt [55,56,99,100]. In this study, the Hordon-Averbach method was used for the modeling of the ω-RCs to estimate the dislocation density [101]. In conventional Hordon-Averbach method, it is assumed that the ω-RC has a Gaussian shape. Therefore, a full width at half maximum (FWHM, $\beta_m$) of the measured rocking curve can be expressed as follows [82],

$$[\beta_m(hkl)]^2 = [\beta_0(hkl)]^2 + [\beta_t(hkl)]^2 + [\beta_r(hkl)]^2 + [\beta_\alpha(hkl)]^2 + [\beta_\varepsilon(hkl)]^2 + [\beta_{\text{inst}}(hkl)]^2$$

(5-1)

where, $\beta_0$ represents X-ray extinction broadening, $\beta_L$ a finite crystallite size broadening, $\beta_r$ a specimen curvature broadening, $\beta_\alpha$ an angular broadening nearby the dislocations, $\beta_\varepsilon$ a strain broadening, and $\beta_{\text{inst}}$ an instrumental broadening. Since the FWHM of the RC of
commercially available silicon single crystal with a dislocation density of 3000/cm² is just 8 arcsec, the x-ray extinction, curvature, and instrumental broadening effects could be safely ignored. The broadening of the RC due to the dislocations and finite crystallite size is given by [102],

\[
(\beta_m)^2 = (\beta_\alpha)^2 + (\beta_\varepsilon)^2 + (\beta_L)^2 = K_\alpha + K_\varepsilon \tan^2 \theta_B + K_L \left( \frac{\lambda}{\sin 2\theta_B} \right)^2
\]

(5-2)

where, \( K_\alpha \), \( K_\varepsilon \), and \( K_L \) are constants, \( \theta_B \) the Bragg angle, and \( \lambda \) the wavelength. If the FWHM values of the several \( \omega \)-RCs are measured at different Bragg angles and Eq. (5-2) is fitted by the least square method, \( K_\alpha \), \( K_\varepsilon \), and \( K_L \) can be estimated. If the dislocations are randomly distributed, the dislocation density can be given as [86],

\[
N_{\text{dis}} = \frac{K_\alpha}{2\pi \ln(2b^2)}
\]

(5-3)

where, \( b \) is the Burgers vector and \( N_{\text{dis}} \) is the dislocation density. However, a pure Gaussian function used for fitting the rocking curves of the strained silicon was not suitable because of the line broadening in the tail region of the diffraction profile. In this study, the X-ray rocking curves were fitted by a Pseudo-Voigt function, which is described by the following equation [56],

\[
P V(x) = I_0[\eta L(x) + (1-\eta)G(x)]
\]

(5-4)

where, \( L(x) \) and \( G(x) \) are Lorentzian and Gaussian functions, and \( \eta \) \((0 \leq \eta \leq 1)\) represents the fraction of the Lorentzian component in Pseudo-Voigt function. Now, since the profile of \( \omega \)-RCs measured from the strained silicon layer is not a pure Gaussian function, but a Pseudo-Voigt function, Eq. (5-2) needs to be modified as following,

\[
[\beta_m(hkl)]^n = [\beta_\alpha(hkl)]^n + [\beta_\varepsilon(hkl)]^n + [\beta_L(hkl)]^n
\]

(5-5)
where, $n$ is a constant that allows for the best fit. If Eq. (5-5) is also fitted by the least square method and then $K_a$ is estimated, the dislocation density of the strained silicon layer can be calculated by Eq. (5-3).

Fig. 5-4 shows a (113) omega rocking curve acquired from annealed strained-Si, which is fitted with Pseudo-Voigt and Gaussian functions. It is clear that a pure Gaussian function does not fit well in the tail region of the diffraction profile because of the absence of a Lorentzian component. Therefore, a Pseudo-Voigt function is more suitable to fit the RCs, as shown previously [100]. In this study, $\omega$-RCs of (113), (004), and (224) planes were analyzed for the estimation of the dislocation density by using Pseudo-Voigt function fitting and the modified Hordon-Averbach method. Notably, the (113) and (224) planes were measured because they require the case of grazing incidence angles, around 2.8° and 8.8°, respectively. Such a small incidence angle results in a large surface interaction volume, therefore being more sensitive to the surface layer. The RCs of the strained layers were fitted with both Voigt and Pseudo-Voigt functions, in addition to Gaussian function, in order to find out the best diffraction line profile shape, as shown in Table 5-2. It was found that while the RCs of as-grown strained silicon have almost a pure Gaussian shape with very small Lorentzian fractions, those of annealed strained silicon have Lorentzian as well as Gaussian shapes due to a higher Lorentzian fraction. It means that the annealing has a strong effect on the line broadening in the tail region of the RCs. In order to estimate the dislocation density, the FWHM values of several RCs were used in the modified Hordon-Averbach method. By optimizing several parameters shown in Eq. (5-5) obtained from the least square fitting, the dislocation density of the strained silicon was calculated and is displayed in Table 5-2. It was found that the dislocation density of the annealed strained silicon is larger than that of the as-grown one, but the fitting parameter ($n$) of the former is smaller than
that of the latter. In the as-grown sample, \( n \) was 1.92 which is quite close to 2, the value used by the conventional Hordon-Averbach method, as shown in Eq. (5-2). In the annealed strained silicon, however, \( n \) was found to be 1.30, which is considerably smaller than 2 because the shape of RCs is no longer pure Gaussian.

This result raised the question on what is the physical meaning of the tail part of the x-ray omega rocking curve. The tail part of the \( \omega \)-RC is related to the finite coherence length which can be defined as an average crystallite size which scatters coherently, and therefore is free of defects [61]. The coherence length can be statistically estimated by using Fourier analysis [52]. First of all, the Fourier coefficients of the diffraction line profile can be determined from the Gaussian and Lorentzian component of the Voigt function and then separated into size and mean squared strain coefficients which are expressed by the following equations [103],

\[
A(L) = \exp(-2LW_L - \pi L^2 W_G^2) \\
A(L) = A_s(L) \exp(-2\pi Q^2 L^2 \varepsilon^2)
\]

where, \( A(L) \) and \( A_s(L) \) are the Fourier and size coefficients, \( W_L \) and \( W_G \) are the FWHM of Lorentzian and Gaussian functions, \( L \), \( Q \), and \( \varepsilon \) are the coherence length, reciprocal lattice spacing and strain, respectively. Finally, the coherence length distribution (\( P(L) \)) can be obtained from the second derivative of the size coefficient [104]. Fig. 5-5 shows the coherence length distribution of annealed and as grown strained silicon. It is found that the mean coherence length of annealed strained silicon is smaller than that of as-grown one due to the generation of misfit defects. Fig. 5-6 shows the surface morphologies and plan-view images of the as-grown and annealed strained silicon obtained from AFM and TEM investigations. The large-scale cross-hatching characteristic [105], which is the presence of misfit defects, are clearly shown in AFM and TEM images, respectively. We clearly see that the annealed strained silicon has a more
cross-hatching patterns than the as-grown, caused by the strain relaxation, consistent with the results obtained from X-ray techniques.

**Conclusion**

In summary, annealed and as-grown strained silicon layers were characterized by using high resolution X-ray diffraction. Although the parallel mismatch between the annealed strain silicon and SiGe buffer layer measured from RSM was very small, the evidence obtained from XRR and ω-RC measurement clearly showed the occurrence of the strain relaxation during annealing process at 800 °C for 30 min. The dislocation density of the strained silicon was estimated from the shape of ω-RCs by using the modified Hordon-Averbach method. Conventional Hordon-Averbach method, in which a rocking curve is fitted by only a Gaussian function, was not appropriate for this experiment due to a significant peak broadening in the tail region. The tail of the rocking curve was fitted well with Voigt or Pseudo-Voigt functions that have Lorentzian as well as Gaussian components. It was found that the dislocation density of annealed strained silicon is larger than that of the as-grown one as a result of strain relaxation. In addition, it was found that the coherence length of the strained silicon decreased after high temperature annealing, which induced a line broadening in the tail region of ω-RCs. The results indicate that XRR and ω-RC are more suitable techniques than RSM to access the strain relaxation when its value is rather small.

**Strained SiGe Grown on Si**

**Experimental Design**

$\text{Si}_{1-x}\text{Ge}_x$ layers with a nominal Ge fraction $x=15$, 20, and 25 % and thickness of 500 and 1000 Å were grown on (100) Si by reduced pressure chemical vapor deposition (RPCVD) at a pressure of 10 Torr and growth temperature of 700 °C using dichlorosilane (DCS, $\text{SiH}_2\text{Cl}_2$) and
germane (GeH₄) as silicon and germanium sources, respectively. This thickness is significantly larger than the critical thickness for SiGe layers with those Ge concentrations [106]. After growth, the layers were annealed in a quartz tube furnace at 800 and 900 °C for 30 min under a N₂ ambient to study the effect of thermal processing on the strain state of the strained SiGe layer. A PANalytical MRD X’Pert system equipped with a 1/2° slit, a mirror and a Ge(220) monochromator on the primary optics and a channel cut Ge (220) analyzer on the secondary optics was employed to collect high-resolution omega-2theta rocking curves (ω/2θRCs) and reciprocal space maps (RSM). For x-ray reflectivity (XRR) spectra acquisition a 1/32° slit and a mirror were used on the primary optics while a parallel plate collimator and a 0.1 mm slit were used on the secondary optics. To confirm the degree of strain relaxation and Ge composition, and investigate the created defects, transmission electron microscopy (TEM) investigations were performed with the aid of a JEOL 200CX. The thickness and composition of the 25% Ge sample was also investigated using Rutherford backscattering spectroscopy (RBS). The effect of the thermal treatment on surface morphology was also investigated by atomic force microscopy (AFM) with a Digital Instrument Nanoscope under tapping mode.

Results and Discussion

Determination of Ge composition, layer thickness, and strain: XRR curves acquired from strained Si₁₋ₓGeₓ layers were obtained using the symmetric θ/2θ configuration with very small angles so that this technique is suitable for the investigation and characterization of thin films. The film density was determined from the position in the XRR curves of the critical angle (θ_C), which is proportional to the electron and mass density [107,108]; the experimental error was estimated to be around 4 % in our study. The diffuse as well as the specular scattering were considered in order to obtain the surface and interface roughness values. The simulation of the XRR curves was performed by using the commercially available Wingixa® software package.
from PANanalytical. For the simulation we used a four-layers model: substrate (Si), interfacial layer (transition layer), Si$_{1-x}$Ge$_x$ layer, and surface contamination layer. The information of the interfacial and strained layers obtained from the simulations for as-grown and annealed samples is presented in Table 5-3 and Table 5-4, respectively. It is clearly shown that both density and thickness of the interfacial layer increase with the increase of Ge fraction. As the interface could not be infinitely sharp, especially when the growing temperature was 700 °C, the higher the change in Ge concentration, the thicker this transition layer is, as expected. The thickness of the grown Si$_{1-x}$Ge$_x$ layers are different from the nominal values, more so for higher Ge fractions. The rather large thickness deviation observed for the sample containing 25% Ge concentration might be caused by an error in the measurement due to surface roughness as a cross section TEM found a (local) thickness value of 510 Å, much closer to the 500 Å nominal value. Since the sample with x=25% Ge had such a large variation of the thickness with respect to the nominal value, we performed a Rutherford backscattering spectroscopy measurement. The result, shown in Fig. 5-7, was modeled using the RUMP program and indicated a composition of Si$_{0.76}$Ge$_{0.24}$ and a thickness of 496 Å, very close to the nominal value. After thermal anneal, it was found that the thickness of the SiGe layers decreased due to unwanted oxidation. However, the increase of the interfacial layer thickness and roughness coupled with the decrease of the Si$_{1-x}$Ge$_x$ layer density points toward a significant Ge interdiffusion [109].

A reciprocal space map (RSM) acquired for the (113) peak region from as-grown Si$_{0.85}$Ge$_{0.15}$ sample is displayed in Fig. 5-8 [58,110]. This diffraction pattern is displayed as a function of scattering vector Q$_X$ parallel and Q$_Y$ perpendicular to the surface. As one can see, there is no measurable relaxation, the SiGe peak being located exactly below the Si peak, at the same Q$_X$ value. Typical ω/20 RC acquired from a sample with 15 % Ge and its simulation
performed with zero relaxation, as found by RSM results, are shown in Fig. 5-9. The SiGe layer thickness and Ge concentration extracted from the ω/2θ RC simulations, along with the values extracted from XRR simulations are presented in Table 5-5. One can note that there is a rather good agreement between these values measured by both x-ray based techniques. A second observation is that for the lowest Ge fraction used in this study, the measured values are closer to the nominal ones, while for the highest value the difference is the largest. The AFM results regarding the samples surface morphology are presented in Fig. 5-10. One can note that for lower Ge concentration the surface is quite smooth, its rms (root mean square) values being around 3 Å. However, the sample contained 25% Ge exhibited a much rougher surface, with a RMS value of 9 Å. The surface also showed an undulation, which might explain the over evaluation of the layer thickness by XRR and ω/2θ scan simulations. Such undulations were previously reported for SiGe and are indications of the relaxation process [111].

The ω/2θ RCs recorded after the thermal anneal were quite different from those recorded from as-grown samples, as shown in Fig. 5-11. The shape of (004) and (113) ω/2θ RCs acquired from annealed Si$_{1-x}$Ge$_x$ layers are different as well as SiGe layer peaks are broader compared to as-grown samples, resulting in the strain relaxation. Especially, the peak shift of annealed Si$_{1-x}$Ge$_x$ toward Si-substrate in (113) ω/2θ RCs is much larger with respective to (004) ω/2θ RCs. The misfit dislocations generated during strain relaxation in strained Si$_{1-x}$Ge$_x$ are a perfect 60° type, $1/2 <110>$ {111}, Burgers vector and slip plane, respectively [106,112]. These dislocations are affecting the x-ray diffraction from asymmetric planes but not from symmetric ones, as one can see in Fig. 5-11. In addition, the amplitude of the oscillations and integrated intensity of Si$_{1-x}$Ge$_x$ peak shown in the annealed samples, especially for higher Ge compositions, were greatly dampened and reduced, an indication of strong Ge interdiffusion and degradation of the
sharpness of the interfaces. Si and Ge atoms diffuse near the interface and this interdiffusion affects the structural factor of x-ray diffracted beam. Zheng et al. showed that the interdiffusivity could be calculated from the decay of integrated intensity of Si$_{1-x}$Ge$_x$ layers with annealing time [113]. Fig. 5-12 shows plan-view TEM images of as-grown and annealed Si$_{1-x}$Ge$_x$ layers. After thermal annealing, the misfit dislocations increased in density indicating that strain relaxation has taken place, which agrees with the observation from the x-ray based techniques. For the highest germanium concentration, 25% Ge, misfit dislocations are already present in the as-grown state, the layer thickness being much larger than the critical thickness [106]. The presence of these defects in the 25% Ge sample in the as-grown state could be another cause of the thickness measurement discrepancy between TEM and x-ray based techniques. It also appears that the simulation of the RCs could be carried out more accurately if the strain relaxation is known from a measurement using a different analysis technique.

**Defects structure in strained SiGe:** Fig. 5-13 (a) shows (004) omega-2theta rocking curves (ω-2θ RCs) of as-grown and annealed at 800 °C for 30 min Si$_{80}$Ge$_{20}$ films 50 nm thick. The RC of as-grown sample shows the well-defined thickness fringes which indicate the formation of an abrupt interface between Si substrate and strained Si$_{80}$Ge$_{20}$ layer. From the simulation of the acquired ω-2θ RC, the film thickness and Ge composition of strained Si$_{1-x}$Ge$_x$ layer were found to be 46.8 nm and 21 %, respectively. However, the RC of Si$_{80}$Ge$_{20}$ layer annealed at 800 °C for 30 min is different from that of as-grown sample. The intensity of annealed Si$_{1-x}$Ge$_x$ layer was reduced and the thickness oscillations were dampened, compared to as-grown sample. In addition, the Bragg peak position of strained layer slightly shifts towards Si-substrate position. These changes indicate a strain relaxation accompanied by misfit defects generation and Ge interdiffusion near the interface [113]. Fig. 5-13 (b) shows plan-view
transmission electron microscopy (PV-TEM) images of as-grown and annealed Si$_{80}$Ge$_{20}$ samples. The as-grown sample does not show any misfit dislocations, indicating that the strained layer was pseudomorphically grown and the interface was abrupt, which is consistent with the results obtained from $\omega$-20 RC investigations. However, the annealed sample shows many misfit dislocations with a cross-hatching pattern which consist of perfect 60° dislocations, $\frac{1}{2}\langle 110 \rangle\{111\}$, Burgers vector and slip plane [112, 114].

An omega rocking curve ($\omega$-RC) investigation was further performed to study the effect of these misfit dislocations on the peak broadening. The full width at half maximum (FWHM) value of the $\omega$-RC has been used as a figure of merit (FOM) for the crystalline quality of the layers. Very small FWHM values, similar to the instrument resolution limit of 0.0021° measured from a high quality Si wafer, and symmetric profile shapes of (004) and (113) $\omega$-RCs that were acquired from the as-grown Si$_{80}$Ge$_{20}$ layer and are displayed in Fig. 5-14 (a) and (b) indicate that the strained layer is a perfect single crystal. The FWHM values of $\omega$-RCs acquired from the annealed sample and shown in Fig. 5-14 (c) and (d) were also similar to those of as-grown sample. However, it needs to be noted that the shape of (113) $\omega$-RC of annealed sample is asymmetric while (004) $\omega$-RC is still symmetric. Therefore, it is found that while (004) $\omega$-RC is not sensitive to the presence of 60° misfit dislocations within the annealed strained layer as shown by TEM results, the profile shape of (113) $\omega$-RC is.

For further study on the defects evolution during strain relaxation, 100 nm thick strained Si$_{75}$Ge$_{25}$ layers with higher strain energy areal density ($E_S$) than 50 nm thick strained Si$_{80}$Ge$_{20}$ samples were grown and then annealed at 900 °C for 30 min. This strain energy areal density can be given as $E_S = \varepsilon^2 Bh$, where $\varepsilon$ is the in-plane strain, B is the Burgers vector and h is the strained layer thickness [115]. The (113) reciprocal space map acquired from the as-grown 100
nm thick Si$_{75}$Ge$_{25}$ sample in Fig. 5-15 indicated a slight strain-relaxation, less than 1.0%, while strain relaxation of annealed sample was 19.1%. The defect structure of as-grown and annealed strained Si$_{75}$Ge$_{25}$ samples has been also studied by using $\omega$-RC as shown in Fig. 5-16. It is found that the $\omega$-RCs of as-grown Si$_{75}$Ge$_{25}$ are very similar to those recorded from annealed Si$_{80}$Ge$_{20}$ layer, as shown in Fig. 5-14 (c) and (d) because the layer thickness of strained Si$_{75}$Ge$_{25}$ is much thicker than the critical thickness for the pseudomorphic growth indicating the generation of 60° misfit dislocations. On the other hand, $\omega$-RCs of annealed Si$_{75}$Ge$_{25}$ sample show a different behavior compared to slightly strain-relaxed sample with 60° misfit dislocations. First of all, it is clearly that the FWHM values of (004) as well as (113) $\omega$-RCs of 100 nm thick Si$_{75}$Ge$_{25}$ annealed at 900 °C for 30 min are much larger than those of slightly strain-relaxed samples. The previous results showed that the (004) $\omega$-RC was not sensitive to 60° misfit dislocations. It is suggested that the misfit defects in annealed strained Si$_{75}$Ge$_{25}$ layer with higher strain energy areal density should be different from 60° misfit dislocations. Second, the shape of both (004) and (113) $\omega$-RCs of annealed sample is almost symmetric. Therefore, it is inferred that the defect structure of highly strain-relaxed SiGe sample is different from that of slightly strain-relaxed sample.

Fig. 5-17 shows cross-sectional transmission electron microscopy (TEM) images of 100 nm thick Si$_{75}$Ge$_{25}$ annealed at 900 °C for 30 min. The strained-SiGe/Si interface is clearly visible and the misfit dislocations lying at the interface and stacking faults in the strained SiGe layer are also shown in Fig. 5-17 (a). Fig. 5-17 (b) shows a high-resolution TEM lattice image of the annealed sample. Typical 60° dislocations present in FCC crystal structure have Burgers vectors $\vec{b}_{60} = 1/2 <110>$ gliding on the {111} closed packed planes. It was experimentally found and theoretically predicted that 60° dislocations will dissociate into two partial dislocations in order
to lower the strain energy [116,117]. The Burgers vectors of these partial dislocations are
\[ \vec{b}_{\theta} = 1/6 <2 \overline{1} \overline{1} > \quad \text{and} \quad \vec{b}_{\theta} = 1/6 <11 \overline{2} > \quad (\theta=30^\circ \text{ or } 90^\circ), \]
where \( \theta \) can be defined as the angle between the dislocation line and its Burgers vector. In addition, it was reported that the
dissociation of 60° dislocations leaded to a different geometry in strain relaxation for the tensile
and compressive strained films [118]. Fig. 5-17 (b) shows stacking faults on \{111\} planes near
the interface which are bounded by partial dislocations. Therefore, the peak broadening of \( \omega \)-
RCs of 100 nm thick strained Si\(_{75}\)Ge\(_{25}\) annealed at 900 °C for 30 min, as shown in Fig. 5-16 (c)
and (d), is due to these partial dislocations associated with the stacking faults.

**Conclusion**

SiGe layers that were grown by RPCVD underwent an anneal treatment at 800 °C for 30
min. The results obtained from XRR and RCs investigations showed that the most important
modification after the thermal treatment was the Ge interdiffusion and misfit dislocations
generation, conducting to wider and rougher interfaces. The strain relaxation was confirmed by
using (113) \( \omega/2\theta \) RCs which are sensitive to the presence of misfit dislocations in strained layers.
At the onset of relaxation the surface morphology exhibited a waviness followed by the
appearance of a cross hatched pattern. These results indicate that x-ray based techniques can be
used to accurately determine Ge content, thickness, and roughness of SiGe layers when the strain
state of the material is known, as seen with the 15 and 20% Ge samples. Once relaxation has
taken place, it is imperative to know the degree of relaxation in order to correctly simulate the
structure of the film.

The result showed that the 60° dislocations generated from slightly strain-relaxed SiGe
layers had an influenced on the profile shape of the (113) \( \omega \)-RC while they did not contribute to
the peak broadening of the (004) \( \omega \)-RC. On the other hand, stacking faults bounded by two
different partial dislocations made both $\omega$-RCs symmetrically broad. Since the presence of the stacking faults in compressively stressed films is unusual, this observation of the stacking faults by using $\omega$-RC contributes to the understanding of defects evolution and process design for high quality strained layers.

**Ion Implantation of Strained Layers**

**Experimental Design**

Si$_{1-x}$Ge$_x$ layers with a nominal Ge fraction $x=0.25$ and a thickness of 50 nm were grown on (100) Si-substrate by reduced pressure chemical vapor deposition (RPCVD) at a pressure of 10 Torr and growth temperature of 700 °C using dichlorosilane (DCS, SiH$_2$Cl$_2$) and germane (GeH$_4$) as silicon and germanium sources, respectively. The Ge composition and layer thickness of Si$_{1-x}$Ge$_x$ measured from Rutherford Backscattering Spectroscopy (RBS, as shown in Fig. 5-7) were 24 % and 49.6 nm, respectively. After growth, Si$^+$ ion implantation with an energy of 12 keV at a fluence of $1 \times 10^{15}$ atoms/cm$^2$ was carried out, followed by thermal annealing in N$_2$ ambient using a quartz tube furnace. Fig. 5-18 shows bright field transmission electron image of implanted SiGe layer annealed at 500 °C for 30 min. The initial amorphous layer thickness after the ion implantation was estimated to be around 28 nm. The amorphous layer began to crystallize during thermal annealing, a process which is called solid phase epitaxy re-growth (SPER) [119]. One can note that the amorphous-crystalline (a-c) interface was not planar but rough, as shown in Fig. 5-18. For comparison reason, the as-grown SiGe layers without ion implantation were also annealed under the same conditions, as those employed for the implanted samples. A PANalytical MRD X’Pert system equipped with 1/2 slit, mirror and Ge (220) monochromator on the primary optics and a channel cut Ge (220) analyzer on the secondary optics was employed to collect high-resolution omega rocking curves ($\omega$-RCs) and reciprocal space maps (RSMs). For
the investigation of the surface morphology, a Digital Instruments Nanoscope atomic force microscopy (AFM) instrument was employed under tapping mode. A JEOL TEM 200CX was used for the cross sectional transmission electron microscopy (TEM) images of SiGe layers and the sample preparation was carried out by using the focus ion beam (FIB) technique.

**Results and Discussion**

First of all, the strain relaxation of annealed SiGe layers without ion-implantation was analyzed to evaluate various possible sources for the dislocations nucleation. Fig. 5-19 shows (113) reciprocal space maps (RSMs) of as-grown and annealed at 800 °C for 30 min Si76Ge24 layers on Si substrate. The reciprocal lattice points (RLPs) are displayed as a function of scattering vector $Q_X$ parallel and $Q_Y$ perpendicular to the surface. It is clearly seen from Fig. 5-19 (a) that the $Q_X$ values of SiGe layer and Si substrate are exactly the same and the shape of SiGe RLP is very sharp and symmetric, indicating that the as-grown layer was pseudomorphically (relaxation=0 %) grown and the interface between the strained layer and substrate was abrupt. During post-growth thermal treatment, the SiGe layer begins to relax due to misfit dislocations generation caused by the thermal budget. In Fig. 5-19 (b), one can note that the SiGe RLP slightly shifts along the relaxation line and seems to be asymmetric. In previous paper, it was reported that the asymmetric RLP of the strained layer was due to the presence of 60° misfit dislocations at the interface [120]. It was also found from RSM results that the strain relaxation of the SiGe layer annealed at 800 °C for 30 min was less than 2 %. This insignificant strain relaxation even after such a high temperature anneal indicates that there exists a kinetic barrier for the generation of the misfit dislocations at the interface because of few sources for the dislocations nucleation. These sources include pre-existing threading dislocations from the Si substrate and growth-related defects induced during the growth of the strained epilayer. The
threading dislocation density of the commercially available Si substrate is less than $10^4$/cm$^3$, which is not enough for an efficient strain relaxation. In addition, one of the growth-related defects in strained SiGe is the surface undulation, which is the formation of a wavy surface characteristic, as shown in Fig. 5-20. It was theoretically predicted and experimentally reported that the surface of strained layers with relatively high Ge concentration becomes undulated to reduce the system energy because the film stress of a wavy surface is smaller than that of the planar surface [121]. In addition, Ge composition near the cusps was larger than that near the troughs, resulting in the lateral modulation of the lattice constant in the SiGe surface [122]. These facts indicate that the cusps can be a preferential site for the dislocations nucleation due to high stress.

Fig. 5-21 shows average peak-to-peak distance and r.m.s. roughness of annealed Si$_{76}$Ge$_{24}$ layers without/with Si$^+$ implantation. As expected, it is shown that the average peak-to-peak distance in these samples decreases with increasing annealing temperature. Note that a change in the peak-to-peak distance with a degree of the thermal budget is almost the same in the Si$_{76}$Ge$_{24}$ films without/with ion-implantation, as shown in Fig. 5-21. It is also found that while the r.m.s. roughness of the samples without ion-implantation increases with the annealing temperature, that of the samples with ion-implantation is almost independent of the temperature even though annealed layers are smoother than as-implanted layer. This difference of the r.m.s. roughness values between the two sets of samples is due to different surface morphology. In Fig. 5-20 (b), the cross-hatch pattern, which is a general characteristic of the strain-relaxed films [123], is clearly seen in the annealed SiGe layers without ion-implantation. However, the AFM image of the annealed layer with ion-implantation does not show any cross-hatch pattern, as one can see in Fig. 5-20 (c).
So far, two possible sources of dislocations nucleation for strain relaxation have been presented: pre-existed threading dislocations from the substrate and surface undulation of the strained layer. However, these sources did not play an efficient role to obtain highly strain-relaxed SiGe layers. Another source for the dislocations nucleation in these samples could be the point defects induced by ion-implantation. Fig. 5-22 shows (113) RSMs of ion-implanted Si$_{76}$Ge$_{24}$ annealed at three different temperatures. The (113) RSM of ion-implanted Si$_{76}$Ge$_{24}$ annealed at 700 ℃ shows that two different layers, a fully-strained layer (defect-free layer) and a relaxed layer (defective layer), co-exist. After ion-implantation, a top SiGe layer of around 28 nm thick was amorphized and there was an amorphous-crystalline interface (a-c interface), as shown in Fig. 5-18. When the top amorphous layer began to crystallize during the SPER process, we believe that most of defects would be nucleated. Especially, dislocation loops can be rather easily nucleated due to a high concentration of point defects. These generated defects propagated into the interface region and the relaxation process was efficiently enhanced, as compared to the samples without ion-implantation. The thickness of the defect-free layer in ion-implanted samples decreased with increasing annealing temperature and finally disappeared after the 900 ℃ anneal, as shown in Fig 5-22. This fact indicates that the propagation of induced defects to the interface is a thermally activated process. Fig. 5-23 shows the degree of strain relaxation and full width at half maximum (FWHM) values of (113) omega rocking curves (ω-RCs) recorded from ion-implanted Si$_{76}$Ge$_{24}$ layers. It is evident that the strain relaxation of ion-implanted Si$_{76}$Ge$_{24}$ layers increases with increasing annealing temperature. The strain relaxation is dramatically increased over 700 ℃ which again demonstrates that there exists an energy barrier for the defects propagation toward the interface. The change of FWHM values of (113) ω-RCs after different thermal treatments needs to be noted. For low annealing temperatures, at which the
layer is a stack of a defect-free and a defective one, the FWHM values of ω-RC increase with increasing temperature. However, FWHM values begin to decrease with increasing temperature over 700 °C, simultaneously with a strain relaxation.

Fig. 5-24 shows cross sectional transmission electron diffraction (X-TEM) bright field images of ion-implanted Si76Ge24 layer after thermal annealing. One can see that almost all defects began to nucleate from the a-c interface during SPER process. The dislocation loops were easily nucleated due to a high concentration of point defects induced by the ion-implantation. It is clearly shown in Fig. 5-24 (a) that there exists a defect-free region between the initial a-c interface and SiGe/Si interface in the implanted layer annealed at 700 °C even though there were few defects observed at the SiGe/Si interface. However, the implanted Si76Ge24 layer annealed at 800 °C was much more defective as shown in Fig. 5-24 (b), where the dislocation loops as well as the misfit dislocations are clearly visible at the SiGe/Si interface. These results are consistent with the previous (113) RSM results of ion-implanted Si76Ge24 layer after thermal treatment, shown in Fig. 5-22.

Evaluating the possible sources for the nucleation of the misfit segments at the SiGe/Si interface, it has been concluded that the pre-existing threading dislocations and surface undulation are not enough to nucleate large concentration of misfit dislocations. In previous work, where 100 nm thick Si76Ge24 layers were annealed at 900 °C for 30 min without ion-implantation, we observed relatively high strain relaxation, which was caused by the stacking faults associated with partial dislocations dissociated from previously generated misfit dislocations [120]. On the other hand, based on the results from this study, the relaxation mechanism of the ion implanted strained SiGe layers after thermal annealing is different: the glissile dislocation loops can be easily nucleated due to a high concentration of point defects.
during solid phase epitaxy re-growth process and they propagate toward the SiGe/Si interface, where they can efficiently lower the kinetic barrier energy for the nucleation of the misfit dislocations. Also, the threading dislocations accompanied with the misfit segments can be easily annihilated after subsequent thermal annealing, as shown in Fig. 5-23.

**Conclusion**

In summary, the defects behavior and relaxation mechanism in strained Si$_{76}$Ge$_{24}$ with and without ion-implantation after thermal annealing were analyzed by considering possible sources for the dislocations nucleation. The strain of SiGe layer without ion-implantation was only slightly relaxed after even high temperature annealing because the pre-existing threading dislocations in the substrate and surface undulation could not act as efficient nucleation sources for the misfit dislocations at SiGe/Si interface. On the other hand, the results showed that the high concentration of point defects in implanted SiGe films helped generating defects during SPER process. These defects propagated to the SiGe/Si interface, where they induced the formation of misfit dislocations, resulting in the enhancement of the strain relaxation. It was also found that the propagation of these dislocations induced during SPER is a thermally activated process. Finally, the dislocations can be easily annihilated after subsequent thermal treatment even though the strain was efficiently relaxed. These results clearly indicate that ion-implantation is a very promising technique for the fabrication of high crystalline relaxed SiGe films.

**Oxidation of Strained-SiGe Layers**

**Experiment Design**

Si$_{1-x}$Ge$_x$ layers with a nominal Ge fraction x=15, 20 and 25 %, and a thickness of 50 nm were grown on (100) Si-substrates by reduced pressure chemical vapor deposition (RPCVD) at a pressure of 10 Torr and growth temperature of 700 °C using dichlorosilane (DCS, SiH$_2$Cl$_2$) and
germane (GeH₄) as silicon and germanium sources, respectively. The Ge composition and layer thickness of Si₁₋ₓGeₓ measured from Rutherford Backscattering Spectroscopy (RBS, shown previously) were very similar to the nominal thickness and composition values. As-grown Si₁₋ₓGeₓ layers were oxidized in a furnace at 800 °C, 900 °C, and 1000 °C for 1 hr under a flow rate of 0.5 L/min of high purity oxygen gas.

A PANalytical MRD X’Pert system equipped with a 1/2° slit, mirror and Ge (220) monochromator on the primary optics and a channel cut Ge (220) analyzer on the secondary optics was employed to collect high-resolution omega-2theta rocking curves (ω-2θ RCs) and reciprocal space maps (RSMs). A JEOL TEM 2010F was used for the cross-sectional scanning transmission electron microscopy (STEM) images and energy dispersive spectroscopy (EDS) for Ge depth profile. The sample preparation was carried out by using the focus ion beam (FIB) technique.

Results and Discussion

Fig. 5-25 shows (113) omega-2theta rocking curves (ω-2θ RCs) of strained-Si₇₅Ge₂₅ layers after thermal oxidation at 800 °C, 900 °C, and 1000 °C for 1 hour. The as-grown film shows intensity oscillation fringes due to the multiple scattering of diffracted x-ray beam along sample normal direction. These oscillations observed from as-grown layers indicate that the interface between the substrate and film is extremely abrupt, so that the as-grown layer was pseudomorphically grown on Si substrate. After the thermal oxidation, the shape of the ω-2θ RCs significantly changes. It needs to be noted that the changes of the ω-2θ RCs of Si₁₋ₓGeₓ (x=15, 20, and 25 %) layers with different oxidation temperatures are very similar, even though those of Si₇₅Ge₂₅ layers are only shown in Fig. 5-25. First of all, from the shape of the (113) ω-2θ RC of strained-Si₇₅Ge₂₅ layer oxidized in 800 °C, it can be inferred that two different SiGe layers co-
exist: a Ge rich layer (GRL) and a Ge deficient layer (GDL), as indicated in Fig. 5-25. Since SiO₂, rather than GeO₂, was preferentially formed during the oxidation due to the large difference of the heat formation of SiO₂ and GeO₂ [124-126], Ge atoms were rejected from the SiO₂, resulting in a Ge pile-up below the oxide. At the same time, Ge diffused into the unoxidized pre-existing SiGe layer, inducing strain relaxation occurred during the oxidation. The strain can be rather easily relaxed by thermal oxidation, compared to N₂ thermal annealing because a large concentration of point defects is generated during the oxidation [127], which lowers the nucleation energy for the generation of misfit dislocations, as shown previously by us. As a matter of fact, the Ge diffusion into the Si substrate at 800 °C is insignificant. It was reported that the activation energy for Ge diffusion in Si₁₋ₓGeₓ (x=20~30 %) alloy was around 3.8~4.3 eV [128,129], so that 800 °C is not enough for Ge atoms to efficiently diffuse into the substrate. However, the existence of GDL indicates that the activation energy for the diffusion of Ge atoms into Si during thermal oxidation is smaller than that under N₂ annealing. Next, the ω-2θ RC of Si₁₋ₓGeₓ layer after the oxidation at 900 °C showed a very broad SiGe layer peak, indicating that Ge atoms diffused deeper into the SiGe, compared to the oxidation in 800 °C. This clearly shows that a GRL still exists in the oxidation at 900 °C as well as 800 °C. Finally, the ω-2θ RC of strained-Si₇₅Ge₂₅ layer after oxidation at 1000 °C showed a different Ge behavior. One can see that the GRL is no longer present and SiGe peak located in the right of a red dot line ranges over Si substrate. The Ge atoms rejected from the oxide are no longer accumulating because they could efficiently diffuse into SiGe at very high temperature. While the Ge segregation dominantly occurred in the oxidation at 800 °C, the Ge diffusion preferentially occurred at 1000 °C. These results from the ω-2θ RCs of strained-SiGe layers
suggest that the competition between Ge accumulation and Ge diffusion into SiGe is strongly dependent on the oxidation temperature.

Fig. 5-26 shows scanning transmission electron microscopy (STEM) image and Ge concentration measured by energy dispersive spectroscopy (EDS), and (113) reciprocal space map (RSM) of strained-Si$_{75}$Ge$_{25}$ oxidized in 800 °C. The TEM image clearly shows the presence of two layers distinguished by the mass contrast in which dark and bright regions in the SiGe film are associated with GRL and GDL, respectively. While initial Ge composition of as-grown SiGe layer was around 25 %, the Ge composition in GRL and GDL, as measured by EDS, was 31.65 % and 19.51 %, respectively. A typical high resolution reciprocal space map (RSM) recorded around the asymmetric (113) reflection from SiGe layer after 800 °C oxidation is shown in Fig. 5-26 (b). In Fig. 5-26 (b), GRL and GDL are located at bottom and top, respectively, with respect to a red dot that indicates the position of the RLP of the as-grown SiGe layer. The presence of both GRL and GDL in the (113) RSM is consistent with the STEM image. On the other hand, it was found from Fig. 5-26 (b) that a large degree of strain relaxation of both GRL and GDL occurred after the thermal oxidation in 800 °C. In a previous study, it was reported that the strain relaxation after N$_2$ annealing in 800 °C was very small and only a few perfect misfit dislocations were generated [120]. This fact indicates that the thermal oxidation process is more efficient than N$_2$ annealing to obtain highly relaxed SiGe layers.

While the Ge pile up in the strained-Si$_{1-x}$Ge$_x$ layers occurred during thermal oxidation for both 800 °C and 900 °C, the SiGe layers oxidized at 1000 °C did not show any Ge pile up, as inferred from the shape of the RCs shown Fig. 5-25. For further investigation of Ge behavior and strain relaxation of SiGe layers after the thermal oxidation at 1000 °C, the (113) RSMs of strained-Si$_{1-x}$Ge$_x$ layers with different Ge compositions were acquired. In Fig. 5-27, the SiGe
RLP of the oxidized film extends over that of Si one, confirming the formation of the Ge graded layer (GGL) for all of Si$_{1-x}$Ge$_x$ samples because the diffusion, rather than the accumulation, of Ge atoms into Si substrate is much more dominant. A weak intensity and broadening of the SiGe RLP indicate that the layer has a mosaic structure in which the layer is tilt or twist along certain direction, causing the modulation of the lattice parameter. What was also noted after the oxidation of strained-Si$_{1-x}$Ge$_x$ layers is a significant degree of the strain relaxation. In the RSM of Si$_{85}$Ge$_{15}$, $Q_X$ values of Si and SiGe RLPs are the same, indicating that their in-plane lattice parameters are still well matched even though the SiGe RLP is very broad. The RLP of SiGe layer shifts to left-upper direction with increasing Ge composition during thermal oxidation.

Finally, the strain of the Si$_{75}$Ge$_{25}$ layer was almost completely relaxed after the oxidation in 1000 °C with a formation of GGL. Therefore, this fact indicates that the strain relaxation induced by thermal oxidation is strongly dependent of the initial Ge composition in as-grown layer because a large concentration of the point defects lowers the activation energy for the dislocation nucleation.

Fig. 5-28 shows scanning transmission electron microscopy (STEM) images of Si$_{85}$Ge$_{15}$ and Si$_{75}$Ge$_{25}$ layers, and Ge depth profile from EDS after thermal oxidation at 1000 °C. In contrast to Fig. 5-26 (a), in which the GRL and GDL co-exist, the dark contrast in the region of SiGe layer after the thermal oxidation at 1000 °C was gradually getting bright along the Si-substrate, indicating that Ge composition in SiGe layer gradually decreases from the Si$_1$-$x$Ge$_x$/SiO$_2$ interface to Si substrate, as shown in STEM images and confirmed by the EDS results in Fig. 5-28. The existence of GGL after the oxidation at 1000 °C confirmed by STEM is consistent with the results from (113) RSMs displayed in Fig 5-27. Ge atoms diffuse deeper into the Si substrate with increasing Ge composition because the activation energy for Ge diffusion in
SiGe layers decreases with increasing Ge composition [129], as one can see Fig. 5-28. In addition, Ge composition of Si$_{85}$Ge$_{15}$ and Si$_{75}$Ge$_{25}$ layers near the SiO$_2$/Si$_{1-x}$Ge$_x$ interface after the thermal oxidation at 1000 °C for 1 hr is around 12 % and 18 %, respectively. Therefore, it is suggested from Fig. 5-28 (c) that the thermal oxidation of strained-SiGe layer with a high Ge composition at high temperature be a promising technique to fabricate relaxed and linear-graded Si$_{1-x}$Ge$_x$ as virtual substrates for strained-Si applications.

**Conclusions**

A Ge graded layer (GGL) was fabricated by using thermal oxidation at high temperatures. It was found that the competition between the Ge accumulation below the oxide interface and diffusion into the remaining SiGe layer was strongly dependent of the oxidation temperature. Ge accumulation occurred during oxidation at 800 °C and 900 °C, but it was no longer found after the oxidation at 1000 °C, for which Ge diffusion preferentially occurred. In addition, it was found that the strain was efficiently relaxed during the thermal oxidation and the initial Ge composition in SiGe layer had a great influence on the degree of strain relaxation. The Ge graded layer fabricated by using thermal oxidation of strained-Si$_{75}$Ge$_{25}$ layer at a high temperature can be used as a virtual substrate for strained Si on fully-relaxed thick SiGe applications.
Table 5-1. Simulations of the XRR curves acquired from the as-grown and annealed strained silicon samples. A model consisting of relaxed SiGe buffer, interfacial, strained silicon, and surface layers were used.

<table>
<thead>
<tr>
<th>Layer</th>
<th>As-grown strained silicon</th>
<th>Annealed strained silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness (Å)</td>
<td>Density (g/cm³)</td>
</tr>
<tr>
<td>Buffer layer</td>
<td>-</td>
<td>3.40</td>
</tr>
<tr>
<td>Interfacial layer</td>
<td>15</td>
<td>2.69</td>
</tr>
<tr>
<td>Strained layer</td>
<td>530</td>
<td>2.33</td>
</tr>
<tr>
<td>Surface layer</td>
<td>5</td>
<td>2.13</td>
</tr>
</tbody>
</table>

Table 5-2. Line profile analysis and calculated dislocation density of as-grown and annealed strained silicon. The diffraction profiles are fitted by Voigt and Pseudo-Voigt functions and fitting parameters are estimated by the least square method.

<table>
<thead>
<tr>
<th></th>
<th>Voigt</th>
<th>Pseudo-Voigt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$W_G$</td>
<td>$W_L$</td>
</tr>
<tr>
<td>As-grown strained-Si/Si$<em>{0.7}$Ge$</em>{0.3}$</td>
<td>(113)</td>
<td>0.151°</td>
</tr>
<tr>
<td>Annealed strained-Si/Si$<em>{0.7}$Ge$</em>{0.3}$</td>
<td>(113)</td>
<td>0.138°</td>
</tr>
</tbody>
</table>

$W_G$: FWHM of Gaussian function
$W_L$: FWHM of Lorentzian function
$W_{pd}$: FWHM of Pseudo-Voigt function
$\eta$: Fraction of the Lorentzian component ($0 \leq \eta \leq 1$)

Table 5-3. XRR simulation results for as-grown Si$_{1-x}$Ge$_x$ samples.

<table>
<thead>
<tr>
<th>Ge concentration (%)</th>
<th>Thickness (Å)</th>
<th>Roughness (Å)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial layer</td>
<td>4</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Strained layer</td>
<td>497</td>
<td>470</td>
<td>579</td>
</tr>
</tbody>
</table>

$^1$ From the reference with [130]
Table 5-4. XRR simulation results for annealed Si$_{1-x}$Ge$_x$ samples.

<table>
<thead>
<tr>
<th>Ge concentration (%)</th>
<th>Thickness (Å)</th>
<th>Roughness (Å)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Interfacial layer</td>
<td>11</td>
<td>20</td>
<td>36</td>
</tr>
<tr>
<td>Strained layer</td>
<td>487</td>
<td>452</td>
<td>530</td>
</tr>
</tbody>
</table>

Table 5-5. SiGe layer thickness and Ge content estimated from XRR and $\omega/2\theta$ RCs simulations and measured by XTEM.

<table>
<thead>
<tr>
<th>Samples</th>
<th>XRR</th>
<th>$\omega/2\theta$ RCs</th>
<th>XTEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness (Å)</td>
<td>Ge content (%)</td>
<td>Thickness (Å)</td>
</tr>
<tr>
<td>15% Ge</td>
<td>497</td>
<td>15.0</td>
<td>490</td>
</tr>
<tr>
<td>20% Ge</td>
<td>470</td>
<td>21.0</td>
<td>468</td>
</tr>
<tr>
<td>25% Ge</td>
<td>579</td>
<td>27.0</td>
<td>580</td>
</tr>
</tbody>
</table>
Figure 5-1. (113) Reciprocal space map of annealed strained-Si/Si$_{0.7}$Ge$_{0.3}$/graded-SiGe/Si-substrate.

Figure 5-2. X-ray reflectivity (XRR) curves recorded from the as-grown and annealed strained-Si/Si$_{0.7}$Ge$_{0.3}$/Graded-SiGe/Si.
Figure 5-3. Raman spectra of strained-Si on SiGe. (a) Raman spectra from the as-grown strained-Si and (b) Si-Si vibrational modes in the strained-Si of as-grown and annealed samples.

Figure 5-4. Curve fitting of (113) rocking curve of annealed strained silicon. (a) Pseudo-Voigt and (b) Gaussian functions were used. $R^2$ is a goodness of fit parameter.
Figure 5-5. The coherence length distribution calculated for the as-grown and annealed strained silicon from the second derivative of the Fourier size coefficient.

Figure 5-6. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) images of strained silicon. (a, b) and (c, d) were obtained from as-grown and annealed strained-Si, respectively.
Figure 5-7. RBS spectrum and its fit using RUMP software [131] for a sample containing a 25% Ge fraction.

Figure 5-8. (113) RSM from a Si_{0.85}Ge_{0.15} layer on (001)Si.
Figure 5-9. ω/2θ RC acquired from a sample with 15 % Ge and its simulation (displaced vertically for better view).

Figure 5-10. AFM micrographs of the as-grown SiGe layers surface.
Figure 5-11. (004) and (113) ω/2θ RCs acquired from the as-grown Si_{1-x}Ge_{x} on Si and after the thermal anneal.

Figure 5-12. Plan-view TEM for strained SiGe samples as-grown and annealed at 800 ºC for 30 min.
Figure 5-13. Omega-2theta rocking curves and TEM images. (a) $\omega/2\theta$ RCs and (b) plan-view TEM images of as-grown and annealed at 800 °C for 30 min Si$_{80}$Ge$_{20}$ films 50 nm thick.
Figure 5-14. (004) and (113) omega rocking curves (ω-RCs) acquired from the as-grown and annealed strained Si_{80}Ge_{20} layers.
Figure 5-15. (113) reciprocal space maps of as-grown and annealed at 900 °C for 30 min 100 nm thick Si75Ge25 layers.

Figure 5-16. (004) and (113) ω-RCs acquired from the as grown and annealed at 900 °C for 30 min Si75Ge25 100 nm thick layers.
Figure 5-17. TEM images of annealed Si$_{75}$Ge$_{25}$ film. (a) Cross-sectional and (b) high resolution TEM images in <110> projection of a 100 nm thick stained Si$_{75}$Ge$_{25}$ annealed at 900 °C for 30 min.

Figure 5-18. Bright field transmission electron microscopy image of implanted Si$_{76}$Ge$_{24}$ layer annealed at 500 °C for 30 min. The SiGe/Si and amorphous-crystalline interfaces are clearly marked in this figure.
Figure 5-19. (113) reciprocal space maps (RSMs) of Si$_{76}$Ge$_{24}$ layers. (a) and (b) were acquired from as-grown and annealed Si$_{76}$Ge$_{24}$ layers. The relaxation line is located between blue (relaxation=0 %) and red (relaxation=100 %) points.

Figure 5-20. Surface undulation of SiGe layers. (a) Schematic of the surface undulation of strained SiGe layer and AFM images of Si$_{76}$Ge$_{24}$ samples annealed at 800 °C for 30 min (b) without and (c) with ion implantation.
Figure 5-21. Average peak-to-peak distance (black) and r.m.s. roughness (blue) of annealed Si\textsubscript{76}Ge\textsubscript{24} layers without/with ion-implantation.

Figure 5-22. (113) RSMs of ion-implanted Si\textsubscript{76}Ge\textsubscript{24} layers after thermal annealing.
Figure 5-23. Strain relaxation and full width at half maximum (FWHM) values of (113) ω-RCs of ion-implanted Si$_{76}$Ge$_{24}$ after thermal anneal. The black and blue lines indicate strain relaxation and FWHM values, respectively.

Figure 5-24. Transmission electron microscopy images of an ion-implanted Si$_{76}$Ge$_{24}$ films. The layers were annealed at (a) 700 °C and (b) 800 °C. The images were taken by using g=220 two beam condition.
Figure 5-25. (113) ω/2θ RCs of as-grown strained-Si$_{75}$Ge$_{25}$ and after oxidation at 800 °C, 900 °C, and 1000 °C for 1hr. Red dot lines indicate the SiGe peak position of as-grown film as a reference.

Figure 5-26. Scanning transmission electron microscopy and reciprocal space map of Si$_{75}$Ge$_{25}$ oxidized in 800 °C. (a) STEM image and Ge concentration measured by EDS and (b) (113) reciprocal space map (the red dot indicates the reciprocal lattice point (RLP) of as-grown Si$_{75}$Ge$_{25}$ layer).
Figure 5-27. (113) reciprocal space maps (RSMs) of strained-Si$_{1-x}$Ge$_x$ layers after the oxidation at 1000 °C for 1 hr.

Figure 5-28. STEM images of oxidized Si$_{75}$Ge$_{25}$ layers and their depth profile. (a) Si$_{85}$Ge$_{15}$ and (b) Si$_{75}$Ge$_{25}$ layers, and (c) Ge depth profile from EDS after the oxidation in 1000 °C.
CHAPTER 6
SUMMARY

Strained-Si/SiGe

The strain relaxation and observation of the structural evolutions in strained-Si/SiGe layers after post thermal processes were investigated using advanced x-ray techniques. These techniques provided a wealth of information about strained layers, such as degree of strain/relaxation, elemental composition, layer thickness, interface roughness, dislocation density, and dislocation behavior. Based on the experimental information, this work showed that the defect behavior in such strained layers was strongly dependent on the thermal processes. For the strain relaxation, the misfit defects should be nucleated at the interface between the strained layer and substrate. The activation energy for the nucleation of the misfit defects depended on the several nucleation source, such as pre-existing threading dislocations from the substrate, surface of the strained layer, point defects induced by ion-implantation and oxidation processes. It was found from this work that the effects of pre-existing threading dislocations and surface step/undulation on the relaxation were not very important so that high temperature N2 annealing induced only a slight relaxation. However, the strain after the implantation or oxidation processes was highly relaxed due to the role of point defects assisted strain relaxation. The generation of the dislocation loops by a large concentration of point defects lowered the activation energy of the misfit dislocation at the interface. The understanding of the relaxation mechanism and defect behavior, highly relaxed and thin Si$_{1-x}$Ge$_x$ layers have been fabricated.

High Crystalline GaN Films

High resolution x-ray techniques were used to acquire detailed information about optimization of the growth conditions for high crystalline GaN films. Especially, a grazing incident x-ray diffraction (GIXD) method was used for the determination of the twist angle
because most defects in GaN films were edge-type threading dislocations. It was found that the crystallinity of GaN films grown by the two-step growth method was strongly dependent on the growth conditions, such as growth temperature and gas flow rate in low temperature and high temperature growth steps. The edge-type threading dislocations can be reduced by optimizing the 3-dimensional growth mode time ($t_{3D}$) in the high temperature island growth step. On the other hand, the screw-type threading dislocation density could be reduced by optimizing the growth temperature in the low temperature nucleation growth.

**P-type ZnO**

Phosphorus-doped ZnO films were characterized using high resolution x-ray diffraction techniques. By analyzing the omega rocking curves, it was found that ZnO films grown on the low temperature buffer layer showed two columnar structures with different in-plane orientation which were surrounded by threading dislocations. For the strain evaluation, a line profile analysis (LPA) using a William-Hall plot and Warren-Averbach method was carried out. The results showed that while the crystallite size was almost the same in all ZnO films, 0.5 at. % P-doped ZnO film showed the highest strain value, compared to 1.0 at. % P-doped ZnO film. This suggested that the internal strain was increased with increasing incorporation of phosphorus atoms due to a mismatch between the atomic radii, resulting in the phosphorus segregation for the strain relaxation. This fact was found to be confirmed by XPS results.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Jung Hun Jang was born in Wonju, Gangwon-Do, South Korea. He earned a bachelor’s degree in Department of Materials Science and Engineering, Hanyang University, Seoul, South Korea, in February 2005. In August 2005, he enrolled in the Department of Materials Science and Engineering, University of Florida, to pursue Ph.D under the guidance of Dr. Valentin Craciun. His main research involved growth and characterization of electronic materials, such as Si, SiGe, ZnO, and GaN. Especially, he focused on the advanced characterization by using x-ray based techniques. During his Ph.D study, he worked in Major Analytical Instrumentation Center (MAIC), University of Florida. He received “Korean Graduate Student Research Award” from University of Florida in 2008. He is author/co-author of 12 journal and conference papers.