SCIENCE AND APPLICATIONS OF III-V GRADED ANION METAMORPHIC BUFFERS ON INP SUBSTRATES

DISSERTATION

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ABSTRACT

High-In InGaAs and InAs material systems are of extraordinary interest for applications of high-speed and infrared devices due to their large carrier mobilities and small band-gaps. However, there is no lattice-matched standard substrate technology for high-In InGaAs and InAs currently and lattice-mismatched direct growth usually leads to high density of threading dislocations, which significantly degrade device performance, particularly minority carrier devices. To obtain device-quality materials, metamorphic graded buffers are required between the substrate and the high-In InGaAs and InAs layer to accommodate the lattice mismatch and filter the dislocations. In other words, metamorphic graded buffers are equivalent to a virtual substrate with tunable lattice constant, supporting materials with desired lattice constant on lattice mismatched substrates. This technique shows the promise of removing the constraints imposed by standard substrates and realizing lattice engineering in semiconductor technology.

Conventional metamorphic graded buffers grown on GaAs and InP substrates are mixed cation materials, which change the group III composition to adjust the lattice constant of the buffers. However, mixed anion graded buffers have potential advantages over mixed cation graded buffers because, during the growth of mixed anion materials, the control of the growth rate is decoupled from that of the chemical composition. This
work focuses on the science and applications of metamorphic mixed anion InAsP graded buffers grown on InP substrates by solid source molecular-beam epitaxy (MBE). The main research activities include the comparison of structural properties between mixed anion and mixed cation graded buffers, the minority carrier lifetime study on InGaAs double heterostructures grown on InP using InAsP graded buffers, and the investigation of high-quality InAs grown on InP using metamorphic InAsP graded buffers.

The first part of this research is the comparison of InAsP (mixed anion) and InAlAs (mixed cation) graded buffers. InAsP and InAlAs step-graded buffers were designed and grown with identical buffer thickness and lattice mismatch (~ 1.3%) with respect to InP substrates. Although the strain relaxation of both buffers were determined to be close to 90% by high-resolution x-ray diffraction, InAsP graded buffers showed smoother surface morphology and lower threading dislocation density compared to InAlAs graded buffers. Atomic force microscopy reveals that the surface roughness (RMS) of InAsP and InAlAs graded buffers were 2.2 nm and 7.7 nm, respectively. With cross-sectional and plan-view transmission electron microscopy, the threading dislocation density was measured to be ~ 4x10^6 cm^-2 for InAsP graded buffers, which is much lower than that for InAlAs graded buffers (> 1x10^7 cm^-2).

Minority carrier lifetime is a very important parameter for the material quality evaluation and better understanding of carrier loss mechanisms. To obtain the information of the minority carrier lifetime, InGaAs double heterostructures (DH) were grown on InAsP and InAlAs graded buffers. Ultra-high photoconductive decay (PCD) was performed on to measure minority carrier lifetimes. Very high carrier lifetimes (4-5 μs) were observed for the InGaAs DH with InAsP graded buffers whereas only ~ 0.5 μs
for that with InAlAs graded buffers, indicating that high quality of the InAsP graded buffers translates into high electronic quality InGaAs with high carrier lifetime. The dependence of lifetimes on the thickness of DHs revealed the excellent InAsP/InGaAs interface quality. In this study, a model combine with wavelength dependent analysis of the initial nonlinear decay observed in PCD data is also presented to explain the possible role of carrier diffusion in PCD characterization.

In view of our previous work of high quality InGaAs/InAsP/InP, it is very promising to extend InAsP graded buffers all the way to support high device quality InAs. As a function of different InAsP graded buffers design, structural properties of overgrown InAs layers, including surface morphology, strain relaxation, and defect structures, were investigated. During the characterization of InAs/InAsP/InP, extraordinarily large epitaxial tilt was found to exist in the relaxed InAs layer. Because the conventional tilt analysis method using double-axis XRD failed to give reliable tilt information, a new tilt analysis method using reciprocal space maps generated by triple-axis XRD has been developed and employed to successfully study the InAs epitaxial tilt.

Transport properties of relaxed InAs grown on InP using InAsP graded buffers have been investigated and correlated with structural properties. During the study, a surface accumulation layer was found in InAs with graded buffers with an electron mobility of 2400 cm²/Vs and a sheet carrier density of 4.05x10¹² cm⁻². Furthermore, 2DEG transport in relaxed InAs layers has been demonstrated using an InAlAs/InAs heterostructures grown on metamorphic InAsP/InP substrates. A peak mobility of 133 000 cm²/Vs was observed at 25 K. In contrast, no 2DEG transport was observed for identical heterostructures using direct-growth buffers, which instead revealed InAs bulk-
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the dominant scattering limitation for these heterostructures. These results demonstrate
the potential of achieve ultrahigh-speed InAs based HEMTs using InAsP graded buffers
on InP.
Dedicated to my parents
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PUBLICATIONS


3. D. Liu, M. Hudait, **Y. Lin**, H. Kim, S. A. Ringel, and W. Lu, “In<sub>0.53</sub>Ga<sub>0.47</sub>As/InAs<sub>0.3</sub>P<sub>0.7</sub> composite channel high electron mobility transistors”, *IEE Electron Lett.* **42**(5), 307-308 (2006).


12. M. K. Hudait, Y. Lin, M. N. Palmisiano, and S. A. Ringel, “0.6 eV bandgap In_{0.69}Ga_{0.31}As thermophotovoltaic devices grown on InAs_yP_{1-y} step-graded buffers by molecular beam epitaxy”, *IEEE Electrical Device Lett.* **24**, 538 (2003).


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CHAPTER 1

INTRODUCTION

1.1 Introduction and motivation

Growth of semiconductor epitaxial layers whose lattice constant is different from that of the original substrates as a means to vary the surface lattice constant to support new device technologies is finding increased interest in many fields. [1, 2, 3, 4, 5, 6] This is largely due to the advances in understanding of how to control strain relaxation by grading of epitaxial layer compositions in ways that minimize the introduction of threading dislocations but simultaneously achieve efficient strain relaxation. The material science of compositionally graded buffers has yielded success at the materials and now at the device levels. Good examples of this are metamorphic SiGe and InGaAs graded buffers used in the GaAs/Si integration and multi-junction tandem photovoltaic devices, respectively.

SiGe graded buffers offer an approach to the integration of III-V compound semiconductor technologies with the conventional Si microelectronic world, which would facilitate many novel technological capabilities, including optoelectronic integrated
circuits and ultra-high bandwidth VLSI. [7] In the current joint research between The Ohio State University and the Massachusetts Institute of Technology, the threading dislocation (TD) density of $1 \times 10^6$ cm$^{-2}$ has been achieved in GaAs grown on Si with this approach. [8, 9] Moreover, recently, high quality InGaP/GaAs solar cells and AlInGaP Lasers/LEDs have been successfully demonstrated on Si substrates using metamorphic SiGe step-graded buffers. [2, 10]

In the photovoltaic technology, metamorphic graded buffers are exploited in device structures to optimize the bandgap profile and thus increase the cell conversion efficiency. In presently dominant InGaP(1.86eV)/In$_{0.01}$Ga$_{0.99}$As(1.40eV) /Ge(0.65eV) lattice-matched photovoltaic systems, the conversion efficiency has reached around 30%. [11] However, theoretical analysis predicts that the conversion efficiency can be increased to 39% by replacing the In$_{0.01}$Ga$_{0.99}$As middle cell with an In$_{0.16}$Ga$_{0.84}$As (1.2 eV) cell. [12] As a result, lattice-mismatched solar cells with metamorphic InGaAs graded buffers have been designed and attracted intensive interest. [13, 14, 15]

As highlighted in Fig. 1.1, high-In InGaAs/InAs-based alloys and heterostructures based on InGaAs, InAlAs and InAsP are of great interest for applications in high-speed electronic and infrared optoelectronic devices, since semiconductor materials in this range of lattice constants display very high electron mobilities, a range of low bandgap energies, and the enticing prospects of ideal band offset energies that are tunable over a wide range. However, there are no suitable lattice-matched substrates to support device-quality epitaxial growth of such high-In InGaAs/InAs-based devices, and direct growth of these materials and devices on standard substrates leads to the formation of high dislocation densities, which significantly degrade the devices performance, especially for
minority carrier devices. Here an alternative solution is to use a graded buffer to transition the lattice from a standard substrate to that of high-In InGaAs/InAs and mitigate the threading dislocations generated during relaxation of the misfit strain.

Figure 1.1 Band-gap vs. lattice constant of semiconductor materials. The highlighted area is the high-In InGaAs/InAs, InAsP and InAlAs alloy region.

For high-In InGaAs/InAs-based devices, InP is generally used as the substrate because it is the least lattice-mismatched. According to Fig. 1.1 shown above, three alloy systems, InGaAs, InAlAs and InAsP, can theoretically extend the lattice constant to any
high-In composition (>53%) InGaAs/InAs on InP substrates. This means that any of these three material systems can potentially function as graded buffers for high-In InGaAs/InAs devices on InP substrates. Because mixed-cation buffers are far more common due to their obvious simplicity, much effort has been devoted to InGaAs/InAlAs graded buffers grown on InP for supporting high-In InGaAs/InAs based devices. [5, 6, 16, 17, 18] However, it has been revealed that the adatom surface mobility competition in the mixed-cation material growth leads to alloy decomposition/branch defects, which severely roughen the surface morphology and degrade the buffer function via blocking dislocation glide. [6, 19, 20] In view of this essential issue in mixed-cation graded buffers, InAsP graded buffers start to attract increasing interest in this research field. As a mixed-anion semiconductor, InAsP is free of the concern of the adatom surface mobility competition.

Compared to InGaAs/InAlAs alloys, the InAsP alloy is a relatively unfamiliar material system. A survey of the literature indicates that much less research work has been performed on this material system. Many key material issues of InAsP bulk material and heterostructures, including As/P competition in crystal growth, strain relaxation, defect formation, and surface morphology are not completely understood. The ability to understand these key issues is also critical for the demonstration of new devices with unique and improved functionality. Hence, in addition to device applications, another motivation of this research is to understand the fundamental material science of this material system.

In this dissertation, an investigation of graded anion III-V buffers based on InAsP will be presented. The prime goal for this research is to establish this as a successful
graded buffer material using solid source molecular beam epitaxy, understand and optimize metamorphic InAsP graded buffer structural properties, correlate with electronic properties to establish likelihood for applications, and ultimately apply to select devices that would reveal the device advantage of anion grading to large lattice constants.

1.2 Background

Like most non nitride III-V compound semiconductors, InAsP alloys crystallize in the zinc blende crystal structure, whose lattice constant spans from 5.8687 Å (InP) to 6.0583 Å (InAs). As mixed-anion alloys, in the lattice structure of InAsP, indium atoms occupy group III sub-lattice positions and As/P atoms randomly take group V sublattice positions. From Fig. 1.1, we can see that the dependence of the bandgap energy and the chemical composition is nearly linear. At room temperature, the energy bandgap of InAs$_y$P$_{1-y}$ can be determined by [21]

\[
E_g (y) = 0.101y^2 - 1.093y + 1.352
\]  

(1.1)

Since the bandgap energy of InAsP ranges from 0.36 eV (InAs) to 1.35 eV (InP), covering most of the infrared wavelength regime, this material system is of special interest in the area of infrared optoelectronic devices. In the 1970s, InAsP was first investigated for the application of injection lasers and photocathodes. [22, 23, 24]

For fiber optics technologies, lattice-matched InGaAsP-based lasers have been the dominant 1.3 µm light sources. Recently, it has been demonstrated that strained-layer semiconductor lasers exhibit lower the threshold current by altering the valence band
structure. [25, 26] As a result, InAsP-based strained multiple quantum well lasers begin to show the trend to replace lattice-matched InGaAsP lasers. The advantages of InAsP over InGaAsP include (1) InAsP is a ternary semiconductor, which is easier to control the chemical composition; (2) InAsP multiple quantum wells provide a larger conduction band offset ($\Delta E_c$). The conduction band offset of InAsP/InP, $\Delta E_c = 0.7\Delta E_g$, in contrast to the conduction band offset of InGaAsP/InP, $\Delta E_c = 0.4\Delta E_g$. [27, 28, 29, 30] This larger band offset significantly improves the high temperature performance of InAsP-based strained quantum well lasers. [31, 32, 33, 34, 35, 36]

However, most previous research work was limited to thin, strained InAsP layers and comparatively little work has been done on bulk, relaxed InAsP with no reports on the use of InAsP to engineer substrate lattice constants. In general, with the relaxing of strain in lattice structures, bulk InAsP layers show significantly different electronic, chemical, and structural properties from thin, strained InAsP layers. To understand fundamental issues of this material system and to explore its potential application in advanced device technology requires investigation of both relaxed and strained InAsP material and its heterostructures. Hence, understanding metamorphic InAsP compositionally graded buffers is the driving force of this study.

1.3 Research objective

The objective for this research is motivated by the “technology-enabling” potential of InAsP metamorphic step-graded buffers in InP-based infrared and high-speed device applications and also by the fundamental material science issues of this relatively unexplored material system. The objective primarily includes two parts. First, this study
shall attempt to understand the complex interrelationships between growth, surface/interface properties, and bulk material properties for InAsP metamorphic step-graded buffers over a wide range of lattice constants between InP and InAs. Second, with obtained instructive understanding and findings, this study shall exploit them to fabricate novel advanced devices that extend beyond the realm of current devices. To accomplish the objective of this research, substantial research work including basic material studies and device optimization is needed. Specifically,

— Extend the lattice constant accessible by metamorphic InAsP graded buffers to cover the range from InP to InAs.

— Understand the fundamental differences between mixed-anion and mixed-cation graded buffers and compare both graded buffers in device applications.

— Determine the impact of InAsP metamorphic step-graded buffers properties, including strain relaxation, morphological features, and defect structures, on the electronic, structural properties of overgrown active layers and optimize the design of InAsP metamorphic step-graded buffers accordingly.

— Fabricate metamorphic devices using InAsP metamorphic step-graded buffers and investigate the correlation between device performances and material properties.

1.4 Outline of this dissertation

The remainder of this dissertation is organized as follows. Chapter 2 will be a review of metamorphic graded buffers. Chapter 3 will introduce crystal growth and characterization techniques utilized in this research, which include solid source molecular-beam epitaxy, x-ray diffraction, transmission electron microscopy, Hall effect,
Chapter 4 covers the crystal growth of InAsP by solid source MBE. The detail growth conditions and the calibration curve of InAsP will be provided. Chapter 5 focuses on the comparison of structural properties of InAlAs and InAsP step-graded buffers, including surface morphology, strain relaxation, and defect structures. Chapter 6 covers the comparison study of minority carrier lifetimes in InGaAs double heterostructures grown on InP with both InAlAs and InAsP step-graded buffers. Additionally, a model will also be developed in this chapter to explain the non-linear behavior of PCD curves obtained in the minority carrier lifetime measurement. The research work in chapters 5 and 6 concentrates on low-As (As composition < 40%) InAsP step-grade buffers with the lattice misfit less than 1.3% with respect to the InP substrate.

From chapter 7 on, InAsP step-graded buffers will be extended to the high misfit regime. Relaxed InAs will be grown on InP using InAsP step-graded buffers. For the material quality evaluation, structural properties of InAs on InP with InAsP graded buffers will be characterized by various experimental techniques. At the end of this chapter, epitaxial tilting in relaxed InAs with InAsP graded buffers will be also discussed. In chapter 8, electrical properties of relaxed InAs grown on InP using InAsP graded buffers will be studied. Moreover, to demonstrate its device application potential, InAs-based heterostructures grown on InP with InAsP step-graded buffers will be designed and investigated, which will be described in chapter 8. Chapter 9 concludes this dissertation by summarizing the research results and presenting some ideas for future work in this area.
1.5 References


2.1 Pseudomorphic and metamorphic growth

When a semiconductor is grown on a substrate with a different lattice constant, a coherently strained layer is obtained first and the mismatch strain is accommodated by the means of elastic deformation of the crystal lattice. This early stage of growth is called pseudomorphic growth. When the thickness of the coherently strained layer exceeds a critical value $h_c$, strain relaxation occurs through the introduction of misfit dislocations at the interface. Thus, the growth evolves into the stage of metamorphic growth. Fig.2.1 schematically shows the stages of pseudomorphic and metamorphic growths. From the viewpoint of energy, the critical thickness is defined to be the layer thickness at which misfit dislocations start to nucleate to relieve the strain energy in the lattice-mismatched layer. [1]
The issue of critical thickness has been studied for decades. The models of van der Merwe [2] and Matthews-Blakeslee (MB) [3] are usually accepted as standard theoretical models in analysis. With Van der Merwe’s model, the critical thickness $h_c$ can be approximately calculated by

$$h_c \approx \left( \frac{1}{8\pi^2} \right) \left( \frac{1-v}{1+v} \right) \frac{a_0}{f}$$

(2.1)
where $\nu$ is the Poisson’s ratio, $a_0$ is the lattice constant of the substrate and $f$ is the lattice misfit. The MB critical thickness is given as the solution of

$$h_c \approx \frac{|b|}{2\pi f \cos \lambda} \left( \frac{1 - \nu \cos^2 \beta}{1 + \nu} \right) \ln \left( \frac{h_c}{|b|} + 1 \right)$$  \hspace{1cm} (2.2)$$

where $|b|$ is the magnitude of the Burgers vector $b$, $\lambda$ is the angle between the Burgers vector and a line that lies in the film/substrate interface normal to the misfit dislocation line, and $\beta$ is the angle between the misfit dislocation line and $b$. Although both models agree with experimental data within a factor of about 2, the key result of the models is that the critical thickness is inversely proportional to the lattice misfit between the substrate and the epitaxial layer. [4, 5]

### 2.2 Fundamentals of metamorphic graded buffers

Typically when misfit dislocations nucleate to relieve the strain in the lattice-mismatched epitaxy, threading dislocations are concomitantly created with the misfit dislocations. [5] Threading dislocations can help to relax the strain by the glide process but they also propagate up towards the active region of electronic and optoelectronics devices and severely degrade device performance and reliability, particularly for minority carrier devices like light emitting diodes (LEDs), heterojunction bipolar transistors (HBT) and photovoltaics. Thus it is of great importance to establish effective techniques to eliminate or reduce the threading dislocation density. In recent years, substantial efforts have been devoted to this research area. Metamorphic compositionally graded
buffers have been demonstrated to be a practical and successful approach to effectively reduce the TD density in lattice-mismatched devices.

Compared to the direct growth on lattice-mismatched substrates, metamorphic compositionally graded buffers have some advantages that help reduce the density of threading dislocations. First, in the growth of graded buffers, dislocations are distributed throughout the entire buffer instead of a single interface. Thus, the probability of pinning by intersecting dislocations, which impedes the glide of threading dislocations, is decreased in graded buffers. Second, the strain in the graded buffer layer is greatly reduced due to spreading the strain profile across the buffer thickness; therefore, the nucleation of dislocation loops is inhibited. The existing threading dislocations are able to glide more easily and relieve the strain. [6] Fig. 2.2 shows cross-sectional TEM images of GaAs grown directly on Si and GaAs grown on Si with SiGe graded buffers. SiGe graded buffers can effectively reduce the TD density from $10^9$ cm$^{-2}$ to $10^6$ cm$^{-2}$, which demonstrates the capability of graded buffers to filter the threading dislocations generated during the relaxation of ~4 % lattice misfit between Si and GaAs.

In the technique of compositionally graded buffers, there are two kinds of common graded buffer designs, one is linear-graded buffers and the other is step-graded buffers. During the growth of buffers, the misfit and the lattice constant of the layer change continuously for the linear-graded buffers and in a stepwise manner for the step-graded buffers. The schematic diagrams of both graded buffers are shown below in Fig. 2.3.
Fig. 2.2 TEM images of (a) GaAs grown directly on Si with the TD density of $10^9$ cm$^{-2}$ [7] and (b) GaAs grown on Si with SiGe graded buffers, the TD density can be reduced to $1 \times 10^6$ cm$^{-2}$ [8].

Fig. 2.3 Schematic diagrams of linearly graded and step-graded buffers, assuming compressive overgrowth to lattice constants larger than that of the substrate.
In practice, both buffer designs have been utilized in device structures to fulfill the function of a virtual substrate and dislocation filter. [9, 10, 11, 12] The most significant difference between linear-graded and step-graded buffers is that linear-graded buffers have no abrupt interfaces while step-graded buffers provide multiple low-mismatch interfaces. These low-mismatch interfaces are able to facilitate the glide of existing threading dislocations to relieve the strain and reduce the nucleation rate of new dislocations. [13] Theoretically, well-designed step-graded buffers have higher efficiency compared to linear-graded buffers in strain relaxation and threading dislocation reduction. The detail of the buffer design theory will be discussed in the next section.

2.3 Theory on the metamorphic step-graded buffer design

In lattice-mismatched epitaxy, when the thin film exceeds the critical thickness, misfit dislocation nucleation accompanies the glide motion of threading dislocations (TDs). During the motion of threading dislocations, the TD density can be reduced through reactions between each other. [14, 15] Since the strain inside the thin film drives threading dislocations to move and react with each other, the introduction of an intentionally strained layer can be used to facilitate the TD reduction process. This is the basic TD reduction mechanism of step-graded buffers. A well-designed graded buffer should relax the misfit strain mostly through the glide motion of existing threading dislocations instead of the misfit dislocation nucleation. However, much theoretical and experimental effort are still needed to further understand threading dislocation behaviors in graded buffers in order to realize an optimal graded buffer design.
Based on the dislocation flow theory, Fitzgerald, et al developed an empirical model to reveal the dependence of the threading dislocation density in compositionally graded buffers on the growth conditions. [16]

\[
\rho_t = \frac{2R_g R_{gr} e^{U/kT}}{|b| B Y^m \varepsilon_{\text{eff}}^m} \propto \frac{R_g R_{gr}}{V}
\]

(2.3)

where \( \rho_t \) is the threading dislocation density, \( B \) is a constant with units of velocity, \( Y \) is the Young’s modulus, \( \varepsilon_{\text{eff}} \) is the strain reduced by dislocation flow, \( m \) is an exponent between 1 and 2, \( R_g \) is the growth rate, \( R_{gr} \) is the grading rate, \( U \) is the activation energy for dislocation glide, \( k \) is Boltzmann’s constant, \( T \) is the temperature, and \( V \) is the dislocation velocity, which can be written as

\[
V = B Y^m \varepsilon_{\text{eff}}^m e^{-U/kT}
\]

(2.4)

Hence, the threading dislocation density in graded buffers is proportional to the growth rate and the grading rate but is inversely proportional to the dislocation glide velocity. In other words, given a fixed growth rate, a larger grading rate can be used for a material system with a larger dislocation glide velocity in its graded buffer design.

Focusing on threading dislocation reaction in graded buffers, Romanov and Speck, et al developed a kinetics approach to describe the TD reduction mechanism. [15, 17, 18, 19] In their model, threading dislocations are reduced by the annihilation reaction
and represented mathematically by a set of first order differential equations. Analogous to the chemical kinetics, the interaction constant for TD reductions is referred to the annihilation radius $r_A$, which denotes the distance necessary for spontaneous reaction between the nearby TDs.

The reaction kinetics model takes into account three kinds of dislocations, (1) TDs that have no obstacles to motion, mobile TDs with the density of $\rho_m$; (2) TDs whose motion is blocked by misfit dislocations, immobile TDs with the density of $\rho_i$, and (3) misfit dislocations with the density of $\rho_{MD}$. In the TD reaction, mobile TDs may encounter other mobile or immobile TDs and annihilate, also mobile TDs may be blocked by MDs and become immobile TDs, and furthermore, MDs are generated through the motion of mobile TDs. Hence, the changes in the TD densities $\rho_m$, $\rho_i$ and the MD density $\rho_{MD}$ are all related to the motion of the mobile TDs. Considering all relations among the three dislocation densities, the model gives the coupled differential equations describing the TD and MD evolution as

\begin{align*}
    d\rho_m &= -\rho_m \rho_{MD} d\lambda - 2r_A \rho_m^2 d\lambda - 2r_A \rho_m \rho_i d\lambda \\
    d\rho_i &= \rho_m \rho_{MD} d\lambda - 2r_A \rho_m \rho_i d\lambda \\
    d\rho_{MD} &= \frac{1}{2} \rho_m d\lambda
\end{align*}

where $d\lambda$ is the differential motion of mobile TDs.
To simplify the calculation, the authors assumed that the TD velocity was linearly proportional to the excess strain present in the thin film and thus the differential motion $d\lambda$ can be related to both the TD velocity and the film growth rate as.

\[
 d\lambda = v dt = \left(\frac{v}{g}\right) dh = \frac{A}{g} \left[ \varepsilon_m (1 - \frac{h_e}{h}) - \rho_{MD} b \right] dh 
\]  

(2.6)

where $v$ is the TD velocity, $h$ is the thickness of the thin film, $g$ is the growth rate, $g = dh/dt$, $A$ is a proportionality constant with units length/time, and $\varepsilon_m$ is the misfit strain.

Combining Eqs (2.5) and (2.6), the authors simplified the differential equations to be

\[
 d\rho_m = -\frac{A}{g} \left[ \varepsilon_m (1 - \frac{h_e}{h}) - \rho_{MD} b \right] \left( \rho_m \rho_{MD} + 2r_A \rho_m^2 + 2r_A \rho_m \rho_i \right) dh 
\]  

(2.7a)

\[
 d\rho_i = \frac{A}{g} \left[ \varepsilon_m (1 - \frac{h_e}{h}) - \rho_{MD} b \right] \left( \rho_m \rho_{MD} - 2r_A \rho_m \rho_i \right) dh 
\]  

(2.7b)

\[
 d\rho_{MD} = \frac{A}{2g} \left[ \varepsilon_m (1 - \frac{h_e}{h}) - \rho_{MD} b \right] \rho_m dh 
\]  

(2.7c)

In Reference 5, numerical solutions to Eqs (2.7) were given. Fig. 2.4 plots the dependence of the normalized misfit dislocation density $\rho_{MD}^* \ (\rho_{MD}^* = \rho_{MD}r_A)$ on the normalized initial misfit strain $\varepsilon_m^* \ (\varepsilon_m^* = \varepsilon_m r_A/b)$. It can be concluded from Fig. 2.4 that the initial misfit strain plays an important role in this TD reduction mechanism. For large initial misfit strains, the TDs will be totally blocked before the film fully relaxes, whereas
for small initial misfit strains, there are extra mobile TDs left in the thin film when the film completely relaxes, which means that mobile TDs are not sufficiently exploited to relax the misfit strain. According to the dependence curve shown in Fig. 2.4, the optimal normalized initial misfit strain can be determined to be \( \sim 0.003 \). [5]

Fig. 2.4 Dependence of the normalized MD density \( \rho_{MD}^* = \rho_{MDrA} \) on the normalized initial misfit strain \( \varepsilon_m^* = \varepsilon_{m\Gamma A}/b \). The optimal initial misfit strain is also indicated in the figure. [5]
Comparing to Fitzgerald’s empirical model, this reaction kinetics approach provides a clearer picture of the metamorphic step-graded buffer design and supports the idea that well-designed step-graded buffers have better performance than linear-graded and direct-growth buffers. In addition, it implies that for materials with larger lattice constants, the optimal misfit strain, namely the grading rate of the step-graded buffers, could be larger. However, since this normalized parameter $\varepsilon_{m^*}$ is still related to the annihilation reaction distance $r_A$, which is difficult to determine theoretically or experimentally. Hence, before this theory can quantitatively applied to guide the design of graded buffers, significant experimental effort must be done to further understanding of the fundamental science of metamorphic graded buffers.

2.4 Current applications of metamorphic step-graded buffers

In addition to the current research of SiGe and InGaAs graded buffers in III-V/Si integration and PV cell optimization, there are other types of graded buffers explored in different electronics and optoelectronics device applications. In GaAs-based devices, InGaAs, InAlAs, InGaP, InAlSb and AlGaAsSb graded buffers have been investigated in applications of field effect transistors, HBTs, quantum well infrared detectors, quantum well/dot lasers, etc. [19, 20, 21, 22, 23, 24] In InP-based devices, InGaAs, InAlAs, and InGaP graded buffers have been used for high-speed devices, quantum-wires optical devices, and TPV converters. [25, 26, 27] Furthermore, graded buffers have also been studied in the integration of III-nitride/Si. For instance, it was reported that AlGaN graded buffers could be grown between GaN and AlN/Si to reduce the crack density and the surface roughness. [28]
In this dissertation, we will concentrate on metamorphic step-graded buffers grown on InP substrates, attempting to merge InAs-based semiconductors, which possess extraordinary electronic properties but whose lattice constant is 3.2% larger than that of InP, with InP substrates. As mentioned before, since InAsP is a less developed material system with advantages over the common mixed-cation material systems, InGaAs and InAlAs, the focus of this research will be on science and applications of metamorphic InAsP step-graded buffers grown on InP substrates.
2.5 References


CHAPTER 3

CRYSTAL GROWTH AND CHARACTERIZATION TECHNIQUES

3.1 Introduction

In this dissertation, a variety of experimental techniques are employed to grow sample structures and characterize the material and electrical properties of the samples. The crystal growth technique used is solid source molecular-beam epitaxy (MBE). The material property characterization techniques include primarily atomic force microscopy (AFM) for the samples surface morphology information, high-resolution x-ray diffraction (HRXRD) for composition and strain relaxation measurements, and transmission electron microscopy (TEM) for defect structure investigation. For electrical property characterization, ultra-high photoconductive decay (UHPCD) and Hall effect are used to measure minority carrier lifetimes and carrier transport properties, respectively. This chapter provides a brief description of each technique mentioned above.
3.2 Molecular-beam epitaxy

Molecular-beam epitaxy (MBE), which was invented in the early 1970s, is one of the most important crystal growth techniques in solid-state device technology. In MBE, thin films are grown by the reactions of several molecular or atomic beams on a heated substrate surface in ultrahigh vacuum (~ $10^{-8}$ - $10^{-10}$ torr). In contrast to other deposition techniques, like liquid phase epitaxy and vapor phase epitaxy, MBE is able to more precisely control the beam fluxes and growth conditions; therefore, it is an ideal method to fabricate sophisticated structures with abrupt interface profiles, such as quantum well devices or advanced transistors. In addition, due to the ultrahigh vacuum environment, samples grown in MBE systems typically have much higher material quality. [1] In Fig. 3.1, a scheme of a conventional MBE system is illustrated.

![Fig. 3.1 Schematic view of a typical MBE system](image)
Conventional MBE systems use solid materials for molecular sources. Therefore they are also referred to as solid source MBE. For III-V compound semiconductor solid source MBE systems, effusion cells are used for group III (gallium, aluminum, and indium) and dopant (usually silicon and beryllium) sources. In the effusion cell, the crucible used is usually made of pyrolytic boron nitride (PBN), which gives a low rate of gas evolution, excellent thermal insulating ability and chemical stability up to 1400°C. For group V sources, like arsenic (As), phosphorus (P), and antimony (Sb), valved crackers are usually adopted due to their larger volume compared to group III sources. In the valved cracker, the flux from a heated group V source is controlled by a valve and group V molecules can be dissociated when the flux moves through a cracking tube, which is located behind the valve. For example, the arsenic flux from a heated As solid source mostly consists of As₄ molecules. After passing through the cracking tube with a temperature around 900°C, the As molecule species are converted from As₄ to As₂. The motivations for the molecular species dissociation are that (1) As₂ has higher incorporation efficiency and (2) Due to simpler incorporation mechanisms, As₂ should result in better crystal quality. [1, 3, 4, 5]

The UHV environment in MBE systems is also ideal for some in situ analysis tools, of which reflection high-energy electron diffraction (RHEED) is the most important one. RHEED allows direct measurement of the surface structure; therefore it can be used to calibrate the growth rate and provide information about the surface morphology. The energy of electrons used in RHEED is in the range of 5 – 40 keV. In MBE systems, the electron beam of RHEED is directed at a low angle (1°-3°) to the
sample surface and the penetration of the beam is restricted to the outmost few atomic layers. That is the reason why RHEED is called a surface analytical technique. [1, 3, 6, 7]  

In general, when an MBE growth is initiated, the intensity of RHEED features shows an oscillatory behavior. [8] A typical example of RHEED intensity oscillations from MBE-grown GaAs (001) surface is shown in Fig. 3.2. In fact, this oscillation effect is usually associated with a layer by layer growth process. In order to obtain a clearer view, a real space representation of this process in relation to RHEED intensity oscillations is schematically illustrated in Fig. 3.3. In the figure, when the layer surface is smooth, the RHEED intensity reaches a maximum; when the growing layer is roughly half complete (roughest), a minimum RHEED intensity is obtained. Thus, the RHEED can provide a continuous and absolute growth rate monitoring with the atomic layer precision. [1]  

![Fig. 3.2 RHEED intensity oscillations from the growth of GaAs. The oscillation period equals to the GaAs growth rate. [1, 8]](image)
Fig. 3.3 Schematic illustration of the formation of the first two complete monolayers in relation to RHEED intensity oscillations. [1, 9]
For diffraction on smooth surfaces, the RHEED pattern is primarily constituted by elongated streaks. [1] However, due to different surface atom rearrangements, the streak patterns display distinct periodicity during the MBE growth. For III-V semiconductor with group V stabilized (001) surface, the typical RHEED patterns is (2x4), which means in the (110) direction, the atom spacing is twice as long as the bulk lattice constant and in the (1-10) direction, the atom spacing is four times of the bulk lattice constant. During the growth of III-V compound semiconductors, the sample surface is usually required to be group V- stabilized in order to obtain an ideal 2-dimensional epitaxial layer, thus (2x4) streaks are the normally desired RHEED patterns in the growth of III-V semiconductors. Fig. 3.4 shows typical (2x4) RHEED patterns from a (001) GaAs surface.

Fig. 3.4 (2x4) RHEED patterns from (001) GaAs surface (a) 2x – in the (110) direction (b) 4x – in the (1-10) direction. [10]
In addition to RHEED, there are some other important in situ optical tools utilized in MBE systems. Optical pyrometry is used to measure the sample growth temperature by monitoring emitted radiation from the sample surface. Furthermore, the fluctuation of temperature profiles from optical pyrometry can provide information on surface roughness. Additional optical characterization techniques, such as spectral ellipsometry, spectral reflectometry and laser interferometry, are also optionally installed to continually examine optical characteristics of the film during MBE growth. [1, 11]

3.3 Atomic Force Microscopy

Atomic force microscope (AFM) is a high-resolution scanning probe microscope, which works by sensing the interaction force between the probe and the sample, and acquiring surface morphology images. In contrast to traditional microscopes, there are no lenses in AFM and the resolution of AFM is limited by the size of the probe rather than the diffraction effect of lenses. [12] This technique was invented by Binnig, Quate, and Gerber in 1986. [13]

Fig. 3.5 shows the configuration of a typical AFM system, which consists of a cantilever probe with a sharp tip mounted to a Piezoelectric (PZT) actuator and photo detectors for receiving a laser beam reflected off the end of the cantilever to provide cantilever deflection feedback. As the tip moves up and down with the contour of the surface, the laser beam deflected from the cantilever provides measurements of the difference in light intensities between photo detectors, which enables the PZT actuator to maintain the scanning tip at a constant force or distance above the sample surface. In the constant force mode, the PZT monitors real time deviation of the distance between the tip
and the sample surface. In the constant distance mode, the deflection force on the sample is recorded. Using computers, the surface image can be generated from the recorded signals. [14]

Fig. 3.5 Configuration of a typical AFM system. The cantilever, laser and photodectors are depicted on the right part. [14]

In AFM, when the tip is close to a sample surface, several interaction forces between the tip and the sample can be present. These forces include (1) van der Waals forces, (2) Coulomb repulsive force, (3) electrostatic force, if both tip and sample carry net charges, and (4) magnetic forces, if both tip and sample have a magnetic moment. [15]
Depending on which force is used as the imaging signal, AFM can be operated in different modes. In the contact mode, the Coulomb repulsive force is used as the imaging signal; while for the non-contact mode, the surface information mainly originates from the attractive van der Waals force. Recently, a new operational mode, termed as the tapping mode, has been explored in AFM technology. The tapping mode combines advantages of the contact and non-contact modes by allowing the cantilever tip to contact the sample for a minimal amount of time during scanning of the sample surface. This technique can increase the imaging resolution and also reduce the damage of tips and samples. [14]

Atomic force microscopy has become an established experimental technique, having significant impact in areas of material and biology sciences. Currently, AFM is capable of imaging the surface with the atomic resolution in direct space. Fig. 3.6 shows a high-resolution AFM image of an InP (110) surface, in which each atom and even atomic defects can be clearly observed. [16] In addition to its applications in the surface morphology, atomic force microscopy can also be exploited to characterize thin film mechanical and physical properties, to analyze microscopic phase distribution in polymers, and to study 3D topography of nanoparticle fabrication. [14, 17]
Fig. 3.6 AFM image of the cleaved InP (110) surface. Atomic defects (a) and adsorbates [(b) and (c)] are labeled in the figure. [16]

3.4 X-ray diffraction

In the area of crystalline semiconductors, x-ray diffraction (XRD) is an important and powerful technique used to characterize structural properties, including lattice constants, strain relaxation, epitaxial tilting, mosaic and curvature effects, as well as defect properties. [18] Compared to other lattice structure characterization techniques, such as transmission electron microscopy, XRD is relatively simple, straightforward, and non-destructive.

Like visible lights and microwaves, x-rays are also transverse electromagnetic waves, but of shorter wavelength. For crystallography, the wavelength range of x-rays commonly used is from 0.5 to 2.5 Å, which is very close to the size of atoms. In Practice,
x-rays are not deviated by refraction and therefore they cannot be focused with lenses.

3.4.1 Introduction to x-ray sources

In general, x-ray sources for diffractometry include laboratory and synchrotron radiation generators. In a laboratory source, x-rays are generated by the impact of accelerated electrons on a solid target. In this case, the output contains the sharp x-ray lines superimposed on a continuous spectrum. However, the intensity of the continuous spectrum is usually much weaker than the x-ray lines. Fig. 3.7 shows the spectrum from a copper sample, which is one of the most common x-ray source metals used in the laboratory x-ray diffractometer. In the spectrum, the Kα lines are from L → K transitions and the Kβ lines result from M → K transitions. In fact, the Kα lines are a doublet, consisting Kα1 and Kα2 lines. Because of its convenient wavelength and high intensity, the Kα1 line is the most popular choice for high resolution diffractometry. Hence in high-resolution x-ray diffraction, the Kα2 line is usually removed by employing a beam conditioner, which will be discussed later in this section.
Synchrotron radiation sources generate x-ray emission by allowing the electron beam to travel in a closed ring, which is called the electron storage ring. Typically, the electron storage ring is under an ultra-high vacuum, in which magnetic fields are used to confine electrons. The principal characteristics of synchrotron radiation are (1) continuous radiation spectrum, (2) high intensity, (3) high degree of polarization, and (4) pulsed time structure. Since the diameter of electron storage rings is around 100m, the installations are normally built on a national scale. [20]
3.4.2 High resolution x-ray diffractometer

Fig. 3.8 shows a schematic of high resolution x-ray diffractometers, which include double-axis and triple-axis configurations. In the double-axis configuration, before it reaches the sample, the incident x-ray is collimated and monochromatized by a beam conditioner, which usually contains apertures and Bragg reflections off crystals. The detector collects all signals diffracted by the sample over its acceptance angle. In contrast to the double-axis setting, the triple-axis x-ray diffractometer uses an analyzer crystal in front of the detector to improve the resolution at the expense of intensity. Because it can provide more detailed information, the triple-axis XRD is receiving more and more attention for research applications. However, for routine characterization in quality control, the double-axis XRD is usually preferred because of its simpler operation, higher intensity and faster measurement. [20]
Fig. 3.8 Schematic of high resolution x-ray diffraction instruments (a) double-axis; (b) triple-axis. [20]
3.4.3 Fundamental principles of x-ray diffraction

The most important theory of x-ray diffraction on crystalline materials is the well-known Bragg’s law, which can be expressed as

\[ n\lambda = 2d \sin \theta \]  

(3.1)

where \( n \) is the order of the diffraction, \( \lambda \) is the wavelength of the X-rays, \( d \) represents the inter-planar spacing of diffracting planes, and \( \theta \) is the angle of the incident X-ray. Fig. 3.9 clearly illustrates the Bragg’s law and all related parameters. Based on the Bragg’s law, the inter-planar spacing, or lattice constant, can be calculated from the incident angle where the diffraction occurs. [20]

Fig. 3.9 Schematic of Bragg’s law. In the figure, the interplanar spacing and the incidence Bragg angle are labeled in the figure. [20]
In general, depending on diffraction planes, x-ray diffraction can be sorted into two categories, symmetric and asymmetric diffractions. In symmetric diffractions, diffraction planes are parallel to the sample surface and thus the incident and exit x-rays are symmetric with respect to the surface normal. Symmetric diffractions are used to determine the perpendicular lattice constant. In asymmetric diffraction, diffraction planes are not parallel to the surface and the incident and exit x-rays are asymmetric to the surface plane. Asymmetric diffractions are used to measure the in-plane lattice constants. For the asymmetric diffraction, since there always exist two similar sets of diffraction planes with the same spacing in a single crystal, two geometries of asymmetric diffractions can be used to measure the in-plane lattice constants of samples, one is the glancing incidence and the other is the glancing exit. \cite{20} The geometries of the glancing incidence and the glancing exit for asymmetric diffractions are illustrated in Fig. 3.10. Due to stronger signals from the epitaxial layer, the glancing incidence geometry should be used for samples with thin epitaxial layers.

Fig. 3.10 Geometries of (a) the glancing incidence and (b) the glancing exit. $\theta_B$ is the Bragg angle and $\phi$ is the angle between the diffraction planes and the surface plane. \cite{20}
For III-V compound semiconductors, the commonly used symmetric and asymmetric geometries are (004) and (115) or (224). Since the (224) geometry has a smaller Bragg angle, stronger signals from the epitaxial layer are typically obtained in the (224) X-ray measurement compared to the (115) geometry. On the other hand, in the case that the epitaxial layer is very thick, the (115) geometry will be chosen in order to get a strong enough signal from the layers underneath and the substrate. Combining results from both symmetric and asymmetric XRD measurements, the strain relaxation ($R$) can be derived using

$$R = \frac{a_i - a_s}{a_{eff} - a_s} \times 100$$  \hspace{1cm} (3.2)

where $a_i$ is the in-plane lattice constant of the epitaxial layer, which is measured by asymmetric XRD measurement; $a_s$ is the substrate lattice constant, and $a_{eff}$ is the fully relaxed lattice constant of the epitaxial layer, which is defined as

$$a_{eff} = \frac{c_i - 2a_i\left(\frac{\nu}{1-\nu}\right)}{1 - 2\left(\frac{\nu}{1-\nu}\right)}$$  \hspace{1cm} (3.3)

where $c_i$ is the perpendicular lattice constant of the epitaxial layer, which is measured by symmetric XRD measurement and $\nu$ is the Poisson’s ratio. [20]
In most cases, $\omega/2\theta$ rocking curve scans with the double-axis XRD setting are used for the sample analysis. The substrate peak in a rocking curve is usually used as the reference and the lattice constant of the epitaxial layer is determined from the peak separation between the substrate and the epitaxial layer. However, when the epitaxial layer is tilted with respect to the substrate, reciprocal space mapping (RSM) with triple-axis XRD setting should be used. Reciprocal space mapping is generated by taking a series of triple-axis XRD $\omega/2\theta$ scans while offsetting the $\omega$ axis between each scan. [21] Compared to rocking curves, reciprocal space mapping is able to distinguish the strain effect from the tilt effect by separating them on different axes in RSMs. Additionally, RSMs provides a direct evaluation of crystal qualities for each epitaxial layer. Fig. 3.11 shows symmetric and asymmetric (the glancing incidence) RSMs of InAsP step-graded buffers grown on InP. In the maps, epitaxial layers with different lattice constants have different $\omega/2\theta$ values. Since they have different tilt angles with respect to the substrate, these layers also have different $\omega_{\text{REL}}$ positions. Similarly, using equations in Reference 20, the perpendicular and in-plane lattice constants can be calculated from symmetric and asymmetric RSMs and strain relaxation of each layer can be determined based on the values of these two lattice constants just calculated.
Fig. 3.11 Symmetric (004) and asymmetric (115) glancing incidence RSMs of 3-step InAsP step-graded buffers grown on InP.
3.4.4 Epitaxial tilt characterized by x-ray diffraction

Lattice-mismatched epitaxy on misoriented substrates commonly leads to epitaxial tilt. So far, epitaxial tilt has been found in several semiconductor material systems, such as InGaAs/GaAs, InAlAs/GaAs, InGaSb/GaSb, InGaAs/GaP, InGaP/GaP, and SiGe/Si. [21, 22, 23, 24, 25, 26, 27, 28] Since Nagai first developed a model to describe this phenomenon in 1974, [29] epitaxial tilt has been investigated for more than 30 years. However, its formation mechanism is still under debate.

Basically, epitaxial tilt is composed of two main contributions, one is called the coherent tilt, which is the consequence of the substrate miscut and lattice mismatch; the other tilt contribution is due to the imbalance of slip systems present in the material during the misfit dislocation nucleation and is only considered for metamorphic material systems. [29, 30] Fig. 3.12 schematically illustrates these two different tilt contributions.

The coherent tilt was first modeled by Nagai. [31] Without considering the strain relaxation, Nagai’s model simply calculated the tilt angle \( \Delta \alpha \) using

\[
\Delta \alpha = \arctan\left[\frac{\Delta a}{a} \tan \theta\right]
\]

(3.4)

where \( a \) is the substrate lattice constant, \( \Delta a \) is the lattice mismatch of the perpendicular lattice constant between the substrate and totally strained epitaxial layer, and \( \theta \) is the substrate miscut angle. [31, 32]
Fig. 3.12 Schematic of two tilt contributions, (a) the coherent tilt and (b) the tilt due to misfit dislocations. [29]

When the epitaxial layer starts to relax, Naigai’s model is no longer valid and the tilt contribution due to misfit dislocations is required to be included. Taking into account of both tilt sources, Riesz generalized the epitaxial tilt $\Delta \alpha$ to be

$$\Delta \alpha = \theta \cdot \left[ f + \varepsilon \frac{2 \nu}{1 - \nu} \right] + (f - \varepsilon) \frac{b_\perp}{b_\parallel} \tag{3.5}$$

where $\theta$ is the substrate miscut angle, $\nu$ is the Poisson ratio of the epitaxial layer, $b_\perp$ and $b_\parallel$ are the perpendicular and parallel components of the Burgers vector, respectively, and $\varepsilon$ is the unrelaxed part of the total misfit $f$, which can be expressed as

$$f = \frac{a_l - a_s}{a_s} \tag{3.6}$$
where $a_l$ and $a_s$ are lattice constants of the epitaxial layer and the substrate. [29] However, due to their simplicity and limitation to general applicability, these models generally fail to accurately predict the tilt both in direction and amplitude. [32] Hence almost all information of the epitaxial tilt is acquired by experimental approaches, such as x-ray diffraction (XRD).

Since it was proposed decades ago, [33, 34] the double axis x-ray diffraction tilt analysis approach has been prevalently used as a primary technique to investigate epitaxial tilt presented in semiconductor hetero-structures. [22, 23, 25, 26, 30, 35, 36] Typically, this approach uses double-axis XRD to take $8\alpha/2\theta$ rocking curve scans in the (004) geometry at 45° azimuthal rotation intervals and then fits the variation of the peak separation between the epitaxial layer and the substrate as the function of the azimuthal angle with a sine curve. As a result, tilt magnitude and direction can be determined from the amplitude and phase of the sine fitting curve, respectively. An example of the tilt analysis performed by double-axis XRD is shown in Fig. 3.13, in which both direction and amplitude of the tilt are indicated.
Fig. 3.13 Tilt analysis using double-axis XRD. The _Tilt_ axis represents the peak separation between the substrate and the epitaxial layer, which has been normalized for the sake of simplicity, and the _Φ_ axis represents the azimuthal angle. _α_ is the amplitude of the epitaxial tilt and the direction of the epitaxial tilt is around _Φ_ = 0°.
Moreover, based on the interference theory, the thin film thickness can also be accurately calculated from thickness fringes appearing in XRD rocking curves. Computer simulation is usually employed to facilitate this calculation process. More detailed information about XRD theories and applications on semiconductors can be found in references 20, 30, and 37.

3.5 Transmission electron microscopy

Transmission electron microscopy (TEM) is an indispensable tool in the characterization of semiconductor materials. Employing transmitted electrons that can be detected and analyzed, TEM provides information related to the atomic structures and defects in samples. [38] In this dissertation, both cross-sectional TEM and plane-view TEM, are used to identify defects and determine defect densities.

In conventional TEM systems, a high-energy electron beam with electron energy around 100 – 1000 keV is employed. The electrons transmitted through the thin sample are focused by magnetic fields (also called electromagnetic lenses) to form TEM images. In general, the TEM lenses column consists of condenser lenses to control the electron illumination of the sample, as well as objective, intermediate, and projector lenses that produce either the micrograph or the diffraction pattern on a fluorescent screen. Fig. 3.14 depicts the lens and aperture setting of the TEM in the operation to acquire (A) a diffraction pattern or (B) a micrograph. In the diffraction mode, the back focal plane of the objective lens is the object of the intermediate lens; while in the imaging mode, the object of the intermediate lens is the image plane of the objective lens. [38, 39]
Fig. 3.14 TEM lens and aperture configurations of (A) the diffraction mode and (B) the image mode. [24]
TEM samples, typically ~ 0.1 – 0.2 µm thick, are usually prepared by the mechanical polishing followed by the ion milling. Recently, focused ion beam (FIB) has also been exploited to do the TEM sample preparation. Basically, FIB uses a heavy ion beam, such as gallium (Ga) ions, to thin the sample down and make observable TEM samples. Fig. 3.15 shows pictures of the sample preparation process using FIB. Because it can be precisely controlled by computers, FIB is simpler and more efficient than the traditional mechanical polishing method. However, since heavy ions are used in FIB, it may generate damage on the surface of samples. Thus, argon ion milling is usually employed to remove the damaged layer after the FIB processing.

![TEM sample preparation by FIB. (a) a thin film made by FIB; (b) the thin film is picked up by a probe.](image)

Fig. 3.15 TEM sample preparation by FIB. (a) a thin film made by FIB; (b) the thin film is picked up by a probe.
The diffraction mode of TEM is very useful in the analysis of crystallographic structures of semiconductor materials, including lattice types and parameters. Compared to x-ray diffraction, the electron diffraction in TEM is much stronger because electrons are charged. In x-ray diffraction, we usually have to rotate the single crystal to observe all the beams. However, a single wavelength in TEM results in many diffracted beams in the TEM due to the shorter wavelengths of high-energy electrons. Typically, the TEM diffraction pattern is an array of spots for single crystals and a series of concentric rings for polycrystalline materials. [38, 39]

The images observed in the TEM are due to the local contrast, which could be diffraction contrast, mass-thickness contrast, or phase contrast. Structural defects can be observed in the diffraction contrast, using bright-field or dark-field mode. In the bright-field mode, images are formed by the direct beam and the defects in the image are seen as dark regions with the bright background. On the other hand, the diffracted beam is used to form images in the dark-field mode and the defects are observed as bright regions with the dark background. [38]

The high-resolution TEM is an advanced TEM imaging technique which combines the direct and diffracted beams to form an image. The interference between these beams generates periodic intensity fringes, which result in the contrast in the high-resolution TEM. Thus the imaging of the high-resolution TEM is based on phase contrast. With this advanced technique, the image resolution of the high-resolution TEM can reach the atomic level, in which individual atoms can be observed. Fig. 3.16 shows a high-resolution TEM image of a grain boundary in germanium. In the image, atoms and lattice structures can be clearly seen and the grain boundary can be easily recognized.
based on the orientation of lattices on each side. Recently, it has been reported that the Titan S/TEM system from FEI achieved the imaging resolution below 0.7 Å, which announces the advent of the sub-Angstrom era for electron microscopy. [40]

Fig. 3.16 High-resolution TEM image of a grain boundary in germanium. Atoms are clearly seen in the image. On different sides of the boundary, the orientation of the lattice structure is evidently different. [39]

3.6 Ultra-high frequency photoconductive decay

Photoconductive decay (PCD) is an important experimental approach used to study carrier recombination mechanisms in semiconductors. Using this approach, recombination lifetimes, which are considered to be a key parameter in evaluation of the semiconductor material quality, can be determined. In contrast to time-resolved photoluminescence (TRPL), the PCD approach can be used to measure recombination lifetimes for not only light-emitting materials but also indirect bandgap semiconductors.
In this dissertation, the PCD technique is used to measure recombination lifetimes in 0.6 eV InGaAs bulk layers to assess their material quality. Although InGaAs is a direct-bandgap semiconductor, it is hard to find a suitable detector for this wavelength range and hence PCD is chosen to do this study instead of TRPL. Since the probe frequency used in this PCD technique is in the ultra-high frequency range (~ 500 MHz), it is termed as ultra-high frequency photoconductive decay (UHFPCD). The purpose of choosing this frequency range is to achieve a large enough penetration depth and obtain recombination lifetimes for bulk materials. [41]

The schematic diagram of UHFPCD is shown in Fig. 3.17. When a light pulse is incident on the measured semiconductor sample, the sample conductivity will change due to photo-generated carriers. This conductivity variation causes an unbalance of the bridge circuit through the induction of coils. Then the unbalanced signal is amplified and sent to a digital processing scope. In other words, the transient photoconductivity information in the semiconductor sample is detected and recorded via measurements of the changing conductivity. Using the transient photoconductivity data obtained, recombination lifetimes of carriers in the semiconductor materials can be derived. [41, 42]
In principle, before the light pulse is turned on, the dark conductivity $\sigma_0$ in the semiconductor sample is given as

$$\sigma_0 = e(n_0\mu_e + p_0\mu_h)$$

(3.7)

where $e$ is the electron charge, $n_0$ and $p_0$ are equilibrium carrier concentrations of electrons and holes, respectively, and $\mu_e$ and $\mu_h$ are the electron and hole mobilities, respectively. The light pulse leads to the photoconductivity $\Delta\sigma$ in the sample, which can be expressed to be
\[ \Delta \sigma = e(\Delta n \mu_e + \Delta p \mu_h) \]  

(3.8)

where \( \Delta n \) and \( \Delta p \) are photo-generated electron and hole concentrations, respectively. To maintain the charge neutrality, \( \Delta n \) should be equal to \( \Delta p \). After the light source is turned off, the photo-generated carrier concentration exponentially decays due to carrier recombination mechanisms.

\[ \Delta n = \Delta n(0) e^{-\frac{t}{\tau}} \]  

(3.9)

where \( \Delta n(0) \) is the initial photo-generated carrier concentration and \( \tau \) is the recombination lifetime. Hence, combining Eqs 3.8 and 3.9, the transient photoconductivity can be expressed as

\[ \Delta \sigma(t) = e(\mu_e + \mu_h)\Delta n(0)e^{-\frac{t}{\tau}} \]  

(3.10)

Assuming electron and hole mobilities are time-independent, the recombination lifetime \( \tau \) can be determined from the dependence of photoconductivity on time via Eq. 3.10. [38, 43]

The light sources used for UHFPCD can be a pulsed laser, a pulsed LED, a xenon flashlamp or laser-driven optical parameteric amplifier. Considering the pulse width of
light sources and the response time of detectors, the minimum resolvable recombination lifetime for UHFPCD is around 10 ns. [41]

3.7 Hall effect

Hall effect has been routinely used for decades to measure carrier transport properties in semiconductors, including carrier types, concentrations, and mobilities. Fig. 3.18 schematically shows a Hall effect measurement, which also helps to explain the fundamental physics in Hall effect. In Hall measurements, when a magnetic field is applied to a semiconductor bar in the Z direction and a current flows in the X direction, a

Fig. 3.18 Schematic of Hall measurements. [38]
Hall voltage will be established across the side of the semiconductor bar due to the Lorentz force. The Hall voltage $V_y$ can be given as

$$V_y = R_H \frac{I_x B_z}{Z}$$

where $I_x$ is the current in the semiconductor, $B_z$ is the magnetic flux density, $Z$ is the thickness of the semiconductor bar, and $R_H$ is called as the Hall coefficient and can be expressed as

$$R_H = -\frac{1}{ne} \quad \text{for n-type semiconductors} \quad (3.12a)$$

$$R_H = \frac{1}{ep} \quad \text{for p-type semiconductors} \quad (3.12b)$$

where $n$ and $p$ are electron and hole carrier concentrations, respectively. [38, 44, 45]

Given the current $I_x$, the magnetic flux density $B_z$, and the semiconductor thickness $Z$, the Hall coefficient can be experimentally determined from the Hall voltage measured. Based on Equation 3.12, the semiconductor type and carrier concentration can be derived from the Hall coefficient. Additionally, the Hall mobility $\mu_H$ can be expressed as

$$\mu_H = \sigma R_H$$

(3.13)
where $\sigma$, also measured experimentally, is the conductivity of the sample. Thus, after obtaining the conductivity and Hall coefficient, the Hall mobility can be determined using Eq. 3.13. [38, 44, 45]

In general, multiple carrier species are present in semiconductor materials, particularly multiple layer device structures. In this case, standard Hall measurements can only provide average values of carrier concentrations and mobilities. To address this issue, a technique, called the quantitative mobility spectrum analysis (QMSA), has been developed to simultaneously characterize the concentration and Hall mobility of each carrier in a multi-carrier system. [46]

For a single-carrier system, the Hall coefficient is field-independent and the conductivity tensor is expressed as

\[
\sigma_{xx} = \frac{n e \mu}{1 + \mu^2 B^2}
\]  
\[
\sigma_{xy} = \frac{n e \mu^2 B}{1 + \mu^2 B^2}
\]

where $n$ and $\mu$ are the concentration and mobility of the carrier, respectively, and $B$ is the magnetic field. For a multi-carrier system, the Hall coefficient measured is the average value of all carriers and the total conductivity tensor is written as

\[
\sigma_{xx} = \sum_{i=1}^{N} \frac{e n_i \mu_i}{1 + \mu_i^2 B^2}
\]
\[ \sigma_{xy} = \sum_{i} \frac{n_{i} e \mu_{i}^{2} B}{1 + \mu_{i}^{2} B^{2}} \]  

(3.17)

In the QMSA technique, the concept of mobility spectrum is used and thus the equations (3.16) and (3.17) can be modified from discrete summations into integrations.

\[ \sigma_{xx} = \int_{-\infty}^{+\infty} \frac{s^{p}(\mu) + s^{n}(\mu)}{1 + \mu^{2} B^{2}} d\mu \]  

(3.18)

\[ \sigma_{xy} = \int_{-\infty}^{+\infty} \frac{(s^{p}(\mu) - s^{n}(\mu)) \mu B}{1 + \mu^{2} B^{2}} d\mu \]  

(3.19)

where \( s^{p}(\mu) \) and \( s^{n}(\mu) \) are hole and electron conductivity density functions.\[47\] By fitting the experimental data of \( \sigma_{xx} \) and \( \sigma_{xy} \), hole and electron conductivity density functions can be calculated. Thus carrier types, concentrations and mobilities can be extracted.\[47, 48\]

Fig. 3.19 provides an example of the QMSA spectrum, which is measured from 1x10\(^{18}\) cm\(^{-3}\) n-type doped InAs grown on InP using 4-step InAsP graded buffers. The thickness of the InAs layer is 1 \( \mu \)m and the Hall measurement was performed at 300 K. From the QMSA spectrum, we can find that, there are two kinds of carriers in the sample: one type is composed of electrons with the sheet concentration of 1.08x10\(^{14}\) cm\(^{-2}\), which agrees with the 1x10\(^{18}\) cm\(^{-3}\) bulk doping when integrated over the layer thickness; the other type is composed of holes with the sheet concentration of 2.08x10\(^{12}\) cm\(^{-2}\). Hall mobilities are determined to be 11809 and 9396 cm\(^{2}\)/Vs for electrons and holes, respectively. Thus, the electrons are the dominant carriers in this structure.
Fig. 3.19 QMSA spectrum of InAs grown on InP using 4-step InAsP graded buffers. The layer thickness is 1 µm and the doping concentration is n-type $1 \times 10^{18}$ cm$^{-3}$. The measurement was performed at room temperature.
3.8 References


4 http://www.ece.utexas.edu/projects/ece/mrc/groups/street_mbe/mbechapter.html


4.1 Introduction

Successful epitaxial growth of mixed-anion III-V$_A$V$_B$ alloys using molecular-beam epitaxy must consider the fact that the group V adatom sticking coefficient is not unity but temperature-dependent, and depends on the particular group V species (e.g. As and P) as its molecular form in the incident beam flux. Phenomenologically, this requires developing calibration curves and a procedure for reproducing growth conditions. Note this is quite unlike for the mixed-cation growth since for this case the sticking coefficient for each cation element (e.g. Ga and In for InGaAs) is unity and compositions are simply controlled by beam flux ratios alone. This chapter describes the MBE growth process and calibration procedures used to create InAsP graded buffers on InP substrates. To generate a basis for discussion, the basic science of mixed-anion versus mixed-cation ternary semiconductors is introduced. This is followed by analysis of grown films using
high-resolution x-ray diffraction (HRXRD) to determine compositions that are used to
generate calibration curves used elsewhere in this research.

4.2 Mixed-anion vs. mixed-cation ternary semiconductors in the MBE growth

During MBE growths of III-V ternary semiconductors, group V elements
frequently desorb from the outmost growth surface whereas group III elements do not. As
a result, the group IIs determine the growth rate of the epitaxial layer and the growth
chamber normally maintains a group V over-pressure condition. In general, the
incorporation of group Vs in the mixed-anion semiconductor alloy (III-V,A,V,B) growth is
strongly dependent on the growth temperature, the growth rate, group III and other group
V elements involved in the growth, resulting in the composition control of mixed-anion
semiconductor alloys much more complicated as compared to that of mixed-cation
(III,A,III,B-V) semiconductor alloys.

Tatsuoka et al. developed a theoretical model to mathematically describe the
incorporation behaviors of group V atoms in mixed-anion alloy growth. [1] In this model,
group V atoms involving the growth were divided into three groups according to their
phases, which are the vacuum phase, the adsorption phase, and the incorporation phase.
Fig 4.1 schematically illustrates these three different phases in the group V atom
incorporation process during the MBE growth. As shown in the figure, the group V atoms
are assumed to be in the molecular form of dimers, like As₂ and P₂. The incident flux
provides group V adatoms during the growth and these adatoms (absorption phase) travel
on the surface. They can be re-evaporated into the vacuum (vacuum phase), or
incorporate into the epitaxial layer (incorporation phase).
The approach of rate equations was used in this model to quantitatively describe the group V incorporation in the mixed-anion (III-VAVB) alloy growth. Assuming the densities of group Vs (VA and VB) adatoms per surface area to be NA and NB, respectively, the rate equations can be written as

\[
\frac{\partial N_A}{\partial t} = f_A - \frac{N_A}{\tau_{IA}} - \frac{N_A}{\tau_{VA}} \tag{4.1}
\]

and

\[
\frac{\partial N_B}{\partial t} = f_B - \frac{N_B}{\tau_{IB}} - \frac{N_B}{\tau_{VB}} \tag{4.2}
\]
where \( f_A(f_B) \) is the incident group V A(B) flux density on the surface, \( \tau_{IA}(\tau_{IB}) \) is the lifetime of the group V A (B) adatoms before the incorporation into the epitaxial layer, and \( \tau_{IA}(\tau_{IA}) \) is the lifetime of the group V A (B) adatoms before the re-evaporation.

At a steady state, namely, \( \partial N_A/\partial t = 0 \) and \( \partial N_B/\partial t = 0 \), the solutions of the equations of (4.1) and (4.2) are

\[
N_A = \frac{f_A}{1/\tau_{IA} + 1/\tau_{VA}} \quad (4.3)
\]

and

\[
N_B = \frac{f_B}{1/\tau_{IB} + 1/\tau_{VB}} \quad (4.4)
\]

Based on these results, the A composition \( y \) in the mixed-anion (III-V_AV_B) alloy can be expressed as

\[
y = \frac{2N_A/\tau_{IA}}{2N_A/\tau_{IA} + 2N_B/\tau_{IB}} = \frac{f_A}{f_A + f_B C_t} \quad (4.5)
\]

Here \( C_t \) is defined to be the relative incorporation coefficient, which is given as

\[
C_t = \frac{1 + \tau_{IA}/\tau_{VA}}{1 + \tau_{IB}/\tau_{VB}} \quad (4.6)
\]
Since the incorporation and re-evaporation lifetimes of group V atoms ($\tau_I$ and $\tau_V$) are a function of growth temperature, group III species, surface orientation, etc., [1] the chemical composition ($\nu$) of mixed-anion semiconductors is dependent on not only the group V fluxes but also the growth conditions.

On the other hand, this model can also be directly applied to the mixed-cation alloy (III$_A$III$_B$-V) growth. Since the sticking coefficient of group III$_A$s is unity, the re-evaporation lifetime for group III$_A$ atoms can be assumed to be infinite. Thus, according to the equations of (4.5) and (4.6), the A composition ($x$) in the mixed-cation (III$_A$III$_B$-V) semiconductor can be simply given as

$$x = \frac{f_A}{f_A + f_B}$$ (4.7)

Here $f_A$ ($f_B$) is the incident group III$_A$ (III$_B$) flux density on the surface. Obviously, the composition control of mixed-cation (III$_A$III$_B$-V) semiconductor alloys is significantly more straightforward as compared to that of mixed-anion (III-$V_A$V$_B$) semiconductor alloys in the growth. Hence, it is understandable why mixed-cation semiconductor materials are far more commonly used in compound semiconductor device applications.

In spite of the complicated composition controlling, mixed-anion semiconductor alloys have their unique advantages over mixed-cation semiconductor alloys in the growth, particularly in the lattice-mismatched growth. Since two group III elements with different surface mobilities take part into the growth of mixed-cation materials, the difference in the surface mobilities may cause randomized nucleation during the growth.
and thus lead to the formation of alloy decomposition/branch defects, which severely roughen the surface morphology and significantly block the glide of threading dislocations. [2, 3] In contrast, mixed-anion semiconductors do not have this issue in the growth because only one group III is involved. Furthermore, in the growth of mixed-anion semiconductors, the group III determines the growth rate and two group Vs control the chemical composition/the lattice constant, hence the lattice constant and the growth rate are decoupled, which offers a potential advantage for the growth of mixed-anion semiconductor alloys. With regard to mixed-anion graded buffers, this advantage also provides more degrees of freedom in the optimization of the strain relaxation in these structures.

In addition, as mentioned in Chap 3, different types of cells are respectively used for group III and group V sources in solid source MBE systems. Conventional effusion cells are used for group III sources and the beam fluxes of the group IIIIs are adjusted by varying the cell temperature. On the other hand, group V sources usually use valved crackers (essentially a second heater zone) to control the species (dimer, tetramer) of the exiting group V molecules, and the fluxes of group Vs are controlled through the adjustment of the valve setting (opening). Using solid source MBE systems, compositional grading in the growth of mixed-anion graded buffers can be simply achieved by changing the valve setting of the group Vs. As opposed to mixed-cation graded buffers growth, the source temperature needs to be adjusted for the composition grading, thus growth interruptions are generally required for the source temperature variation and these stops may compromise interface quality of device structures.
Overall, although more efforts are needed for the chemical composition control, due to the relatively scarcity of this approach in solid source MBE growth, compositionally graded mixed-anion alloys show great promise as high-quality graded buffer materials in contrast to mixed-cation alloys since, as described earlier, the growth rate is decoupled from the rate of introducing lattice strain.

4.3 Crystal growth of InAsP

A Varian Gen II solid source MBE, which is part of the UHV cluster housed in the Semiconductor Epitaxy and Analysis Laboratory (SEAL) at The Ohio State University, was employed to grow InAsP samples. Fig 4.2 shows a picture of this MBE system. In this system, molecular beams are generated using conventional effusion cells for group III elements (Al, Ga and In) and valved cracker sources for phosphorus (P) and arsenic (As). The molecular form of As used in the growth was As$_2$ due to the reasons described in Chapter 3. Considering its lower cracker temperature and thus a lower growth chamber background pressure, P$_4$ was initially used as the phosphorus source in the InAsP sample growth. However, when P$_4$ molecules condense on the cold walls of the MBE chamber interior, white phosphorus forms, which is a serious safety concern during maintenance because of its pyrophoric properties. [4] In contrast, P$_2$ molecules condense on the cold walls as red phosphorus, which is much safer than white phosphorus. In view of this fact, during the evolution of our group’s usage of P-based MBE, the P source for the InAsP growth was switched from P$_4$ to P$_2$ by increasing the cracker temperature from 800 °C to 950 °C. However, in certain cases that will be noted, P$_4$ based epitaxy was also
performed as a result of this lab-safety driven transition that occurred during the early parts of this research.

![Varian Gen II MBE system in Electronic Materials and Devices Laboratory at The Ohio State University](image)

**Fig. 4.2** Varian Gen II MBE system in Electronic Materials and Devices Laboratory at The Ohio State University

Although some calibration results of the InAsP growth have been published by other researchers, [5, 6, 7, 9] they either were not carried out by solid source MBE, or did not extend to high As content InAsP alloys due to their complicated, nonlinear group V element incorporation as discussed early in this chapter. Hence, in order to explore InAsP step-graded buffers to support semiconductor materials with lattice constants between InP...
and InAs, a complete calibration curve from low As content to high As content needed to be created using solid source MBE.

4.4 Experimental results and discussions

During the growth of InAsP alloys, the indium flux was fixed to provide a growth rate ~ 0.8 µm/hr, which was calibrated using reflective high-energy electron diffraction (RHEED) intensity oscillations. Since InP is used as the substrate in this research, we chose to fix the P/In ratio and increase the As/In ratio to achieve the composition/lattice constant grading during the growth of InAsP graded buffers. As mentioned above, initial films were grown using P₄ and later we switched to P₂. Here, calibrations were made using both forms of P. Based on low-temperature photoluminescence and Hall effect results obtained from InP testing samples, the P₄/In and P₂/In flux ratios were chosen to be 7/1 and 12/1, respectively. Before the growth of InAsP, a 2000 Å InP layer was always deposited to smooth the surface of the InP substrate. During the InAsP growth, the growth temperature at the surface of the growing layer was determined by optical pyrometry. We refer to this as the “IR” temperature and for our growths, the IR growth temperature was nominally maintained at 485°C. Well-developed (2x4) RHEED patterns, similar to the RHEED patterns shown in Fig. 3.4 in the last chapter, were usually obtained throughout the entire growth under these growth conditions, indicative of an ideal two-dimension growth.

Since epitaxial tilting is usually present in graded buffer structures, [10, 11] reciprocal space mapping (RSM) by triple-axis x-ray diffraction (TAXRD) was used to account for the epi-layer tilt in order to accurately measure the chemical composition of
InAsP alloys for calibration purposes. Details of TAXRD and RSM were described in Chapter 3 and this method allows the separate determination of lattice constant and strain, enabling accurate determination of the InAsP composition even in the presence of the lattice mismatched growth. Here the symmetric (004) and asymmetric (115) glancing incidence RSMs were obtained. The X-ray diffractometer used was a Bede D1 system, employing a Cu Kα1 source, which was monochromated and collimated by two channel cut silicon crystals and a 0.5 mm slit. An analyzer crystal together with a 1 mm slit is used to reduce the acceptance angle of the detector and improve the measurement resolution.

Fig. 4.3 shows InAsP composition calibration results, which include data for both P₄ and P₂. Because the V/III ratio is a more relevant parameter for determining the group V incorporation in the mixed-anion alloy growth, [12] the X-axis of the figure uses the As₂/In flux ratio instead of the arsenic flux. Here, in order to better analyze the data in Fig. 4.3, the equation (4.5) is modified to be

\[
y_{As} = \frac{f_{As}}{f_{As} + f_P C_t} = \frac{(f_{As} / f_{In})}{(f_{As} / f_{In}) + (f_P / f_{In}) C_t}
\]  

(4.8)

where \( y_{As} \) is the As composition in InAsP, \( f_{As} \), \( f_P \), and \( f_{In} \) are the fluxes of arsenic, phosphorus, and indium, respectively. Now we can use the equation (4.8) to directly interpret the measured data in Fig. 4.3.
Fig. 4.3 Composition calibrations of InAsP alloys grown by solid source MBE at 485 °C. The compositions were measured by triple-axis X-ray diffraction. Both P₄ and P₂ results are included in the figure.

As mentioned before, the P/In flux ratios of 12/1 and 7/1 were selected in the InAsP growth for P₂ and P₄, respectively. Hence, the equation (4.8) can be rewritten to be

\[ y_{As} = \frac{f_{As} / f_{ln}}{(f_{As} / f_{ln}) + 12C_t(P_2)} \quad \text{for } P_2 \quad (4.9) \]

and

\[ y_{As} = \frac{f_{As} / f_{ln}}{(f_{As} / f_{ln}) + 7C_t(P_4)} \quad \text{for } P_4 \quad (4.10) \]
Fig. 4.3 shows that, given a fixed As/In flux ratio, very close As compositions in InAsP were obtained for different P species with different P/In flux ratios. Comparing both equations of (4.9) and (4.10), we can conclude that the relative incorporation coefficient \( C_t \) of \( P_4 \) is larger than that of \( P_2 \) and the ratio of \( C_t (P_4) \) and \( C_t (P_2) \) should be very close to 12/7.

In addition, by fitting the measured data, we found that the dependence of \( y_{As} \) on \( f_{As}/f_{In} \) in Fig. 4.3 approximately follows an exponential decay curve rather than a hyperbolic curve, implying that the relative incorporation coefficient \( C_t \) is not a constant but a function of the As flux. This certainly would be a very interesting future study. As the primary part of this future work, the P/As incorporation in InAsP should be investigated as a function of growth conditions, including growth temperature, P/In flux ratio, and the growth rate. In the meanwhile, theoretical modeling and calculations are also required to further understand the effect of P on As incorporation and vice versa. However, even without this information at this point, this calibration curve can be used to guide the growth of InAsP layers with As compositions from 10% to 90% and provides enough of a database for the InAsP step-graded buffer growth discussed later. Here we would like to point out that, to our knowledge, no research work on the As/P incorporation behavior in high-As InAsP alloys grown by solid source MBE has been published so far.
4.5 References


4 EMDL P handing manual.


CHAPTER 5

MIXED-CATION VERSUS MIXED-ANION III-V STEP-GRADED BUFFERS
FOR LATTICE-ENGINEERED SUBSTRATES ON INP

5.1 Introduction

Perhaps the most important fundamental aspect of this research is to generate knowledge regarding the fundamental differences between mixed-anion (III-$V_A V_B$) and mixed-cation (III$_A$III$_B$.V) step-graded buffers and the potential advantages of the former for substrate engineering in between common substrate material lattice constants, particularly InP and InAs. A series of experiments were undertaken to directly investigate III-V anion and cation based graded layers with the goal of obtaining most efficient strain relaxation, with a minimum of threading dislocations and surface roughness, as these are requisite for engineered substrate technology. Here, graded InAsP and InAlAs were grown on identical InP substrates, and their structural properties were compared as a function of compressive misfit with respect to InP. By ensuring nominally identical misfit between the terminal layer and the initial substrate, direct comparisons can be developed and quantified. The focus in this chapter is on the “lower misfit” regime
of these alloys on InP, i.e. for misfits below 1.5%. In subsequent chapters, higher misfit up to InAs on InP (3.5%) are described.

### 5.2 MBE growth of InAlAs and InAsP step-graded buffers

Figure 5.1 shows schematics for the In\(_x\)Al\(_{1-x}\)As and InAs\(_y\)P\(_{1-y}\) metamorphic step-graded buffers designed and grown for this study. Both buffers were grown on semi-insulating (001) InP substrates, with identical total lattice mismatches between the top layer and the InP substrate of ~ 1.2% and total buffer thicknesses of 2.7 \(\mu\)m. This particular misfit (i.e. equilibrium lattice constant of the final layer in the grade stack) was chosen since it is lattice-matched to a particular composition of InGaAs that our group is exploring in parallel for low bandgap thermophotovoltaic energy conversion devices. [1, 2] Before discussing the results, it must be made clear that even though the misfit was nominally identical in these studies, optimum growth conditions for each type of buffer, as alluded to in chapter 4 are not similar. For the In\(_x\)Al\(_{1-x}\)As step-graded buffer growth, the As/III flux ratio was maintained all the time at 24/1 and the beam fluxes of In and Al were independently adjusted to achieve the step-grade. To suppress the formation of In droplets, the IR growth temperature was intentionally reduced from 525 °C to 505 °C with increased In-content in the buffer layers. These are high growth temperatures relative to those published for InAlAs where no lattice grading is employed, since our goal is to promote maximum relaxation efficiency via dislocation glide, which is strongly temperature dependent, but this must be balanced by surface decomposition which becomes more problematic as In content is increased. This is why the growth temperature must be continuously reduced as In content is increased, and is one of the
primary complication for graded cation growth using In-containing compounds in MBE growth. On the other hand, for the InAs$_{y}$P$_{1-y}$ step-graded buffer growth no temperature changes are used since the In flux is constant and we can safely choose a substrate temperature based on material quality alone and not lattice relaxation (which is dictated by $V_A/V_B$ ratio only). For growths using P$_4$ (which are those described in this chapter only) the P$_4$/In ratio was fixed at 7/1. The growth temperature ~ 485 °C, was kept throughout the entire buffer structure growth. Note that similar conditions were used with P$_2$ based growth, the exception being the P$_2$/In flux ratio is now 12:1.

Fig. 5.1 Scheme of (a) InAlAs and (b) InAsP step-graded buffers. The total thicknesses of both buffers are 2.7 µm and the misfits of the top layer are ~ 1.2% with respect to the InP substrate.
Both reflective high-energy electron diffraction (RHEED) and pyrometer data were recording during growth of both types of graded buffers. While RHEED intensity oscillations are used to determine growth rates, here we captured the RHEED images during growth to observe surface reconstructions and general atomic quality. Additionally, we recorded the surface temperature continuously during growth by in-situ pyrometry. The combination of these provides very telling information regarding graded buffer quality, well prior to conducting complex ex-situ studies.

During the In$_x$Al$_{1-x}$As buffer growth, RHEED patterns were clear (2x4) initially and turned to slightly blurry, indicative of the roughening of the surface morphology. In contrast, a clear (2x4) RHEED pattern was consistently observed in the growth of the InAs$_y$P$_{1-y}$ step-graded buffers, qualitatively suggesting that InAs$_y$P$_{1-y}$ buffers have a smoother surface. Routinely, an optical pyrometer (IRCON, Model: V-12C05), with the detecting wavelength ranging from 0.91 – 0.97 µm, was used to monitor the real-time substrate surface temperature during both buffer growths. Fig 5.2 shows the measured surface temperature profiles for In$_x$Al$_{1-x}$As and InAs$_y$P$_{1-y}$ graded buffers. From the In$_x$Al$_{1-x}$As surface temperature profile shown in the figure, we can find the intentionally decreased growth temperature for each In$_x$Al$_{1-x}$As layer and the impact of the growth interruption between the step-graded layers to adjust the In and Al fluxes. Obviously, the surface temperature profile of the InAs$_y$P$_{1-y}$ graded buffers has less fluctuation as compared to that of the In$_x$Al$_{1-x}$As graded buffers. Since the fluctuation appearing in the surface temperature profile is caused by the surface light scattering effect, it suggests that the In$_x$Al$_{1-x}$As buffer surface is rougher than that of the InAs$_y$P$_{1-y}$ buffers. Hence, the real-
time temperature profile data are in good agreement with the RHEED results for surface morphology of both types of graded buffers.

Fig. 5.2 Surface temperature profiles measured by optical pyrometry for InAlAs and InAsP step-graded buffers. Due to different growth rates, the growth time was different for these step-graded buffers with identical thickness. [1]

5.3 Surface morphology of InAlAs and InAsP step-graded buffers

Both Nomarski microscopy and AFM were used to examine the surface morphology of both step-graded buffers. Figs 5.3 (a) and (b) shows the Nomarski images of InAsyP1-y and InxAl1-xAs step-graded buffers, respectively. As shown, a well-
developed uniform crosshatch pattern can be seen on the surface of InAs$_y$P$_{1-y}$ step-graded buffers, indicative of effective strain relaxation via dislocation glide. [3, 4, 5] For In$_x$Al$_{1-x}$As step-graded buffers, although a strong crosshatch pattern is also found on the top surface, it is with a significantly more grainy background in contrast to that on the surface of InAs$_y$P$_{1-y}$ step-graded buffers. More quantitative surface morphology comparisons of both buffers are provided by AFM images, which are shown in Figs 5.3 (c) and (d). As a result, the background difference between two buffers is more evident in AFM images and the root mean square (rms) surface roughness was measured to be 2.2 nm and 7.3 nm for InAs$_y$P$_{1-y}$ and In$_x$Al$_{1-x}$As step-graded buffers, respectively. Hence, the Nomarski and AFM results are in good agreement with the conclusions obtained from RHEED observations and surface temperature profiles. As discussed in the last chapter, the reason for the significantly rougher surface of In$_x$Al$_{1-x}$As step-graded buffers is suggested to be the difference in surface mobility of In and Al atoms and this roughening mechanism becomes more noticeable in higher-In content InAlAs layers. [6] In contrast, since only one group III is involved, there is no surface mobility deviation of group III atoms in the mixed-anion material growth that affects growth rate to a first order. Furthermore, due to the group-V rich environment maintained during the growth, the group V incorporation is relevant to the surface lifetime rather than the surface mobility of group V atoms. Hence, the roughening mechanism due to different atom surface mobilities is not present in the mixed-anion growth. Experimentally, the observation of smooth surface morphology of InAs$_y$P$_{1-y}$ step-graded buffers using both in situ (RHEED and optical pyrometry) and ex situ (Nomarski and AFM) characterization techniques strongly supports this argument.
Fig. 5.3 Nomarski microscopy images of (a) InAs$_{0.4}$P$_{0.6}$ and (b) In$_{0.7}$Al$_{0.3}$As, and AFM images of (c) InAs$_{0.4}$P$_{0.6}$ and (d) In$_{0.7}$Al$_{0.3}$As layers grown on InP substrates using In$_{x}$As$_{y}$P$_{1-y}$ and In$_{x}$Al$_{1-x}$As step-graded buffers, respectively. [1]
5.4 Strain relaxation in InAlAs and InAsP step-graded buffers

To obtain more detailed insight into the difference between cation and anion III-V graded layers from the perspective of strain relaxation, we performed very extensive investigations of bulk structural properties using reciprocal space maps (RSMs) obtained via triple-axis x-ray diffraction. Figs. 5.4 and 5.5 show the (004) and (115) glancing incidence RSMs for both InAs$_y$P$_{1-y}$ and In$_x$Al$_{1-x}$As buffers, respectively, with identical total misfit and total layer thickness. In the figures, the diffraction peaks of the substrate and buffer layers are indicated.

From the RSMs, the measured perpendicular and in-plane lattice constants of the top InAs$_y$P$_{1-y}$ layer were determined to be 5.9523 and 5.9419 Å, respectively. Using the measured lattice parameters, the As composition in the top layer was calculated to be 40% and the degree of relaxation of the InAs$_{0.4}P_{0.6}$ layer was found to be ~ 90% using the equations (3.2) and (3.3) in the chapter 3. Similarly, the perpendicular and in-plane lattice constants of the top In$_x$Al$_{1-x}$As layer were determined to be 5.9438 and 5.9266 Å, respectively. The In composition of the top layer was determined to be 70% and the relaxation of the top In$_{0.7}$Al$_{0.3}$As layer was calculated to be ~ 87%, which is similar to the relaxation of the top InAs$_y$P$_{1-y}$ layer if taking account of measurement errors. Hence, we can draw a conclusion that both InAs$_y$P$_{1-y}$ and In$_x$Al$_{1-x}$As step-graded buffers effectively relax the total 1.2% misfit strain and high relaxation is achieved in the top layers for both types of buffers.
Fig. 5.4 Symmetric (004) and asymmetric (115) glancing incidence reciprocal space maps of InAs$_{0.4}$P$_{0.6}$/InAs$_{y}$P$_{1-y}$/InP.
Fig. 5.5 Symmetric (004) and asymmetric (115) glancing incidence reciprocal space maps of $\text{In}_{0.7}\text{Al}_{0.3}\text{As}/\text{In}_{x}\text{Al}_{1-x}\text{As}/\text{InP}$.
5.5 Defect structures in InAlAs and InAsP metamorphic step-graded buffers

As discussed in Chapter 2, an ideal graded buffer is desired not only to relax the misfit strain but also to effectively glide the threading dislocations to achieve a minimum defect density in overgrown layers. Although both graded buffers have been determined to be ~ 90% relaxed in the last section, the investigation of threading dislocations/defects is required to provide a further evaluation of both graded buffers. In this section, cross-sectional TEM was performed to investigate defect structures inside relaxed In$_x$Al$_{1-x}$As and InAs$_y$P$_{1-y}$ step-graded buffers. All TEM samples were prepared using the conventional polishing and ion milling method.

Figs. 5.6 (a) and (b) show representative cross-sectional TEM images of In$_x$Al$_{1-x}$As and InAs$_y$P$_{1-y}$ step-graded buffers, respectively. The chemical compositions of all buffer layers are labeled in the images. For In$_x$Al$_{1-x}$As graded buffers, defect structures are obviously seen in the top In$_{0.68}$Al$_{0.32}$As layer from the TEM image at the resolution scale. These defect structures are suggested to be either alloy decompositions/composition modulations [7, 8, 9] or branch defects [10, 11], instead of simple threading dislocations. It has been reported that these defects have strong interdependence with surface morphology and severely block the glide of threading dislocations during the strain relaxation of graded buffers. [8, 9, 10] In fact, similar type of defects has also been observed in other mixed-cation graded buffers, such as InGaAs and InGaP. [10] Hence, although the origins of these defects are not totally clear yet, it is believed to be an inherent phenomenon related to mixed-cation graded buffers. [11] In contrast, in the cross-sectional TEM image of InAs$_y$P$_{1-y}$ step-graded buffers there are no defects visible in the top InAs$_{0.4}$P$_{0.6}$ layer, suggesting that the threading dislocation (TD)
density is below the statistical limit in typical cross-section TEM fields of view, i.e. < 1x10^7 cm^-2. To obtain an accurate value of the TD density in the top InAs_{0.4}P_{0.6} layer, we prepared samples for plan-view TEM. Fig. 5.7 shows a (220) bright-field plan-view TEM images, in which threading dislocations are indicated. According to plan-view TEM results, the average TD density in the relaxed top InAs_{0.4}P_{0.6} layer was determined to be 4x10^6 cm^-2. [12]

5.6 Conclusions

In this chapter, surface morphology, strain relaxation, and defect structures of InAs_{y}P_{1-y} step-graded buffers have been compared with those of In_{x}Al_{1-x}As step-graded buffers. Although both buffers achieve similar strain relaxation of ~ 90% determined by HRXRD, InAs_{y}P_{1-y} step-graded buffers show smooth surface and lower density of threading dislocations as compared to In_{x}Al_{1-x}As graded buffers. Using AFM, the rms surface roughness of In_{x}Al_{1-x}As and InAs_{y}P_{1-y} graded buffers was characterized to be 2.2 nm and 7.3 nm, respectively. Cross-sectional TEM revealed that significantly higher density of defects was present in the In_{x}Al_{1-x}As graded buffers in contrast to the InAs_{y}P_{1-y} graded buffers. Furthermore, plan-view TEM demonstrated that the threading dislocation density in the top InAsP layer was around 4x10^6 cm^-2. Based on all these characterization results, we can draw a conclusion that mixed-anion alloys display their fundamental excellence in structural properties as III-V graded buffer materials.
Fig. 5.6 Cross-sectional TEM images of (a) an $\text{In}_{0.69}\text{Ga}_{0.31}\text{As}$ layer grown on a step-graded $\text{In}_x\text{Al}_{1-x}\text{As}$ buffers and (b) an $\text{InAs}_{y}\text{P}_{1-y}$ layer grown a step-graded $\text{InAs}_y\text{P}_{1-y}$ buffers. [1]
Fig. 5.7 Plan-view TEM micrograph (bright field) of InAs$_{0.4}$P$_{0.6}$ layer grown on step-graded InAs$_y$P$_{1-y}$ buffers. Threading dislocations are labeled in the figure with a, b, c, etc. [12]
5.7 References


CHAPTER 6

COMPARISON OF INALAS AND INASP METAMORPHIC STEP-GRADED BUFFERS WITH LOW (<1.5%) MISFIT: APPLICATIONS TO ELECTRONIC HETEROSTRUCTURES AND DEVICES

6.1 Introduction

In chapter 5, the growth and structural properties qualities of InAlAs and InAsP metamorphic step-graded buffers were compared, revealing fundamental differences between mixed-anion and mixed-cation graded buffers. From those studies, InAsP metamorphic step-graded buffers exhibited smoother surface morphology and lower defect density as opposed to InAlAs metamorphic step-graded buffers at the same lattice misfit with respect to InP substrates. This chapter is the second part of the mixed-cation vs. mixed-anion graded buffer comparison for low misfit (< 1.5%), focusing on the comparison of electronic properties and device characteristics between devices grown on InAlAs and InAsP graded buffers.

This chapter focuses on minority carrier recombination lifetimes obtained from lattice-mismatched InGaAs-based double heterostructures (DH) grown on both types of
graded buffers since carrier lifetimes are extremely sensitive to defect densities and provides a direct indication of device applicability.

6.2 Recombination lifetime study in InGaAs DHs grown on InAsP graded buffers and InAlAs graded buffers

In this section, the fundamental science of carrier recombination lifetimes is briefly introduced first. After that, the recombination lifetime study of InGaAs DHs on InAsP graded buffers are discussed and followed by the recombination lifetime comparison between two different graded buffers. Finally, a diffusion model is developed to explain the non-linear behavior observed in photoconductivity decay (PCD) data during the recombination lifetime measurements.

6.2.1 Fundamentals of carrier recombination lifetime in semiconductors

In principle, a semiconductor in thermal equilibrium always has time-independent net carrier concentrations. Although electrons are continuously excited from the valence band into the conduction band (the electron-hole pair generation) and jump back to the valence band from the conduction band (the electron-hole recombination), the generation rate is equal to the recombination rate so that the net carrier concentrations are in dynamic equilibrium. If the equilibrium is disturbed, for example, by a light with the photon energy larger than the bandgap of the semiconductor, excess carriers (electrons and holes) will be generated, which increases the carrier concentration; after turning off the light, the increased carrier concentrations will decay back to the equilibrium
concentrations via carrier recombination. This decay process can be described mathematically by

\[ \Delta n(t) = \Delta n(0) \exp\left( -\frac{t}{\tau_n} \right) \quad (6.1) \]

where \( \Delta n(0) \) is the initial excess carrier concentration and \( \tau_n \) is the carrier recombination lifetime. [1, 2]

In principle, carrier recombination in bulk semiconductors primarily consists of three recombination mechanisms, Shockley-Read-Hall (SRH) recombination, radiative recombination, and Auger recombination. Therefore the bulk recombination lifetime \( \tau_B \) is expressed to contain three terms and each term is associated with a recombination mechanism, [3]

\[ \frac{1}{\tau_B} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{Rad}} + \frac{1}{\tau_{Auger}} \quad (6.2) \]

where \( \tau_{SRH} \), \( \tau_{Rad} \), and \( \tau_{Auger} \) are SRH, Radiative, and Auger Recombination lifetimes, respectively. Fig. 6.1 schematically illustrates three recombination mechanisms.
Since the carrier recombination at deep levels in the bandgap was first studied by Shockley, Read and Hall, this recombination mechanism is usually termed as Shockley-Read-Hall recombination. The SRH recombination lifetime is given by

$$\tau_{SRH} = \frac{\tau_p (n_0 + n_1 + \Delta n) + \tau_n (p_0 + p_1 + \Delta p)}{p_0 + n_0 + \Delta n}$$

(6.3)

where $p_0$ and $n_0$ are the equilibrium hole and electron concentrations, $\Delta n$ and $\Delta p$ are the excess carrier concentrations, and $n_1$, $p_1$, $\tau_n$, and $\tau_p$ are defined respectively as below.
\[ n_1 = n_i e^{(E_T - E_i)/KT}; \quad p_1 = n_i e^{-(E_T - E_i)/KT} \]  

\[ \tau_p = \frac{1}{\sigma_p \nu_{th} N_T}; \quad \tau_n = \frac{1}{\sigma_n \nu_{th} N_T} \]  

(6.4a)  

(6.4b)

where \( N_T \) and \( E_T \) are the density and energy level of deep-level impurities, respectively, \( \sigma_p \) and \( \sigma_n \) are the capture cross section for electrons and holes, respectively, and \( \nu_{th} \) is the thermal velocity of carriers. [3]

The equation 6.3 can be simplified accordingly at some specific conditions. For p-type semiconductors \( (p_0 >> n_0) \), with the assumption of \( n_1 \) and \( p_1 << p_0 \), the SRH recombination lifetime at the low injection level \( (\Delta n = \Delta p << p_0) \) can be written as

\[ \tau_{SRH} = \tau_n \]  

(6.5)

Similarly, for n-type semiconductors \( (n_0 >> p_0) \), with the assumption of \( n_1 \) and \( p_1 << n_0 \), the SRH recombination lifetime at the low injection level is given as

\[ \tau_{SRH} = \tau_p \]  

(6.6)

In other words, at the low injection level, the SRH recombination lifetime is equal to the minority carrier lifetime. At the high injection level \( (\Delta n = \Delta p >> p_0, n_0, p_1, \text{ and } n_1) \), the SRH recombination lifetime becomes
\[ \tau_{SRH} = \tau_n + \tau_p \quad (6.7) \]

Hence, the high injection SRH lifetime is always theoretically longer than the low injection SRH lifetime. [3]

Since the SRH recombination is closely related to densities of deep levels, which are generally caused by defects in semiconductors, the SRH lifetimes or the minority carrier lifetimes are usually used as a critical evaluation factor for the material quality of semiconductors.

The process through which carriers recombine from band to band with photon emission is called radiative recombination, which is very important for direct bandgap semiconductors. The radiative recombination lifetime is written as

\[ \tau_{Rad} = \frac{1}{B(p_0 + n_0 + \Delta n)} \quad (6.8) \]

where B is the radiative recombination coefficient. At the low injection level, the radiative recombination lifetime can be given as

\[ \tau_{Rad} = \frac{1}{Bp_0} \text{ for p-type semiconductors} \quad (6.9a) \]

\[ \tau_{Rad} = \frac{1}{Bn_0} \text{ for n-type semiconductors} \quad (6.9b) \]

while at the high injection level,
\[ \tau_{\text{Rad}} = \frac{1}{B \Delta n} \]  

(6.10)

In general, the radiative recombination lifetime is independent of the defect density of semiconductors. [3, 4]

The Auger recombination lifetime is given as

\[ \tau_{\text{Auger}} = \frac{1}{C_n \left(n_0^2 + 2n_0 \Delta n + \Delta n^2\right) + C_p \left(p_0^2 + 2p_0 \Delta n + \Delta n^2\right)} \]  

(6.11)

where \( C_n \) and \( C_p \) are the Auger recombination coefficients. At the low injection level, the Auger recombination lifetime can be approximated to be \( 1/C_p n_0^2 \) (p-type semiconductors) or \( 1/C_n n_0^2 \) (n-type semiconductors) in contrast to \( 1/(C_p + C_n) \Delta n \) at the high injection level. Since \( C_n \) and \( C_p \) are very small (on the order of \( 10^{-31} \text{ cm}^6/\text{s} \)), the Auger recombination is usually a negligible component of the total carrier recombination when the doping concentration or the injection level is not high.

The recombination lifetimes measured in double heterostructures should consider the surface/interface recombination contribution. Assuming that both hetero-interfaces of DHs have a same recombination velocity \( S \), the lifetime measured can be approximately given as

\[ \frac{1}{\tau_m} = \frac{1}{\tau_B} + \frac{2S}{d} \]  

(6.12)
where $\tau_m$ is the recombination lifetime measured and $d$ is the well thickness of DHs. Theoretically, according to the equation 6.12, the bulk recombination lifetime and the surface/interface recombination velocity can be determined from the dependence of the recombination lifetimes measured on the DH well thickness.

Photoconductive decay (PCD) and time-resolved photoluminescence (TRPL) are the most popular recombination lifetime measurement techniques in the semiconductor area. Since TRPL requires a detector that can sense emitted photons, this is a limitation for low bandgap materials like InGaAs due to lack of good IR detectors. Conventionally, other techniques are used that do not have this limitation, like PCD. In this study, the PCD technique was used to do the recombination lifetime investigation. The detailed information of the PCD measurement can be found in chapter 2.

6.2.2 Recombination lifetime investigation of lattice-mismatched InAsP/InGaAs DHs grown on InAsP step-graded buffers

InAs$_{0.32}$P$_{0.68}$/In$_{0.68}$Ga$_{0.32}$As/InAs$_{0.32}$P$_{0.68}$ double heterostructures were grown by solid source MBE. The molecular forms of As and P used in the growth were As$_2$ and P$_2$, respectively. All samples were grown on semi-insulating (001) InP substrates and the entire structure was unintentionally doped. The DH structure is schematically shown in Fig. 6.2. Before the DH growth, a 2000 Å InP buffer was deposited, followed by an InAs$_y$P$_{1-y}$ compositionally step-graded buffer consisting of 4 steps, each of 4000 Å thickness, with compositions shown in Fig. 6.2. The misfit between the final step in the buffer (InAs$_{0.32}$P$_{0.68}$) and the InP substrate is $\sim$ 1%. Triple-axis x-ray diffraction (TAXRD) confirmed that $> 90\%$ strain relaxation was achieved with this buffer design.
Following the buffer growth, a series of InAs$_{0.32}$P$_{0.68}$/In$_{0.68}$Ga$_{0.32}$As/InAs$_{0.32}$P$_{0.68}$ DH structures with InGaAs well thicknesses of 0.5 µm, 1 µm and 2 µm were grown on the InAs$_y$P$_{1-y}$ buffers, achieving a nominal lattice-matched condition with the final InAs$_{0.32}$P$_{0.68}$ step of the buffer. Each DH structure included a 300 Å top InAs$_{0.32}$P$_{0.68}$ barrier layer to complete the DH structure.

Ultra-high frequency PCD measurements at room temperature were made on all DH structures to monitor the photoconductivity decay within the InGaAs wells in order to gain insight into the carrier recombination in these DH structures. The description of this technique can be found in Chapter 3. A range of excitation wavelength was used as
described below. By fitting the decay after the optical excitation pulse was removed, PCD lifetimes were quantified.

Fig. 6.3 PCD data obtained for DHs with well thicknesses of 0.5 µm, 1 µm and 2 µm at 300 K. The solid lines are data fits to the LLI regime of the PCD response.

Fig. 6.3 shows PCD data obtained for 0.5 µm, 1 µm and 2 µm thick DH structures. The wavelength of the excitation pulse selected in the measurement was 2000 nm (0.62 eV), slightly higher than the band-gap of the In$_{0.68}$Ga$_{0.32}$As well layer (0.60 eV) and below the InAs$_{0.32}$P$_{0.68}$ bandgap (1.0 eV), in order to confine band-absorbed photo-carrier generation within the InGaAs wells. The incident photon flux of the excitation
pulse was $\sim 2 \times 10^{10}$ photons/cm$^2$. Assuming an absorption coefficient $2 \times 10^4$ cm$^{-1}$ for the In$_{0.68}$Ga$_{0.32}$As well layer at the wavelength of 2000 nm, [5] the 1/e penetration depth of 2000 nm photons inside the InGaAs well layer is $\sim 0.5$ µm. Based on these data, the initial injection level is calculated to be $\sim 4 \times 10^{14}$ cm$^{-3}$, which can be considered equal to the initial photogenerated carrier concentration, assuming the quantum efficiency is 100%. Since the photoconductivity can be expressed as

$$\Delta \sigma = e \mu \Delta n$$  \hspace{1cm} (6.13) $$

where $e$ is the electronic charge, $\mu$ is the photogenerated carrier mobility and $\Delta n$ is the concentration of photogenerated carriers, the PCD signal is proportional to the concentration of photogenerated carriers so that the initial injection level can be also considered as the starting value of the PCD curve. The unintentional background doping of the InGaAs well layer was n type $\sim 1 \times 10^{15}$ cm$^{-3}$, which was determined by electrochemical Capacitance-Voltage profiling. In Fig. 6.3, the initial injection level and the background doping values are indicated. Fitting the low injection level regime of PCD data denoted by the solid line fitting in Fig. 6.3, low injection level PCD lifetimes ($\tau_{PCD}$) were determined to be $\sim 5$ µs, 4 µs and 4 µs for 0.5 µm, 1 µm and 2 µm thick InGaAs well DH structures, respectively. The lack of dependence of lifetimes on DH well layer thickness implies a low recombination velocity, $S$, at the InAsP/InGaAs interfaces such that the usual expression from which the bulk minority carrier lifetime in the InGaAs well, $\tau_B$, can be extracted according to the equation 6.12 is no longer valid. That is, for $S \ll d/2\tau_B$, we have $1/\tau_{PCD} \approx 1/\tau_B$. Hence, we can consider the 4-5 µs low
injection level PCD lifetime to reasonably approximate the minority carrier lifetime in the bulk, relaxed InGaAs layer. Fig. 6.4 shows the cross-sectional TEM of the DH structure. At the resolution level, a very smooth, defect-free InAsP/InGaAs interface can be observed in the image, which further demonstrates the excellent quality of the InAsP/InGaAs interface.

![Cross-sectional TEM of the InGaAs DH grown on 4-step InAsP graded buffers](image)

Fig. 6.4 Cross-sectional TEM of the InGaAs DH grown on 4-step InAsP graded buffers

### 6.2.3 Diffusion model for the initial fast decay of PCD curves

It is obvious from the PCD behavior shown in Figs. 6.3 that the carrier recombination does not yield single-slope exponential decays as expected for ideal
UHFPCD measurements. The fast initial decay observed for all three DH structures may be explained by several phenomena. First, a high value for S at the upper InAsP/InGaAs interface can yield multi-exponential photoconductivity decay due to the higher concentration of photogenerated carriers near the upper interface that would dominate the initial part of the photoconductivity decay. However, the observed lack of DH thickness dependence by PCD lifetimes from Fig. 6.3 demonstrates that the influence of interface recombination is negligible (i.e. interface recombination is very low), eliminating this possibility. A second plausible explanation then is photogenerated carrier diffusion that can occur during the transient time window observed here as a result of the initially non-uniform carrier generation profile that is dictated by the absorption coefficient of the InGaAs layer at the excitation wavelength. The non-uniform concentration profile induces minority carrier diffusion in the InGaAs layer until a uniform concentration distribution is reached throughout the InGaAs layer. Once a uniform carrier distribution is reached, the photoconductivity decay becomes dominated by carrier recombination and the PCD curve becomes a steady decay curve from which the carrier recombination lifetime can be derived. As shown below, Fig. 6.5 schematically illustrates the photogenerated-carrier distribution profile at different stages during the photoconductivity decay process.
Fig. 6.5 Photogenerated carrier profiles at different stages during the photoconductivity decay process.

To establish the reasonableness of this explanation, the diffusion relaxation time, which is defined as the characteristic time for the diffusion process to be complete, can be roughly estimated if we consider a simple diffusion model in which the initial \((t = 0)\) concentration profile of photogenerated carriers \(C(x, 0)\), is approximated by

\[
C(x,0) = C_0, \quad 0 \leq x \leq h \\
C(x,0) = 0, \quad h < x \leq l.
\]  \(6.14\)
In this expression, $h$ represents the absorption depth of incident photons entering the InGaAs well layer in the PCD experiment and $l$ is the thickness of InGaAs well layer. For the purpose of estimation, we assume $\partial C/\partial x = 0$ at the boundaries and only one reflection occurs at the lower InGaAs/InAsP interface for diffusing carriers. Under these simplifying conditions, the carrier concentration $C(x, t)$ can be written as

$$C(x,t) = \frac{1}{2}{C_0}\{\text{erf}\left(\frac{h - x}{2\sqrt{Dt}}\right) + \text{erf}\left(\frac{h + x}{2\sqrt{Dt}}\right) + \text{erf}\left(\frac{h + 2l - x}{2\sqrt{Dt}}\right) + \text{erf}\left(\frac{h - 2l + x}{2\sqrt{Dt}}\right)\} \quad (6.15)$$

where $D$ is the diffusion constant of electrons in this case. [6] Since the carrier concentration $C(x, t)$ is a sum of error functions, it is expected that the dependence of $C(x, t)$ on $t$ should not be linear on a logC-t plot, which is consistent with the initial part of the measured PCD data in Fig. 6.3. If we use a value for the electron mobility in the In$_{0.68}$Ga$_{0.32}$As layer of 6000 cm$^2$/Vs based on mobility data measured in MBE-grown mismatched InGaAs with similar composition and doping concentration, a diffusion relaxation time for the 2 µm thick DH is estimated to be $\sim 5$ µs. Given the simplifying approximations used in this demonstration and that the diffusion relaxation time characterizes completion of the diffusion process, this time is consistent with the initial decay period prior to the dominance of low injection level recombination-limited decay in Fig. 6.3. It should be noted, however, that due to the absorption depth approximation employed, this simplified model cannot be used to determine the diffusion relaxation time for DH structures with well thickness less than the absorption depth calculated, such as for the 0.5 µm DH.
Additional support for this argument is provided by Fig. 6.6, which compares only the initial (0-2 μs) PCD response of the 2 μm thick DH sample as a function of excitation wavelength at 1500 nm, 1800 nm and 2000 nm. For diffusion to be important in the PCD behavior, the different initial concentration gradients that result from the dependence of the carrier generation profile on the wavelength-dependent absorption coefficient should be evident. Hence progressively reduced diffusion should be observed for increasing wavelengths (lower absorption coefficient). This trend is clearly seen in Fig. 6.6 for the three excitation wavelengths. The 1500 nm and 1800 nm excitation produce substantially larger diffusion enhanced decay in overall photoconductivity, as
measured by the magnitude of PCD reduction in this nonlinear 0-2 µs regime, compared to the PCD response in the same time window using near bandgap (2000 nm) excitation (note that 2000 nm corresponds to 0.62 eV and the In$_{0.68}$Ga$_{0.32}$As bandgap is measured to be 0.60 eV). From this, we conclude that a diffusion process that influences the overall PCD magnitude is consistent with the observed nonlinear decay in the PCD response of these materials.

6.2.4 Recombination lifetimes for InGaAs DHs grown on InAlAs graded buffers

Similar to the DH lifetime studies just described using graded anion InAsP buffers, identical DH structures were also grown on graded cation InAlAs buffers on InP, where the InAlAs buffers were grown as described in chapters 4 and 5, in order to directly assess the impact of the two lattice grading strategies on electronic material quality. Specifically, lattice-mismatched In$_{0.69}$Ga$_{0.31}$As DHs were grown on semi-insulating semi-insulating (001) InP substrates that were offcut by 2° toward <110> using both InAsP and InAlAs step-graded buffers. [7] For this specific comparison the InGaAs DH structure was comprised of a 2 µm thick In$_{0.69}$Ga$_{0.31}$As layer surrounded by InAs$_{0.32}$P$_{0.68}$ barrier layers for the anion buffer structure and by In$_{0.68}$Al$_{0.32}$As barrier layers for the cation buffer structure. The InAsP step-graded buffers followed the growth structure shown in Fig. 6.2 and In$_x$Al$_{1-x}$As step-graded buffers (x = 0.52 – 0.68) consist of 4 graded layers, with a total thickness of 1.3 µm.

Fig. 6.7 plots PCD data of InGaAs DHs for both graded buffers from which recombination lifetimes were found to be ~ 5 usec using the graded InAsP buffer and ~ 0.5 usec for the graded InAlAs buffer. The factor of ~ 10 improvement in carrier lifetime
for the graded anion structure is extraordinary, and completely consistent with the greater degree of structural perfection in the bulk (lower dislocation density) and surface (lower degree of surface roughness) of the graded anion buffers described in chapter 5. Hence, one can expect that full devices based on lattice mismatched III-V materials should be superior for the graded InAsP buffers as opposed to the more usual InAlAs buffers on InP. The discussion in section 6.3 reveals this to be very clear.

Fig. 6.7 PCD curves of InGaAs DHs with the well thickness of 2 µm on both InAsP and InAlAs graded buffers. The recombination lifetime obtained from InAsP-buffered DHs is much longer than that for InAlAs-buffered DHs.

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6.3 Conclusions

High PCD recombination lifetimes of 4-5 $\mu$s have been demonstrated for $\sim$ 1% mismatched InGaAs on InP using InAs$_{y}$P$_{1-y}$ step-graded buffers. In addition, outstanding interface quality is demonstrated in this lattice-mismatched heterostructure such that the InAsP/InGaAs interface recombination velocity $S$ is low to the point where DH thickness dependence of net PCD lifetimes is not observed. Conversely, for identical lattice-mismatched InGaAs grown on InAlAs step-graded buffers the PCD recombination lifetime was measured to be only $\sim$ 0.5 $\mu$s. The inferior material quality of InAlAs graded buffers is suggested to be the reason for this significantly shorter recombination lifetime. A model combined with wavelength-dependent analysis of the initial nonlinear decay observed in PCD data is also presented to explain the possible role of carrier diffusion in PCD characterization. In summary, this investigation demonstrates that superior material properties of InAsP step-graded buffers translate to better electronic properties in overgrown InGaAs layer with higher recombination lifetimes. Based on these results, excellent devices using InAsP graded buffers are expected, and in fact recently high-performance thermophotovoltaic cells using InAsP step-graded buffers have been successfully achieved. [8, 9]
6.4 References


7 R. N. Sacks and S. A. Ringel, unpublished.


CHAPTER 7

GROWTH AND STRUCTURAL PROPERTIES OF HIGHLY MISMATCHED INASP STEP-GRADED BUFFERS AND VIRTUAL INAS GROWN ON INP

7.1 Introduction

In the previous chapters, we have demonstrated that InAsP step-graded buffers can be used to support high-quality lattice-mismatched InGaAs materials and devices on InP substrates with low to moderate lattice misfit, i.e. $f < 1.5\%$, for As anion content of up to around 40\%. Extension across the entire range of lattice constants made accessible by the InAsP alloy, i.e. out to InAs, would generate a critical achievement, since the electron mobility of InAs is two times of that of lattice matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ and an order of magnitude higher than that of electrons in Si. [1, 2] Currently there exists no InAs electronic device technology that exploits its outstanding transport properties due to the large lattice constant mismatch between InAs and any available substrate technology. Relaxed InAs has a lattice constant that is 3.2\% larger than that of an InP substrate, and achieving controlled relaxation of the lattice strain associated with this misfit has relegated the use of InAs to the realm of inserting thin strained layers within InP/InGaAs...
lattice matched devices. [3, 4] The low thickness required to maintain a fully strained layer, which limits the ability for electronic devices to utilize high mobility electrons at an appreciable carrier density, for instance. It is clear that were there a way to generate “bulk-like” InAs in a wafer form, or for that matter any InAsP alloy with a lattice constant between InP and InAs with high As content, an InAs device technology analogous to InP or GaAs would be conceivable. The remaining chapters of this dissertation focus on various aspects of creating high As content virtual InAsP and InAs “substrates” via the extension of grading InAsP layers on InP to high As content values. This chapter focuses on growth and structural analysis of InAs grown on InP with InAsP graded buffers.

7.2 InAsP graded buffer design for metamorphic InAs on InP

According to the dislocation flow theory discussed in chapter 2, the glide velocity of threading dislocations in the buffer layer is one of the most critical factors in the graded buffer design. Considering that InAs has a weaker bond strength and an lower dislocation glide activation energy compared to InP [5, 6, 7], the dislocation glide velocity in InAs should be higher than that in InP based on equation (2.4) in chapter 2. In view of this observation, it is reasonable to speculate that the dislocation glide velocity $V$ should be higher in higher-As InAsP alloys. Based on this, initial growths with no attempt to optimize the misfit profile were designed with a relatively high grading rate in the upper regions of the buffer, since from a device perspective minimizing the total graded buffer thickness is important as this can influence thermal resistance of electronic devices.
7.2.1 4-step InAsP graded buffers: design, crystal growth, and surface morphology

Fig. 7.1 illustrates the schematic cross-section and the misfit profile of the first InAsP graded buffer designed for InAs on InP. The total buffer thickness was 1.6 µm and consisted of 4 InAsP graded layers having nominal (based on calibration growth runs and XRD data) As compositions of 10%, 25%, 50%, and 90% on the anion sublattice. The graded buffers were followed by a 1 µm thick InAs layer.

<table>
<thead>
<tr>
<th>Buffer Thickness (µm)</th>
<th>Misfit % (respect to InP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4 µm InAs$<em>y$P$</em>{1-y}$ $y = 0.5$</td>
<td>0.0</td>
</tr>
<tr>
<td>0.4 µm InAs$<em>y$P$</em>{1-y}$ $y = 0.25$</td>
<td>0.5</td>
</tr>
<tr>
<td>0.4 µm InAs$<em>y$P$</em>{1-y}$ $y = 0.1$</td>
<td>1.0</td>
</tr>
<tr>
<td>1 µm InAs$<em>y$P$</em>{1-y}$ $y = 0.9$</td>
<td>1.5</td>
</tr>
<tr>
<td>0.4 µm InAs$<em>y$P$</em>{1-y}$ $y = 0.5$</td>
<td>2.0</td>
</tr>
<tr>
<td>1 µm InAs top layer</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Fig. 7.1 Schematic diagram of 4-step InAsP graded buffers for InAs grown on InP. On the right side, the misfit as a function of the buffer thickness is also plotted.

To characterize transport properties using Hall effect it is necessary to separate the InAs layer from the InAsP graded buffers from the electrical perspective. Much more of this will be discussed in detail later in chapter 8 but the essence is to ensure that the
conductivity of the layer of interest, in this case the InAs cap layer, has a conductivity much higher than that of the underlying graded buffers and substrate. Here, the InAs layer was intentionally n-doped with Si to a concentration of $1 \times 10^{18}$ cm$^{-3}$. The InAsP graded buffers and the InAs layer were grown at 485 °C and 500 °C, respectively, as determined by optical pyrometry, and are unintentionally doped.

During MBE growth, a clear 2x4 RHEED pattern initially developed, which gradually blurred toward the end of the growth run (high As content regime), indicative of surface roughening. This was confirmed, ex-situ with Nomarski microscopy after growth of the entire structure that shows no pronounced cross-hatch morphology that is otherwise indicative of ideal relaxation via glide of long misfit dislocations, [8] suggesting very short dislocation misfit segments and high defect densities are present. Fig. 7.2 shows the Nomarski image. In looking at the misfit profile of Fig. 7.1, the large jump in misfit (1.2%) between the InAs$_{0.5}$P$_{0.5}$ and InAs$_{0.9}$P$_{0.1}$ layers is suspicious since high misfit at a single interface will nucleate at high density of misfit dislocations before glide effectively relaxes strain over long distances. Ultimately, a high initial threading dislocation density will block dislocation glide and can generate dislocation pileups.
Fig. 7.2 Nomarski image of surface morphology for InAs grown on InP using a 4-step InAsP graded buffer by Nomarski microscopy.
7.2.2 5-step InAsP graded buffers: buffer design, surface morphology, and defect structures

With this initial information, a 5-step InAsP graded buffer was then designed based on the performance of the 4-step graded buffer structure. In this new buffer structure, one more misfit step was added so that the maximum misfit at any one step in the buffer stack is reduced from 1.2% to 0.8%. The structure is shown in Fig. 7.3, with nominal As compositions (on the anion sublattice) of 10%, 25%, 40%, 70%, and 90% for the 5 steps between the InP substrate and InAs cap layer. To make a direct comparison with the 4 step structure for electrical measurements, the thickness and doping of the top InAs layer were kept the same. Fig. 7.4 shows the Nomarski image of the InAs layer

![Schematic diagram of 5-step InAsP graded buffers for InAs grown on InP. On the right side, the misfit as a function of the buffer thickness is also plotted.](image-url)
Fig. 7.4 Nomarski image of surface morphology for InAs grown on InP using a 5-step InAsP graded buffer by Nomarski microscopy.
grown on InP with this 5-step InAsP buffer. In contrast to Fig. 7.2, well-developed surface crosshatch morphology is clearly evident, indicative of effective strain relaxation via glide of long misfit dislocation segments, similar to earlier observations for the lower part of the InAsP graded buffer.

Cross-sectional transmission electron microscopy (TEM) was used to characterize structural defects present in the InAs layer with the 5-step InAsP graded buffer. TEM samples were prepared by focused ion beam, which was described in chapter 3. Figure 7.5 (a) shows the cross-sectional TEM image, in which the InAs layer and InAsP graded buffers can be clearly identified. From the images at this resolution, there are no threading dislocations visible in the InAs layer, indicating the threading dislocation density is below 1x10^7 cm^-2. In order to demonstrate the impact of the InAsP step-graded buffers on defect densities in the overgrown InAs layer, an identical 1 µm InAs layer was grown directly on InP using a single step InAs buffer with the same thickness as the 5-step InAsP graded buffer (1.5 µm). Fig. 7.5 (b) shows a representative cross-sectional TEM image obtained for this single step structure, threading dislocations can be observed throughout the entire InAs layer, from the abrupt InAs/InP interface to the top surface of the InAs layer. This reveals the presence of a high density of threading dislocations for the direct-growth sample (~ 5x10^8 cm^-2) as would be expected for single step growth of thick InAs on InP due to the large lattice mismatch (>3%). [9] Hence, these TEM results demonstrate the high material quality of InAs grown on a 5-step InAsP graded buffer and verify the high efficiency of InAsP graded buffers in migrating threading dislocations during strain relaxation.
Fig. 7.5 Cross-sectional TEM images of InAs grown on InP with (a) a 5-step InAsP graded buffer, (b) a direct-growth InAs buffer. The TD densities are below $1 \times 10^7$ cm$^{-2}$ and $\sim 5 \times 10^8$ cm$^{-2}$ in the InAs layer with/without the InAsP graded buffers, respectively.
7.2.3 6-step InAsP graded buffers: buffer design and surface morphology

As discussed above, high material-quality InAs has been achieved on InP substrates with a 5-step InAsP graded buffer. In addition, InAs-based high-speed devices built on these virtual InAs substrates have recently demonstrated excellent device performance. The detailed information of InAs-based devices using a 5-step InAsP graded buffer will be discussed later in chapter 8. However, in the cross-sectional TEM image of InAs grown on 5-step InAsP graded buffers – Fig. 7.5(a), defect structures can still be observed in the top two InAsP graded layers (InAs\textsubscript{0.70P0.30} and InAs\textsubscript{0.90P0.10}), particularly in the InAs\textsubscript{0.70P0.30} layer, in contrast to other layers in this 5-step buffer structure. Since the lattice mismatch between InAs\textsubscript{0.45P0.55} to InAs\textsubscript{0.70P0.30} layers is the largest (0.8%) in this buffer design, it is likely that this 0.8% grading jump could still be too aggressive for InAsP step-graded buffers. Based on these results, a new InAsP graded buffer structure has recently been developed and is still under investigation right now as part of the ongoing studies in this material in our research group.

This new structure is shown in Fig. 7.6, with nominal As compositions of 15%, 30%, 45%, 60%, 75%, and 90% for the 6 steps between the InP substrate and InAs cap layer. With one more buffer layer, the largest lattice mismatch in is approximately 0.5% in this buffer design. In order to find the optimal buffer thickness, this total thickness of this structure is further reduced to 1.2 \( \mu \text{m} \) to investigate the buffer thickness impact on structural properties in the overgrown InAs. Same as the last two buffer structures, the InAsP buffer layers were followed by 1 \( \mu \text{m} \) InAs. Fig. 7.7 shows the Nomarski image of the InAs layer (with a 10 nm thick InAlAs cap layer) with a 6-step InAsP graded buffer, in which well-developed crosshatch patterns can be clearly observed as expected.
Fig. 7.6 Schematic diagram of 6-step InAsP graded buffers for InAs grown on InP. On the right side, the misfit as a function of the buffer thickness is also plotted.

Fig. 7.7 Nomarski image of surface morphology for InAs (with a 10 nm thick In$_{0.8}$Al$_{0.2}$As cap) grown on InP using a 6-step InAsP graded buffer by Nomarski microscopy.
7.2.4 Strain relaxation and mosaic structures in the InAs layer with InAsP graded buffers

With the comparison of surface morphologies suggesting different bulk structural properties, reciprocal space maps (RSM) were obtained using high-resolution XRD measurements on all three buffer structures mentioned above to explore if there is a correlation with the quality of the relaxed layers. Based on symmetric and asymmetric RSMs, the InAs layers were determined to be nearly totally relaxed (>97%) on all three buffers. However, comparison of the (004) symmetric RSMs, shown in Fig. 7.8, reveals that different broadening (mosaicty) in the $\omega_{\text{rel}}$ (rocking curve) scan direction was found in the InAs layers grown on different graded buffers. As one of the common crystalline imperfections, mosaic structures are microscopic misorientations in a single crystal and therefore create diffraction broadening effects in XRD measurements. [10] In general, mosaicity can be quantified using the full width at half maximum (FWHM) of rocking curve scans. In view of this, rocking curves of the InAs layer are also measured for all structures and shown in Fig. 7.8. FWHM values of InAs rocking curves are determined to be 2133, 1846, and 1808 arcsec for the 4-step, 5-step, and 6-step InAsP graded buffers, respectively. This indicates that greater mosaicity exists in the InAs layer with 4-step InAsP graded buffers in contrast to that with the 5-step or 6-step buffers. On the other hand, with the least mosaicity, the InAs layer grown on 6-step InAsP graded buffers is suggested to have the most uniform microstructure among all three graded structures.
InP
InAs
InAs_yP_{1-y}

(a)

FWHM - 2133 arcsec

XRD Intensity (A.U.)

ω_rel (arcsec)

InP
InAs
InAs_yP_{1-y}

(b)

FWHM - 1846 arcsec

XRD Intensity (A.U.)

ω_rel (arcsec)
Fig. 7.8 Symmetric RSMs for 1 \( \mu \)m relaxed InAs grown on (a) 4-step InAsP graded buffers (b) 5-step InAsP graded buffers, and (c) 6-step InAsP graded buffers. XRD rocking curves of the InAs layer on all three buffers are also included.

As crystal imperfections, mosaic structure in epitaxial layers has been reported to strongly affect carrier transport properties such as carrier mobilities in semiconductor materials. [11, 12] Hence, it would be expected that carrier transport in the InAs layer with a 4-step InAsP graded buffer could be more strongly affected by mosaicity as compared to those with a 5-step or 6-step graded buffer. The detailed discussion of
transport properties of the InAs layer grown on InAsP step-graded buffers will be presented later in chapter 8.

Before leaving this topic, it is important and at first surprising to note that there is significantly less mosaicity observed for InAs directly grown on InP, i.e. without a graded buffer. Fig. 7.9 shows an (004) RSM of a 2.5 µm thick InAs grown directly on InP. The InAs FWHM value is determined from its rocking curve to be ~ 250 arcsec, almost an order of magnitude less than that obtained from InAs with an InAsP graded buffer. This is opposite of what might intuitively be expected given the much lower threading dislocation density for the graded structures. The explanation for this apparent anomaly may lie in the different modes of strain relaxation for high versus low misfit interfaces. According to the data obtained, it appears that the threading dislocation glide process leads to the formation of a mosaic structure. Since the glide distance of threading dislocations for direct InAs on InP epitaxy is relatively short due to the high misfit at the single interface, glide plays a much less dominant role in relaxing the strain in this structure. The lack of threading dislocation glide and the narrow XRD peak width indeed do suggest that the dislocation glide process directly impacts crystalline mosaic spread in the graded buffer.

The conclusion from this argument and collection of data is that the measure of mosaic spread for graded buffers should not be used to gauge overall material quality when compared to high misfit relaxation. The opposite trend of threading dislocation density proves this point and subsequent sections and chapters support this notion via electrical property comparisons. The device investigation described in chapter 8 will indicate that threading dislocations have more severe impact on high-speed device
performance as compared to mosaic spread, which appears to be a secondary issue if an issue at all.

Fig. 7.9 (004) RSM for 1 µm relaxed InAs directly grown on InP. The FWHM of the XRD rocking curves for the InAs layer is determined to be ~ 250 arcsec.

7.3 Tilt analysis on InAs grown on InP using InAsP step-graded buffers

During the structural property investigation of relaxed InAs with InAsP graded buffers, we observed a significant epitaxial tilt present in the InAs layer and InAsP buffers as well. For metamorphic structures, epitaxial tilt is primarily caused by a nonzero net out-of-plane Burgers vectors due to the imbalance between dislocation glide/nucleation in different directions, and thus it is closely related to the strain
relaxation mechanism for graded buffer structures. [13, 14, 15] Therefore, the investigation of epitaxial tilt could help create a better understanding of the fundamental science of strain relaxation in graded buffers and also provide more data for the buffer design optimization. In this section, epitaxial tilt in the metamorphic InAs layer grown on InP with InAsP step-graded buffers is characterized using high-resolution x-ray diffraction (XRD).

7.3.1 Tilt analysis using the conventional method

The x-ray diffractometer used in this investigation is a Bede D1 system, employing a Cu Kα1 source, which is monochromated and collimated by two channel cut silicon crystals and a 0.5 mm slit. Initially, the conventional tilt analysis method (the double-axis XRD method), which was described in details in chapter 3, was used to characterize epitaxial tilt in the metamorphic InAs layer. During double-axis XRD scans, the slit used in front of the x-ray detector was fixed at 0.5 mm and the sample was mounted with the [1T0] direction along the x-ray incidence beam, at which the azimuthal angle is defined to be 0 degree (Φ = 0°). All tilt analysis measurements were performed at room temperature.

During the tilt analysis using the double-axis XRD method, it was found that the InAs layer peak could only be observed on the rocking curves at certain but not all azimuthal angles. Additionally, for some scans in which the peak could be observed, the intensity of the epitaxial peak was relatively weak. As an example, Fig. 7.10 shows the double-axis XRD tilt analysis result of the InAs layer grown on the 5-step InAsP graded...
buffer, whose structure is shown in Fig. 7.3. Based on the fitting, the magnitude and direction of the epitaxial tilt in the InAs layer with respect to the InP substrate is \(~ 86\) arcsec at an azimuthal angle of \(~ 145\) degrees with respect to the \([110]\) direction of the substrate.

Fig. 7.10 Tilt analysis data and the fitting curve using the double-axis XRD method.

<table>
<thead>
<tr>
<th>(\Phi)</th>
<th>0</th>
<th>45</th>
<th>90</th>
<th>135</th>
<th>180</th>
<th>225</th>
<th>270</th>
<th>315</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak separation</td>
<td>–</td>
<td>3915</td>
<td>3907</td>
<td>–</td>
<td>–</td>
<td>3885</td>
<td>4005</td>
<td>–</td>
</tr>
</tbody>
</table>

Obviously in Fig. 7.10, the sine curve does not fit the data very well due to the absence of epitaxial peaks at some azimuthal angles and also the weak peak intensity in
some double-axis XRD scans. This suggests that the double-axis XRD tilt analysis method has poor applicability in this situation, causing significant error in tilt analysis data. In fact, when the epitaxial layer is tilted with respect to the substrate, a single rocking curve is theoretically unable to pass through both the substrate and the epitaxial peaks given an ideal detector. However, since the acceptance angle of the detector cannot be indefinitely small, the epitaxial peak can still be practically observed in measurements but at the price of losing intensity if the epitaxial tilt is not considerably large. In the extreme case that the epitaxial tilt is too large to be covered in the acceptance angle, the epitaxial peak would disappear in the curve scanned. This is what happened in our data at the azimuthal angles of 0, 135, 180, and 315 degrees. By realizing this, it is understandable why poor sine fittings are usually obtained when the double-axis XRD tilt analysis method is performed on a sample with large epitaxial tilt.

7.3.2 Tilt analysis using the reciprocal space map method

To solve this problem, we developed a new tilt analysis method, which use reciprocal space maps (RSMs) generated by triple-axis XRD. Compared to double-axis XRD, triple-axis XRD is able to separate lattice strain and epitaxial tilt. [16] The new method basically employs two symmetric RSMs at two orthogonal azimuthal angles which have a 90 degree separation. As schematically plotted in Fig. 7.11(a), the components of the total epitaxial tilt, $\mu$ and $\nu$, which actually are the projections of the total epitaxial tilt $\Delta \alpha$ at two orthogonal planes, can be obtained from these two symmetric RSMs. In order to help better understand the geometric relationship between all these parameters, the total epitaxial tilt with respect to the substrate and its two projected
components, $\mu$ and $\nu$, are depicted in Fig. 7.11(b). Based on this geometrical model, the magnitude and direction of epitaxial tilt can be calculated by

$$\Delta \alpha = \arccos\left[\frac{1}{\sqrt{1 + \tan^2 \mu + \tan^2 \nu}}\right]$$  \hspace{1cm} (7.1)

and

$$\Psi_{\text{tilt}} = \tan \frac{\nu}{|\tan \nu|} \arccos\left[\frac{-\tan \mu}{\sqrt{\tan^2 \mu + \tan^2 \nu}}\right]$$  \hspace{1cm} (7.2)

respectively, where $\Psi_{\text{tilt}}$ is defined to be the angle between the [1T0] direction and the projection of the epitaxial layer normal $\mathbf{n}$ on the (001) plane, which denotes the direction of the epitaxial tilt.
Fig. 7.11 (a) Schematic of symmetric reciprocal space maps at $\Phi = 0$ and $90^\circ$; (b) Geometrical model of the epitaxial tilt between the epitaxial layer and the substrate.
Table 7.1 Tilt analysis data of the InAs layer grown on different InAsP graded buffers by the RSM tilt analysis method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu$</th>
<th>$\nu$</th>
<th>Tilt magnitude</th>
<th>Tilt direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-step</td>
<td>-5368</td>
<td>-1555</td>
<td>5598</td>
<td>17</td>
</tr>
<tr>
<td>5-step</td>
<td>3955</td>
<td>-2870</td>
<td>4880</td>
<td>144</td>
</tr>
<tr>
<td>6-step</td>
<td>-4017</td>
<td>2872</td>
<td>4924</td>
<td>-37</td>
</tr>
</tbody>
</table>

To measure the epitaxial tilt using this new method, symmetric (004) RSMs at the azimuthal angles of 0 and 90° were performed on all three InAs/InAsP/InP samples mentioned above and are shown in Fig. 7.12, in which tilt components, $\mu$ and $\nu$, of the InAs layer are indicated. Table 7.1 lists tilt components ($\mu$ and $\nu$) obtained from RSMs and magnitude and direction (with respect to [110] direction) of epitaxial tilt calculated using equations (7.1) and (7.2) for each sample. Tilt analysis data show that the InAs layer grown on the 4-step InAsP graded buffer has larger epitaxial tilt as compared to other two samples. It is interesting to find that the epitaxial tilt as a function of graded buffers is consistent with the mosaicity results discussed in the last section, implying that the formation of both epitaxial tilt and mosaicity may be closely related to an imbalance of threading dislocation glide in graded buffers. As mentioned early, the imbalance of threading dislocation glide at different directions would result in a net out-of-plane
Burger vector. [13] Macroscopically, this out-of-plane Burger vector could tilt the epitaxial layer with respect to the substrate. On the other hand, it could also lead to microscopic misorientations in the epitaxial layer, i.e. mosaicity. Hence, large epitaxial tilt should always accompany large mosaicity in the epitaxial layer. However, no correlation between tilt directions and buffer structures can be derived according to these tilt analysis data.
Continued
Fig. 7.12 (004) reciprocal space maps of InAs grown on InP with (a) 4-step InAsP graded buffers, (b) 5-step InAsP graded buffers, and (c) 6-step InAsP graded buffers at the azimuthal angles of 0 and 90 degrees. Tilt components, $\mu$ and $\nu$, are indicated in RSMs.

To further demonstrate the correlation between the tilt and threading dislocation glide, epitaxial tilt in the InAs layer grown directly on InP was also characterized using the new tilt analysis method. Fig. 7.13 shows symmetric (004) RSMs at the azimuthal angles of 0 and 90° for a 2.5 µm thick InAs layer grown directly on InP, in which tilt components, $\mu$ and $\nu$, are measured to be -531 and -159 arcsec, respectively. Using equations (7.1) and (7.2), the epitaxial tilt in the InAs layer is determined to be 554 arcsec.
at an azimuthal angle of ~ 17 degrees with respect to the [110] direction of the substrate. Thus, the magnitude of epitaxial tilt present in the direct-growth InAs sample is approximately one order lower as compared to that in graded buffer samples. Similar to the mosaicity results, this can be understood by realizing that the threading dislocation glide does not play an important role in the strain relaxation process for direct-growth InAs on InP. Since nearly no threading dislocation glide occurs, the imbalance of threading dislocation glide at different directions in direct-growth samples is accordingly reduced, which leads to significantly smaller epitaxial tilt in direct-growth samples in contrast to graded buffer samples.

Fig. 7.13 (004) reciprocal space maps of a 2.5 μm InAs grown directly on InP at the azimuthal angles of 0 and 90 degrees. Tilt components, $\mu$ and $\nu$, are indicated in RSMs.
7.4 Conclusions

InAsP graded buffers have significant impact on structural properties of InAs grown above, including surface morphology, threading dislocation densities, mosaicity, and epitaxial tilt.

In InAsP step-graded buffers, misfit must be less than 1.2% pre interface to achieve ideally cross-hatch patterns on the overgrown InAs surface, which indicates effective threading dislocation glide in graded buffers. For 1.5 µm thick InAsP graded buffers with the largest interface misfit of 0.8%, a threading dislocation density was determined to be < 1x10^7 cm^-2 in the overgrown InAs layer using TEM. In contrast to a threading dislocation density of 5x10^8 cm^-2 in InAs with an identical thickness InAs direct-growth buffer, this result demonstrates the high efficiency of InAsP graded buffers in migrating threading dislocations.

A larger misfit interface graded buffer leads to greater mosaicity and epitaxial tilt in the InAs layer grown above. Based on data obtained, it appears that the formation of both mosaicity and epitaxial tilt in graded buffer samples is related to the imbalance of threading dislocation glide at different directions. Strongly supporting this explanation, mosaicity and epitaxial tilt in direct-growth InAs samples were observed to be significantly less than those in graded buffer samples due to nearly no threading dislocation glide involved in the strain relaxation process for direct-growth samples.

During the epitaxial tilt characterization in graded buffers, a new tilt analysis method using RSMs was developed. In contrast to the conventional method, the magnitude and direction of epitaxial tilt in InAs with InAsP graded buffers were successfully determined with higher accuracy using this new approach.
7.5 References


CHAPTER 8

TRANSPORT PROPERTIES AND APPLICATIONS OF VIRTUAL INAS SUBSTRATES FOR ULTRA HIGH-SPEED 2DEG ELECTRONICS

8.1 Introduction

In chapter 7, structural properties of relaxed InAs grown on InP with InAsP step-graded buffers were studied as a function of graded buffers. It has been demonstrated that different InAsP graded buffer structures lead to overgrown InAs with different surface morphology, defect structures, and epitaxial tilt. Due to the obvious impact of the buffer design on structural quality, it is of interest to see if and how this may translate to observed differences in electrical quality and properties of InAs with InAsP graded buffers. In this chapter, transport properties of InAs are investigated for several buffer designs using Hall effect measurements. Additionally, in order to explore potential high-speed metamorphic InAs-based device applications, two-dimensional electron gas (2DEG) structures are investigated based on InAlAs/InAs fabricated on virtual InAs, with results being correlated to structural properties.
8.2 Transport properties of relaxed InAs grown on 4-step and 5-step InAsP graded buffers

As discussed in the last chapter, a greater degree of mosaic spread was observed in relaxed InAs using the 4-step graded buffer as compared to the 5-step sample. Furthermore, the lack of a well-developed cross-hatch pattern on the 4-step sample surface suggests higher threading dislocation densities. Since both mosaicity and threading dislocation pileups affect carrier transport, [1, 2, 3] it is useful to perform an electrical property study for the relaxed InAs layer grown on both buffers.

Temperature-dependent Hall measurements were made on the InAs cap for both types of graded buffer designs, which were illustrated in Figs 7.1 and 7.3, respectively. Sheet carrier densities of the InAs layer were measured to be \( \sim 1 \times 10^{14} \) cm\(^{-2}\) for both samples, independent of measurement temperature. Integrating over the thickness of the InAs layer (1 \( \mu \)m), this sheet carrier concentration agrees well with the expected value of the bulk doping (\( 1 \times 10^{18} \) cm\(^{-3}\)). Fig. 8.1 shows electron mobilities as a function of measurement temperature for the relaxed InAs layer in each case. With similar doping concentration in the relaxed InAs layer, higher electron mobilities were obtained from the 5-step InAsP graded buffer sample as compared to the 4-step InAsP graded buffer sample, indicating that superior structural properties (fewer defects and reduced mosaicity) appear to translate into improved electronic properties (high electron mobilities) for the relaxed InAs grown on the 5-step InAsP graded buffer. Note that electron mobilities achieved in the relaxed InAs with the 5-step InAsP graded buffer are comparable to the theoretical mobility value predicted for bulk InAs at this doping level. [4, 5] Therefore, we chose this 5-step buffer design to become the new baseline for the
exploration of metamorphic InAs-based high-speed devices grown on InP substrates. However, before moving toward that end result, it is necessary to first consider the issue of surface accumulation for InAs layers, which has been widely reported and has significant effect on electrical property characterization.

![Dependences of electron mobilities on temperature for metamorphic InAs layers on both 4-step and 5-step InAsP graded buffers.](image)

**Fig. 8.1** Dependences of electron mobilities on temperature for the metamorphic InAs layers on both 4-step and 5-step InAsP graded buffers.

### 8.3 The surface electron accumulation layer issue for InAs

It has been suggested for more than 30 years that surface states pin the Fermi level above the conduction band edge and form an electron accumulation layer on the free InAs surface. [6, 7, 8, 9, 10, 11, 12] Independent of the bulk doping of the InAs layer, the sheet carrier density of this accumulation layer is usually on the order of $10^{12}$
Given the fact that these prior efforts have all focused on either InAs with very high defect density due to high mismatched direct epitaxy [6, 7, 8, 9] or bulk InAs wafers [10, 11, 12], the relaxed InAs grown on graded buffers created in this dissertation research provides an opportunity to explore the universality of this observation. That is, what role does the microstructure quality of InAs have on surface accumulation via surface Fermi level pinning, if any? In this section, combining conventional Hall effect measurements and quantitative mobility spectrum analysis (QMSA), the issue of the surface accumulation layer is addressed for relaxed InAs grown on InP with InAsP graded buffers. Detailed information regarding QMSA can be found in chapter 3 and other references. [13, 14, 15]

Assuming the existence of the surface accumulation layer, we should consider the InAs layer as a two-conduction layer system during Hall effect measurements, one being the doped bulk InAs layer and the other the surface accumulation layer. However the QMSA spectra obtained for the n-type 1x10^{18} cm^{-3} InAs layer grown on either the 4-step or the 5-step InAsP graded buffer show the presence of only a single channel conduction, as seen in Fig. 8.2. In fact, the sheet carrier density for this channel derived from the measurement is 1.02x10^{14} cm^{-2}, far larger than the ~10^{12} cm^{-2} concentration observed for surface accumulation layers on InAs. Moreover, if we integrate this 2-D concentration to be distributed over the entire 1 µm InAs layer thickness, we obtain the bulk electron carrier concentration due to the intentional Si doping of 1x10^{18} cm^{-3}. 

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Fig. 8.2 QMSA spectrum of a 1 µm thick InAs layer grown on a 5-step InAsP graded buffer on semi-insulating InP. The dominant carriers are electrons from the InAs bulk layer. The peak of holes is also observed in the spectrum.

If it is correct that the electron transport detected with QMSA is indeed due to bulk InAs conduction, then the measured carrier density should depend upon layer thickness, since there would be no change expected in the presumed surface accumulation layer. To perform this evaluation a second sample identical to that used for the transport measurements thus far was grown, with the only difference being the relaxed InAs layer thickness was increased from 1 to 2 microns. Table 8.1 lists sheet carrier concentrations for both samples as a function of the InAs layer thickness. As seen, the measured sheet carrier concentration varies proportionally with the layer thickness, proving the somewhat controversial result that lateral transport is dominated by the bulk
electrons and not by a surface accumulation layer. While at first this appears to contradict the earlier Hall measurement results on InAs bulk and highly defective material, [6, 7, 8, 9] the impact of intentional doping must first be accounted for to generate a complete understanding. What can be concluded with certainty at this point is that for n-type 1x10^{18} \text{ cm}^{-3} \text{ InAs layers}, the surface accumulation layer, if present, has no impact on Hall measurements and Hall data obtained only reflect transport properties of carriers in the bulk InAs layers.

Table 8.1 Sheet carrier concentrations of 1 \mu m and 2 \mu m metamorphic InAs layer grown on InP substrates using 5-step InAsP graded buffers.

<table>
<thead>
<tr>
<th>Run #</th>
<th>InAs thickness</th>
<th>Sheet carrier concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSU1687</td>
<td>1 \mu m</td>
<td>1.04x10^{14} \text{ cm}^{-2}</td>
</tr>
<tr>
<td>OSU1695</td>
<td>2 \mu m</td>
<td>2.04x10^{14} \text{ cm}^{-2}</td>
</tr>
</tbody>
</table>

To explore deeper, the conductivity of the InAs layer itself must be considered. The probable reason for the absence of the surface accumulation layer conduction in Hall measurements so far is probably the significantly higher conductivity of the bulk InAs layer in contrast to that of the surface accumulation layer. For n-type semiconductors, the conductivity \sigma can be written as
\[ \sigma = en\mu \]  \hspace{1cm} (8.1)

where \( e \) is the electron charge, \( n \) is the electron concentration, and \( \mu \) is the electron mobility. [16] For the surface accumulation layer, the sheet carrier concentration is typically reported to be on the order of \( 10^{12} \, \text{cm}^2 \) and the electron mobility around 4000 \( \text{cm}^2/\text{Vs} \). [17] In contrast, the bulk InAs layer has a sheet carrier concentration of \( 1 \times 10^{14} \, \text{cm}^2 \) and the electron mobility of \( \sim 1 \times 10^4 \, \text{cm}^2/\text{Vs} \) based on the measured data. Hence, the conductivity of the bulk InAs layer is more than 2 orders of magnitude higher than that of the surface accumulation layer and thus the transport of the bulk InAs layer dominates in Hall measurements.

To verify this logic, 1 \( \mu \text{m} \) thick, relaxed InAs layers were grown on a 5-step InAsP buffer identical to the structure shown in Fig. 7.3 but with an n-type (Si) doping level reduced to a value of \( 1 \times 10^{17} \, \text{cm}^{-3} \). Fig. 8.3 shows the resultant room temperature QMSA spectrum in which two types of conduction electrons are now evident. One set of conduction electrons is present with a sheet carrier concentration of \( 1.12 \times 10^{13} \, \text{cm}^2 \) and an electron mobility of \( 20287 \, \text{cm}^2/\text{Vs} \), which correlates with the 1 \( \mu \text{m} \) thick n-type \( 1 \times 10^{17} \, \text{cm}^{-3} \) bulk InAs layer. The second set of conduction electrons has a much lower sheet carrier concentration of \( 4.05 \times 10^{12} \, \text{cm}^2 \) and an electron mobility of \( 2400 \, \text{cm}^2/\text{Vs} \). These values match those expected for the InAs surface accumulation layer reported in other works and clearly reveal how the doping of the InAs layer itself obscures the presence of this layer.

As a conclusion, the surface accumulation layer is present in relaxed InAs grown on InP using an InAsP step-graded buffer and the apparent lack of its detection for highly doped InAs is easily explained by its relatively low conductivity with respect to that of
bulk InAs. Therefore, the universality of the presence of the surface accumulation layer is confirmed, but its role can be diminished through doping.

![Graph](image)

**n-type 1x10^{17} cm^{-3}**

Fig. 8.3 QMSA spectrum of 1 µm InAs with the n-type doping of 1x10^{17} cm^{-3}, in which the surface accumulation layer conduction can be observed.

### 8.4 InAlAs/InAs heterostructures on relaxed InAs virtual substrates

With the additional understanding gained regarding the InAs bulk transport properties and their measurements, we now turn to the use of these relaxed InAs layers to support 2DEG structures based on simple InAlAs/InAs heterostructures. To date, all such “device” structures using InAs as transport channels have done so based on thin,
strained InAs where the InAs layer thickness reduces power handling in such device structures. This section provides a discussion of the transport properties of InAlAs/InAs heterostructures grown on InP using an InAsP graded buffer, which are enabling for eventual InAs FETs on virtual InAs.

8.4.1 Sample structure of In0.8Al0.2As/InAs heterostructures grown on a 5-step InAsP graded buffer

The In0.8Al0.2As/InAs heterostructure with the InAsP step-graded buffer is schematically depicted in Fig. 8.4. The InAsP step-graded buffer used in this study consists of five unintentionally doped layers, each of 3000 Å, with layer compositions shown in the figure. The detailed growth information of this InAsP buffer can be found in that last chapter. The buffer layers are followed by 1 µm InAs layer, which completes the virtual InAs substrate, capped with a 10 nm In0.8Al0.2As to finish the heterostructure. The 10 nm In0.8Al0.2As cap layer is well below its critical thickness (~ 30 nm) on relaxed InAs so that a high quality barrier confinement can be provided for a 2DEG structure. In Fig. 8.4, a schematic band diagram of an InAlAs/InAs 2DEG structure is also illustrated. In order to diminish the effect of buffer during electrical characterization of the heterostructure discussed later, both the InAlAs and InAs layers were doped with Si at a concentration of 1x10^{18} cm^{-3}. Nominal growth temperatures for the In0.8Al0.2As/InAs heterostructure were 500 °C, as determined by optical pyrometry.
8.4.2 2DEG in In$_{0.8}$Al$_{0.2}$As/InAs heterostructures with an InAsP graded buffer

Temperature-dependent Hall (van der Pauw) measurements were performed from 25 to 300 K to explore carrier transport properties within the InAlAs/InAs heterostructures. In order to ensure that the measured transport properties are unambiguously attributed to the heterostructure region without interference from possible parallel conduction through the underlying, conductive InAsP step-graded buffers, we chose to intentionally dope the InAlAs/InAs heterostructure to a high enough level
such that electron transport within these very low resistivity layers would dominate the van der Pauw measurement. Separate resistivity measurements confirmed that the doped InAlAs/InAs resistivity of $\sim 5 \times 10^{-4} \, \Omega \cdot \text{cm}$ was approximately 2 orders of magnitude lower than that of the undoped InAsP graded buffer region. We note that such a doping scheme would not be included for an optimized FET, but here it serves the purpose of revealing the impact of material quality on relaxed InAs transport properties. QMSA was also employed here to isolate the spectrum of carriers solely attributable to the InAs in order to determine the carrier mobility and the sheet carrier concentration specifically for that layer. The measured dependence of both the electron mobility and sheet carrier concentration on temperature are shown in Fig. 8.5, indicating the presence of a dominant 2DEG. The maximum measured electron mobility is 133 000 cm$^2$/Vs at 25 K and the mobility displays a strong and monotonic decrease with increasing temperature. At room temperature (300 K), the mobility is $\sim 28000 \, \text{cm}^2/\text{Vs}$ with measured 2DEG sheet carrier concentration of $1.1 \times 10^{12} \, \text{cm}^{-2}$, with the source of channel electrons likely being both the InAlAs barrier and the doped InAs bulk layer. Note that this large sheet carrier density is achieved in spite of the relatively low confinement provided by the $\text{In}_{0.8}\text{Al}_{0.2}\text{As} (E_g = \sim 0.79 \, \text{eV})$ barrier in these simple test structures.
Fig. 8.5 Temperature dependence of electron mobilities and sheet carrier concentrations for the In$_{0.8}$Al$_{0.2}$As/InAs heterostructure grown on InP with an InAs$_y$P$_{1-y}$ step-graded buffer.

It is instructive to compare these results with those obtained from a nominally identical InAlAs/InAs heterostructure grown directly on a single step InAs buffer on InP, to reveal the impact of the InAsP step-graded buffer on the 2DEG transport properties observed in relaxed InAs layers. Figure 8.6 shows a schematic for this single step structure. The Hall effect measurements made on these samples revealed a very different behavior, with no evidence for 2DEG transport in the InAlAs/InAs heterostructures grown without benefit of the graded buffer. Here the electron mobility is approximately
temperature-independent with a value of \(\sim 14000 \text{ cm}^2/\text{Vs}\) and the sheet carrier concentration is \(\sim 1.0 \times 10^{14} \text{ cm}^{-2}\), which implies that the Si-doped InAs bulk layer and not a thin 2DEG channel, dominates carrier conduction (noting that this sheet carrier concentration translates to \(\sim 1 \times 10^{18} \text{ cm}^{-3}\) when integrated over the 1 \(\mu\)m InAs layer thickness). Due to the high doping of the InAs layer, impurity scattering plays the most important role in the bulk carrier transport and thus leads to the insensitivity of electron mobility on temperature, consistent with the assignment of a bulk-dominated transport mechanism for this sample.

![Fig. 8.6 Schematic cross-section of In\(_{0.8}\)Al\(_{0.2}\)As/InAs heterostructures grown on InP with an direct-growth InAs buffer.](image)

| 10 nm In\(_{0.8}\)Al\(_{0.2}\)As n type 1x10\(^{18}\) cm\(^{-3}\) |
| 1 \(\mu\)m InAs layer n type 1x10\(^{18}\) cm\(^{-3}\) |
| 1.5 \(\mu\)m n-d InAs |
| InP substrate |
Fig. 8.7 directly compares the electron mobility behavior as a function of temperature for InAlAs/InAs heterostructures grown on the step-graded and single step buffer. The large difference in mobility characteristics can be understood by realizing that the \( \text{In}_{0.8}\text{Al}_{0.2}\text{As/InAs} \) heterostructure is a multi-conduction-channel system, in which carriers are concentrated at the \( \text{In}_{0.8}\text{Al}_{0.2}\text{As/InAs} \) heterointerface and also within the InAs bulk layer. With the \( \text{InAs}_y\text{P}_{1-y} \) step-graded buffer present, a high-mobility 2DEG forms at the InAlAs/InAs interface and these high-mobility 2D carriers dominate the Hall measurements. On the other hand, the obvious domination of transport by the InAs bulk layer in the heterostructure without the graded buffer layers suggests the lack of a parallel high-mobility 2DEG transport region.

### 8.4.3 Impact of threading dislocations on the 2DEG mobility

It is clear from the discussion above that the buffers are essential to observe the presence of 2DEG transport in overgrown \( \text{In}_{0.8}\text{Al}_{0.2}\text{As/InAs} \) heterostructures. The probable reason for the vanishing 2DEG in InAlAs/InAs heterostructures grown on relaxed InAs layers on mismatched substrates without a graded buffer is its much higher TD density, which is consistent with earlier work also on \( \text{In}_{0.8}\text{Al}_{0.2}\text{As/InAs} \) heterostructures but grown instead on non-graded InAs/GaP substrates. [19]
According to Matthiessen’s rule, the 2DEG mobility $\mu_{2DEG}$ can be expressed as

$$\frac{1}{\mu_{2DEG}} = \sum_i \frac{1}{\mu_i} \quad (8.2)$$

where $\mu_i$ represents the mobility contribution from different scattering mechanisms, which include alloy scattering, interface scattering, background impurity scattering, and...
charged threading dislocation scattering, etc. Here, since we want to focus on the impact of charged dislocation scattering, the equation (8.2) can be re-written to be

\[
\frac{1}{\mu_{2DEG}} = \frac{1}{\mu_0} + \frac{1}{\mu_{TD}}
\]  

(8.3)

where \(1/\mu_{TD}\) is the threading dislocation scattering contribution and \(1/\mu_0\) represents the summation of all other scattering contributions.

Based on a model described in Ref. 20, the charged threading dislocation scattering time for 2DEG can be approximately given as

\[
\tau_{2D}^{TD} \approx \frac{2\hbar^3 e^2}{\epsilon_0^2 c_0^2} \frac{1}{N_{TD} \pi^2 m^* e^4 f^2} \frac{1}{(1.84k_F^2 q_{TF} - 0.25)}
\]

(8.4)

where \(N_{TD}\) is the threading dislocation density, \(f\) is the fraction of filled states, which is assumed to be 1 in this model, \(c_0\) is the lattice spacing in the (001) direction, \(k_F\) is the Fermi wave vector, which is defined as

\[
k_F = \sqrt{\frac{2\pi n_s}{m}}
\]

(8.5)

where \(n_s\) is the 2DEG sheet carrier concentration, which can be determined experimentally using Hall measurements, and \(q_{TF}\) is the 2D Thomas Fermi wave vector,
\[
q_{TF} = \frac{2}{a_B^*}
\]  

(8.6)

where \(a_B^*\) is the effective Bohr radius. [20] Hence the contribution of the threading dislocation scattering can be expressed as

\[
\mu_{TD}^{2D} = \frac{e\tau_{TD}^{2D}}{m^*} \approx \frac{2\hbar^3 e^2 e_b^2 e_c^2 k_F^4}{N_{TD} \pi^2 (m^*)^2 e^3 f^2} \cdot \frac{1}{\left(\frac{1.84k_F}{q_{TF}} - 0.25\right)}
\]  

(8.7)

Based on TEM results shown in chapter 7, the threading dislocation densities for InAs with/without the InAsP step-graded buffer were below 1x10^7 cm^-2 and ~5x10^8 cm^-2, respectively. If we assume that the threading dislocation density in the InAs layer with InAsP buffers is 1x10^7 cm^-2, increasing the threading dislocation density to 5x10^8 cm^-2 reduces the calculated mobility of electrons in the 2DEG region to below 10000 cm^2/Vs, which is lower than the measured carrier mobility (14000 cm^2/Vs) for the InAlAs/InAs heterostructure grown on the direct growth InAs buffers. The calculated results are shown in Fig. 8.7, together with experimental data for comparison purposes. We can thus conclude that bulk carrier transport dominates the Hall measurement in the absence of threading dislocation density-reducing graded buffers due to the very low 2DEG mobilities at this higher threading dislocation density, demonstrating the need for threading dislocation reduction to achieve high mobility InAs channels.
8.5 Conclusions

In conclusion, transport properties of relaxed InAs grown on InP using InAsP graded buffers have been investigated using conventional Hall effect and QMSA. Higher electron mobilities were observed in InAs with a 5-step InAsP graded buffer in contrast to the 4-step sample, indicating that superior structural properties (fewer defects and reduced mosaicity) translates into high electronic properties (high electron mobilities) for the relaxed InAs grown on the 5-step InAsP graded buffer. Additionally, a surface accumulation layer was found in InAs with graded buffers with an electron mobility of 2400 cm²/Vs and a sheet carrier density of 4.05x10¹² cm⁻². Due to its relatively low conductivity, this surface conduction layer could be obscured in Hall effect measurements for highly doped InAs with graded buffers.

2DEG transport in relaxed InAs layers has been demonstrated using an InAlAs/InAs heterostructures grown on metamorphic InAsP/InP substrates. This is the first reported InAs 2DEG achieved using relaxed epitaxial InAs materials. At room temperature, an electron mobility of 28 000 cm²/Vs was measured with a sheet carrier density of 1.1x10¹² in spite of using a relative low band gap In₀.₈Al₀.₂As carrier confinement layer. A peak mobility of 133 000 cm²/Vs was observed at 25 K. In contrast, no 2DEG transport was observed for identical heterostructures using direct-growth buffers, which instead revealed InAs bulk-limited transport characteristics. Model calculations based on measured threading dislocation densities reveal that dislocation scattering within the relaxed InAs channel is the dominant scattering limitation for these heterostructures, demonstrating promise for the use of relaxed, virtual InAs substrates based on graded InAsP/InP in future InAs HEMT device applications.
8.6 References


CHAPTER 9

CONCLUSIONS

9.1 Summary

This dissertation provides a systematic study on material science and potential for device applications of mixed-anion InAsP step-graded buffers grown on InP substrates, which includes background, buffer design, crystal growth, and material and device characterization.

All samples used in this study were grown by solid source molecular-beam epitaxy. First of all, the composition calibration of InAsP, ranging from 5% As to 90% As, was carried out to provide a roadmap for this research. To our knowledge, it is the first time that such large range calibration has been achieved for InAsP using solid source molecular-beam epitaxy.

In the low-misfit regime of InAsP step-graded buffers (the As composition < 40% and the misfit < 1.3%), InAsP step-graded buffers were compared with mixed-cation InAlAs step-graded buffers in structural properties. In principle, mixed-anion semiconductor materials have more degrees of freedom than mixed-cation semiconductor
materials in crystal growth due to the decoupling of the growth rate and the chemical composition during the growth of mixed-anion materials. Our experimental results have proven this to be true for MBE growth. This work has demonstrated that InAsP step-graded buffers exhibited smoother surface morphology and lower defect density in contrast to InAlAs step-graded buffers. The TEM results (cross-section and plan-view) indicated that InAsP step-graded buffers graded out to InAs$_{0.4}P_{0.6}$ on InP, a 1.3% total misfit, have yielded low threading dislocation densities in the $\sim 4 \times 10^6$ cm$^{-2}$ range. InAlAs structures show evidence for alloy decomposition and/or complex defects such as branches and stacking faults. No such defects were seen using InAsP over identical misfit ranges.

In order to optimize and understand InGaAs/InAsP/InP heterostructures from the viewpoint of electronic device application, minority carrier recombination was studied using photoconductive decay (PCD) in InAsP/InGaAs double heterostructures grown on InAsP step-graded buffers. High minority carrier lifetimes of $4 - 5 \mu$s close to the radiation limit were measured, indicating the ability of InAsP step-graded buffers in achieving high material quality mismatched InGaAs layers. Analysis of the recombination lifetimes suggests that very low interface recombination velocities were achieved at InAsP/InGaAs interfaces. During this study, a photogenerated carrier diffusion model was proposed to explain the initial nonlinear decay observed in PCD data for these heterostructures.

Based on results obtained in the first (low misfit) stage of the research, InAsP step-graded buffers were extended all the way to support metamorphic InAs on InP substrates, i.e. virtual InAs substrates. Different buffer designs have been firstly
compared and evaluated based on their structural properties. In contrast to 4-step graded
buffer structures, 5-step and 6-step samples exhibited superior surface morphology, lower
defect densities, and less mosaicity, indicative of higher material quality. In addition, a
large epitaxial tilt is observed in relaxed InAs grown on InP using InAsP step-graded
buffers. Because the conventional double-axis XRD tilt analysis method fails to provide
reasonable results due to the existing large tilt, a new tilt analysis method using reciprocal
space mapping has been developed. Using this new method, the epitaxial tilt were
determined to be 5598, 4880, 4924 arcsec for 4-step, 5-step, and 6-step samples,
respectively. As a result, the new method offers an alternative for the tilt characterization
of crystalline materials and provides more reliable results as compared to the
conventional method for samples with a large epitaxial tilt.

Transport property investigation revealed that InAs grown on the 5-step graded
buffer has higher electron mobilities as compared to that grown on the 4-step buffer,
demonstrating superior structural properties (fewer defects and reduced mosaicity)
translates into high electronic properties (high electron mobilities) for the relaxed InAs
grown on the 5-step InAsP graded buffer. During the transport property investigation, a
surface accumulation layer has been confirmed to be present on the surface of the
metamorphic InAs layer. Due to its relatively low conductivity, the existence of the
surface accumulation layer has little impact on transport properties of the highly doped
InAs layer in Hall measurements.

2DEG transport in relaxed InAs layers have been demonstrated using an
InAlAs/InAs heterostructure grown on metamorphic InAsP/InP substrates. At room
temperature, an electron mobility of ~ 28000 cm²/Vs was measured by Hall effect with a
sheet carrier density of $1.1\times10^{12}\text{cm}^{-2}$ in spite of using a relatively low bandgap In$_{0.8}$Al$_{0.2}$As carrier confinement layer. In contrast, no 2DEG transport was observed for identical heterostructures grown on InP with an InAs direct-growth buffer. This fact, combined with both TEM measurements and model explanation reveal the need for reduced threading dislocation density to achieve the maximum electronic quality and potential performance for InAs HEMT structures grown on InP and the promise of using InAsP buffers for this purpose. This is the first report of 2DEG behavior in epitaxial, relaxed InAs.

### 9.2 Recommendations for future work

Future work should focus on several key areas. First is the continued optimization of InAsP step-graded buffers for supporting high material quality InAs and other III-AsP materials with lattice constants between that of InP and InAs, grown on virtual InAsP substrates. This includes working to thin the buffer and optimizing number of steps, and so on. Second is the need to understand issues of doping levels and different Al content barriers in order to optimize 2DEG properties in general and apply these structures to generate new device structures made available by the high quality lattice-tunable substrate. And finally, the notion of anion sublattice engineering is generically of interest for other virtual substrates. In particular the lattice constant range between GaAs and InP can be accessed using InGaAsP grading on the AsP sublattice. These are each described briefly below.
9.2.1 Optimization of InAsP metamorphic step-graded buffers

Based on the previous efforts to understand and optimize InAsP metamorphic buffers, systematic study should be conducted to achieve lowest threading dislocation densities at minimal buffer thickness and highest quality metamorphic InAs layers on InP. Basic growth experiments to investigate buffer strain relaxation should occur and the impact of experimental variables, including grading rate, number of steps, step thickness, growth temperature, etc., on structural and electronic properties of InAsP buffers should be evaluated. Similar to the previous work, triple-axis XRD and TEM (cross-sectional and plan-view) studies should be made so that buffer strain relaxation and dislocation densities can be related to the growth and structure properties. AFM should be employed to monitor the surface roughness and evolution of crosshatch features through this series of experiments. In addition, temperature-dependent Hall measurements should be used to systematically study carrier transport in bulk InAs layers on InAsP step-graded buffers in order to understand their electronic properties, which is required for the future design and fabrication of InAs-based device application.

Recently, a 6-step InAsP graded buffer with a total thickness of 1.2 µm has been designed based on structural investigation results of the 5-step InAsP graded buffer. The buffer structure of this 6-step graded buffer was shown in Fig. 7.6. \( \text{In}_{0.8}\text{Al}_{0.2}\text{As/InAs} \) heterostructures, consisting of a 10 nm \( \text{In}_{0.8}\text{Al}_{0.2}\text{As} \) cap and a 1 µm InAs layer, were grown on the 6-step graded buffer and 2DEG transport in InAlAs/InAs heterostructures was characterized and compared to that of 5-step samples. Because the growth of the 6-step sample was performed just after the MBE opening maintenance, another 5-step sample, with the identical structure as shown in Fig. 8.4, was also grown in order to
provide a fair comparison. Both samples were unintentionally doped in this study.

Figures 9.1 (a) and (b) show 2DEG mobilities and sheet carrier concentrations for both samples, respectively. In spite of using a thinner buffer layer, higher 2DEG mobilities were obtained in the 6-step sample in contrast to the 5-step sample, particularly in the low temperature range. Because the threading dislocation scattering increases with decreasing temperature, [1, 2, 3] this phenomenon may implies that lower densities of threading dislocations are present in the 6-step structure as compared to the 5-step structure. TEM work is still ongoing through others in our group. On the other hand, slight buffer impact can be seen in temperature dependences of 2DEG sheet carrier concentrations, as shown in Fig. 9.1 (b). These results strongly demonstrate that more improvements on InAsP step-graded buffers are possible. Hence, in the future the thickness and grading rate of InAsP graded buffer should be further optimized based on characterization results of both structural and electrical properties.
Fig. 9.1 Comparisons of (a) 2DEG mobilities and (b) sheet carrier concentrations between InAlAs/InAs heterostructures with 5-step and 6-step InAsP graded buffers.
9.2.2 InAs-based HEMT using InAsP metamorphic step-graded buffers

Table 9.1 compares 2DEG mobilities and sheet carrier concentrations (Room temperature) obtained from InAlAs/InAs heterostructures grown on InAsP step-graded buffers with those from other InAs-based HEMTs where thin and strained InAs layers are used. Based on the fact that 2DEG transport in InAlAs/InAs heterostructures grown on InP using InAsP step-graded buffers is already as good if not better than current InAs-based HEMTs, we should explore InAs HEMTs without need for a strained InAs channel using standard InP substrate technology. This means that power handling, high speed, and manufacturability are possible simultaneously for first time.

Table 9.1 Comparison of 2DEG properties for InAlAs/InAs heterostructures with other HEMT structures.

<table>
<thead>
<tr>
<th>Device materials</th>
<th>Device type</th>
<th>Mobility (cm²/νs)</th>
<th>Sheet carrier density (cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InAs-inserted InAlAs/InGaAs [4]</td>
<td>HEMT</td>
<td>16 500</td>
<td>1.96 x10¹²</td>
</tr>
<tr>
<td>InAs-inserted InAlAs/InGaAs [5]</td>
<td>HEMT</td>
<td>12 500</td>
<td>3.5 x10¹²</td>
</tr>
<tr>
<td>InAs/InAlAs [6]</td>
<td>Heterostructure</td>
<td>28 000</td>
<td>1.1 x10¹²</td>
</tr>
</tbody>
</table>

In this upcoming research work, all HEMT device parameters, such as the spacer thickness, doping level, doping type (modulation or § doping), etc. will need to be optimized according to transistor device performance. Since there are no lattice-matched
materials available for InAs as the barrier layer in HEMT structures, a completely strained, lattice-mismatched InAlAs layer may still be selected as the barrier layer. In this case, because the barrier layer influences the band-offset, the lattice-misfit of the active region interface, and the Schottky barrier performance, the selection and optimization of the barrier layer for InAs-based HEMT structures will become a key issue in this future study. So far, we have already begun to look into these next generation structures with Prof. Wu Lu and his group at OSU.

The initial optimization has already been performed on InAlAs/InAs heterostructures using the 5-step InAsP graded buffer. This work includes effort to understand the impact of (I) doping level and (II) Al mole fraction in the InAlAs barrier layer on 2DEG in InAlAs/InAs heterostructures, which are discussed briefly in the following part of this section.

(I) Doping effect on 2DEG in InAlAs/InAs heterostructures

Following the sample structure shown in Fig. 8.4, unintentionally doped InAlAs/InAs heterostructures were grown on InP using the 5-step InAsP step-graded buffer (the background doping was determined to be \( \sim 1 \times 10^{16} \text{ cm}^{-3} \) in the InAlAs/InAs heterostructure). 2DEG transport properties in this sample were studied using Hall effect and compared to the n-type \( 1 \times 10^{18} \text{ cm}^{-3} \) sample. Fig. 9.2 (a) and (b) show comparisons of electron mobilities and sheet carrier concentrations between both samples, respectively. It is interesting to find that the doping change has little impact on the 2DEG mobilities based on data shown in Fig. 9.2 (a), implying that the impurity scattering does not play an
Fig. 9.2 Comparisons of (a) 2DEG mobilities and (b) sheet carrier concentrations between undoped and n-type $1 \times 10^{18}$ cm$^{-3}$ doping InAlAs/InAs heterostructures.
important role in 2DEG transport in InAlAs/InAs heterostructures. On the other hand, the
2DEG sheet carrier concentrations reduce as expected when the doping level in the
InAlAs/InAs heterostructures decreases, indicating that the source of channel electrons is
likely either the InAlAs barrier or the doped InAs layer or both. In order to figure out the
main source of 2DEG electrons, samples with doping only in the barrier but not InAs or
vice versa should be grown and investigated later. Furthermore, a spacer layer should be
added into InAlAs/InAs heterostructures to finish a standard HEMT structure. In the
meanwhile, the doping level should be optimized accordingly with the variation of the
spacer thickness.

(II) Effect of the Al content in the barrier layer on 2DEG in InAlAs/InAs
heterostructures

In contrast to the lattice-matched 2D EG heterostructures, like AlGaAs/GaAs
structures, changing of the Al content in InAlAs/InAs heterostructures not only modifies
the band offset but also it varies the misfit strain at the hetero-interface. Hence, it is of
special interest to study the impact of the Al content in the barrier layer on 2DEG
transport in the InAlAs/InAs heterostructure.

InAlAs/InAs heterostructures, with 20%, 30%, and 40% Al mole fractions in the
barrier layer were grown on InP with the 5-step InAsP graded buffer. In order to maintain
high material quality, the thickness of the barrier layer in each sample structure was
chosen to be 10 nm, which is well below the critical thicknesses for all three Al content
InAlAs barrier layers on relaxed InAs. Using Hall effect measurements, 2DEG transport
properties were measured and compared. Figure 9.3 shows the temperature dependence
of 2DEG mobilities for all samples. Clearly, 2DEG mobilities decrease with increasing the Al composition in the InAlAs barrier layer. This could be explained by an increase in the number of scattering centers in the higher-Al InAlAs barrier layer. [7] When the Al composition increases to 40%, no 2DEG was observed in the InAlAs/InAs heterostructure and Hall data only reflect carrier transport in the bulk InAs. The possible reason for this phenomenon is likely due to the large lattice misfit (~2.6%) between the \( \text{In}_{0.6}\text{Al}_{0.4}\text{As} \) barrier and relaxed InAs. Since the lattice misfit is too large to maintain a two-dimensional growth mode, the degraded barrier layer and the InAlAs/InAs interface could not support high mobility 2DEG in the structure. [8]

Fig. 9.3 Comparison of 2DEG mobilities of InAlAs/InAs heterostructures grown on InP using a 5-step InAsP graded buffer with different Al compositions. No 2DEG was observed in the 40% Al InAlAs/InAs heterostructure.
Fig. 9.4 shows 2DEG sheet carrier concentrations as a function of temperature for both the 20% and 30% Al InAlAs/InAs heterostructures, which clearly reveals different temperature dependences of sheet carrier concentrations for different samples. The reason for this phenomenon has not been completely understood yet. It could be caused by the different material quality of the InAlAs barrier layer due to different Al content and also different misfit strain, or it could be related to different amount of oxygen incorporated in the InAlAs barrier layer. Further analysis using high-resolution TEM and secondary ion mass spectrometry will be required to further clarify this issue.

Fig. 9.4 Comparison of 2DEG sheet carrier concentration between the In$_{0.8}$Al$_{0.2}$As/InAs and In$_{0.7}$Al$_{0.3}$As/InAs heterostructures grown on InP using a 5-step InAsP graded buffer.
As discussed early in this section, a high Al content barrier would degrade or even eliminate 2DEG in InAlAs/InAs heterostructures. However, HEMT devices usually need a high Al content InAlAs barrier (large bandgap) for the fabrication of a high-quality Schottky contact. To compromise this conflict, a two-layer InAlAs barrier could be tried on potential InAlAs/InAs HEMT structures. Fig. 9.5 schematically illustrates the two-layer barrier structure, the lower layer with low Al content used to maintain a high quality 2DEG and the higher layer with high Al content used to provide a large bandgap for the Schottky contact requirement. Hence, this two-layer barrier design can simultaneously satisfy demands from both sides. Based on 2DEG transport properties, the thicknesses and compositions of this two-layer structure should be optimized accordingly.

Two-layer InAlAs barrier

![Two-layer InAlAs barrier diagram](image)

Fig. 9.5 Schematic diagram of a two-layer InAlAs barrier for InAs HEMTs
9.2.3 Anion graded InGaAsP metamorphic step-graded buffers on GaAs

By analogy with the work shown here using the group V sublattice to grade between InP and InAs, one can envision using InGaAsP to achieve a similar approach between the equilibrium GaAs and InP lattice constants. Many technologies are desiring heterostructures in this range but the lack of conventional substrate wafers continue to impose limitations. We suggest exploring InGaAs$_{y}$P$_{1-y}$ metamorphic buffers on GaAs as an extension of the anion grade concept from InAsP metamorphic buffers on InP. Taking advantage of the fact that In$_{0.49}$Ga$_{0.51}$P is lattice matched to GaAs, the lattice constant of InGaAsP metamorphic buffers can be expanded by incrementally substituting As for P on the anion sublattice. The optimal buffer designs for this quaternary buffer on GaAs may be quite different from the InAsP metamorphic system owing to some key material dependent differences, such as dislocation interactions, dislocation nucleation rates, and dislocation glide barriers. Issues like these are compelling and direct comparisons of strain relaxation and dislocation features on each substrate in parallel will generate considerable new information about lattice engineering in III-V semiconductors.
9.3 References


75. F. J. Giessibl, Reviews of Modern Physics, 75, 949 (2003).


108. EMDL P handing manual.


133. R. N. Sacks and S. A. Ringel, unpublished.


