Optimization of Metamorphic Materials on GaAs Grown by MBE

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Abstract

Advanced epitaxial technologies such as molecular beam epitaxy (MBE) and metal-organic vapor phase epitaxy (MOVPE) have enabled the idea of semiconductor heterostructures, which built up the foundation of the fast developing information and communication technology nowadays. Lattice mismatch has been a problem limiting designs of semiconductor heterostructures. Restricted by the availability of large and high-quality commercial substrates, only a small range of materials with a lattice constant close to certain substrate, such as GaAs and InP, could be chosen. Metamorphic growth is one of the solutions by which a virtual substrate with a desired lattice constant can be obtained after growing a mismatched but nearly relaxed buffer layer on a conventional substrate. The main challenges of this method are the rough interface and a high threading dislocation (TD) density in the active region of the devices. The TD problem is more severe for optoelectronic devices, such as lasers, which have a large device area, and therefore can easily contain TDs in the active region. Although there have been notable progresses for metamorphic optoelectronic devices in recent years, further reduction of the TD density is still required to improve the performance and make them competitive with existing products.

In this work, we investigate and optimize growth schemes of metamorphic buffer layers grown on GaAs substrate by MBE. Effects of both n- and p-type doping on material quality in alloy graded InGaAs buffers with different parameters, such as grading profiles, grading slopes, In compositions and thicknesses are studied systemically. Moreover, further TD reduction by nitrogen incorporation in metamorphic buffers is demonstrated. The physical origin is found to be due to both the strain and the lattice hardening effect. These results show that by proper designs of the metamorphic buffers there are great potentials to further improve the quality of metamorphic heterostructures and enhance the performance of metamorphic optoelectronic devices.

Keywords: metamorphic, heterostructures, molecular beam epitaxy, alloy graded buffer, threading dislocation, InGaAs, GaAs
List of papers

Appended papers:


Other papers not included in this thesis:


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Göteborg

May 2010
### List of acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>2D</td>
<td>two-dimensional</td>
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<tr>
<td>3D</td>
<td>three-dimensional</td>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>AR</td>
<td>anisotropic ratio</td>
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<td>FEM</td>
<td>finite element method</td>
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<td>FIB</td>
<td>focused ion-beam</td>
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<td>FWHM</td>
<td>full-width-at-half-maximum</td>
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<tr>
<td>HEMT</td>
<td>high-electron mobility transistor</td>
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<tr>
<td>LAG</td>
<td>linear alloy grading graded</td>
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<td>LTG</td>
<td>linear source temperature grading/graded</td>
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<td>MBE</td>
<td>molecular beam epitaxy</td>
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<td>MD</td>
<td>misfit dislocation</td>
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<tr>
<td>M-LTG</td>
<td>mirrored linear source temperature grading/graded</td>
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<tr>
<td>MOCVD</td>
<td>metal-organic chemical vapour deposition</td>
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<td>MOVPE</td>
<td>metal-organic vapor phase epitaxy</td>
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<td>PL</td>
<td>photoluminescence</td>
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<td>QD</td>
<td>quantum dot</td>
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<td>QW</td>
<td>quantum well</td>
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<td>RHEED</td>
<td>high-energy electron diffraction</td>
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<td>RMS</td>
<td>root mean square</td>
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<td>SL</td>
<td>superlattice</td>
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<td>TD</td>
<td>threading dislocation</td>
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<td>TEM</td>
<td>transmission electron microscopy</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XTEM</td>
<td>cross-sectional transmission electron microscopy</td>
</tr>
</tbody>
</table>
# Table of Contents

Abstract ....................................................................................................................................... i  
List of papers ............................................................................................................................ iii  
Acknowledgement ..................................................................................................................... v  
List of acronyms ...................................................................................................................... vii  
Table of Contents ...................................................................................................................... ix  
1 Introduction ........................................................................................................................ 1  
   1.1 Background and motivation ........................................................................................ 1  
   1.2 Overview of metamorphic growth .............................................................................. 3  
   1.3 Vision of this thesis ..................................................................................................... 3  
2 Strain relaxation in heterostructures ................................................................................... 5  
   2.1 Lattice mismatch and strain ....................................................................................... 5  
   2.2 Ways of strain relaxation ............................................................................................ 6  
      2.2.1 Formation of 3D islands ....................................................................................... 6  
      2.2.2 Misfit dislocations ............................................................................................... 7  
      2.2.3 Cracks .................................................................................................................. 8  
      2.2.4 Coherent elastic deformation ............................................................................... 9  
   2.3 Dislocations in zincblende crystals ........................................................................... 10  
      2.3.1 Formation of dislocation half loops ................................................................... 10  
      2.3.2 Glide and interactions of 60° dislocations ......................................................... 11  
      2.3.3 Formation of edge dislocations .......................................................................... 13  
3 Alloy-graded metamorphic buffer layers and doping effect ............................................ 15  
   3.1 Strain relaxation in alloy graded buffer layers .......................................................... 16  
      3.1.1 “Dislocation-free” region and residual strain .................................................... 16  
      3.1.2 Step-like strain relaxation .................................................................................. 18  
   3.2 In segregation ............................................................................................................ 19  
      3.2.1 Theoretical model ............................................................................................... 19  
      3.2.2 Edge type TD formation caused by In segregation ............................................ 20  
      3.2.3 Doping effect on In segregation ........................................................................ 21  
3.3 Doping effect on dislocation kinetics .......................................................................... 23  
3.4 Design of alloy-graded buffers for optoelectronic devices .......................................... 24
1 Introduction

1.1 Background and motivation

An idea called “semiconductor heterostructures” has brought us an irresistible new everyday life style with mobile phone, computer, internet, high resolution TV etc, and also the Nobel Prize in Physics to Zhores I. Alferov and Herbert Kroemer in 2000. The idea is that if one can put layers of different semiconductor crystals with different bandgaps, refractive indices etc, on top of each other, the performance of the devices should be superior to the conventional ones.

Realization of this idea was implemented by the development of epitaxial technology, which has paved the road to the fast developing information and communication technology nowadays [1]. The epitaxy of heterostructures, namely heteroepitaxy, has already become a common technology for the semiconductor industry. There are several existing epitaxial growth methods, among which molecular beam epitaxy (MBE) and metal-organic vapor phase epitaxy (MOVPE) have emerged to be the most advanced and widely applied techniques for both research and industrial production. They have advantages over other methods such as flexibility with material combination, excellent uniformity and precise control of doping, alloy composition and thickness for growth of very thin layers [2]. Thanks to MBE and MOVPE, many quantum heterostructure devices have been realized both in laboratories and as real products with high performance such as different types of semiconductor lasers [3,4,5,6], high-electron mobility transistors (HEMTs) [7] and high efficiency multi-junction solar cells [8,9], etc.

Modern heteroepitaxy provides a great freedom on designing heterostructures. However, at a very high evolution pace, the freedom soon meets some practical limitations, the most crucial one of being lattice mismatch. Semiconductor materials are single crystals with own characteristic crystal structures and lattice constants. If one thin layer of crystal is grown onto a substrate with a different lattice constant, the atoms in the epi-layer will be forced to align with the lattice below [10]. This phenomenon is called pseudomorphic growth and the epi-layer is fully strained in this case. The strain force or energy will be accumulated while the epi-layer is growing thicker until a critical point [11], at which the strain starts to relieve by formation of three-dimensional (3D) islands on the growth front or misfit dislocations (MDs) inside the crystal. The MDs are often in the form of section of lines lying at the interface and leave threading components called threading dislocations (TDs) through subsequent heterostructures. In most cases, the TDs have an adverse effect that can kill devices.

All heteroepitaxy growth must start from a substrate, which should have a relatively large area, very smooth surface, high uniformity, low dislocation density and affordable price. These criterions filter out most of the possibilities and leave for example Si (001), Si (111), GaAs (001), InP (001), 6H-SiC (0001), 4H-SiC(0001) and sapphire (0001) wafers as standard
commercially available substrates [2]. The restriction of the substrate choice gives a severe limitation on design of epi-layers. Only the materials with a lattice constant very close to that of substrate can be employed as building blocks of heterostructures and devices. Fig. 1-1 shows a diagram of bandgap vs. lattice constant for most common binary III-V compounds and group IV crystals. Taking GaAs or InP substrates for instance, only the combinations within the grey area can be chosen to design devices except some very thin layers such as a quantum well (QW). However, even the thickness of a very thin QW (<10 nm) is still limited by the critical thickness relative to the substrate. For example, a 1.3 μm pseudomorphic In_xGa_{1-x}As QW laser can never be realized when directly grown on a GaAs substrate. The minimum In composition needed from the strained bandgap of bulk InGaAs is 45.5% but it has a critical thickness of less than 3 nm on a GaAs substrate [12]. Other practical applications requiring the solutions to the substrate problem are Ga(Al)N growth for visible and ultraviolet light emission [13], extending laser and detector wavelength on GaAs to above 1.3 μm [14,15,16,17,18,19,20,21], integration of GaAs and/Si based devices on Si [22,23,24,25,26,27,28,29] and multiple junction solar cells [9,30,31] etc.

Metamorphic growth is one of the possible solutions to go beyond the substrate limitation. In this approach, a buffer layer is first grown on top of a standard substrate. This buffer layer should be thick enough that the strain is mostly relaxed. Then a virtue substrate or template with a desired lattice constant and acceptable quality is obtained, on which a prescribed device can be grown without strain relaxation. The metamorphic growth offers a large freedom for design of electronic and optoelectronic devices.
1.2 Overview of metamorphic growth

After the first experiments with the idea of metamorphic growth in the 1970s and 80s [32,33], there has been extensive studies in different material systems such as InGaAs on GaAs [34,35], SiGe on Si [36], AlGaAsSb on GaAs [37], InGaP on GaAs [38], GaAs on Si [39], etc.

The early tries to make metamorphic devices were mainly aimed on lasers [33,40,41,42]. However after the first arising in the 1990s [43,44], metamorphic HEMTs were found to be compatible with those based on InP [45] and have become the most successful metamorphic devices - the only type that has been commercialized. Nowadays, metamorphic technique plays an important role in GaN related high bandgap applications as well as in multiple junction solar cells that have shown the highest conversion efficiency [8, 9].

There have been remarkable progresses for the metamorphic lasers working at telecom wavelength range in recent years. The first approach was the demonstration of quantum dot (QD) lasers emitting at 1.27- 1.34 μm [46] initially by the research groups from University of New Mexico, USA and from Ioffe Institute, Russia, together with Technical University of Berlin, Germany [47]. The laser performance has been improved and the lasing wavelength has been push to around 1.5 μm [15,17,18,20,49,50,51,52,53]. Another approach is based on metamorphic QWs [21,42,54,55,56].

Our group has been working on metamorphic QW lasers at telecom wavelength since 2003 and has made remarkable breakthroughs including the demonstration of the world first 1.34 μm InGaAs QW lasers under continuous wave excitation [57,58] and the world first 1.55 μm metamorphic InGaAs QW lasers at room temperature [59] in collaboration with Institute of Semiconductors, Chinese Academy of Sciences, China.

1.3 Vision of this thesis

Although great progresses have been made for the metamorphic technology, the performance of the metamorphic optoelectronic devices can still hardly compete with the conventional counterparts. The rough interface and the high TD density are the main challenges of the metamorphic growth, and they can be more severe for optoelectronic devices. Since optoelectronic devices, such as lasers, commonly have a much larger device size (1 μm to 1 mm) than the electronic devices like HEMT (gate length in 100 nm or smaller), it is very easy for device structures to contain TDs in the active regions. Metamorphic buffers must be further optimized in order to reduce the TD density and interface roughness, and consequently enhance the optical quality and improve the device performance to make them competitive with existing products.
Use of an alloy graded buffer is one of the most successful metamorphic growth schemes and has been extensively investigated for several material combinations under different growth conditions [61, 62, 63, 64, 65, 66]. By continuously changing the alloy composition in the buffer layer, dislocations can be mostly confined in the bottom part of the buffer layer leaving a nearly dislocation free and fully strained top layer which acts as a virtual substrate with a desired lattice constant. In our previous work we have found that doping can have a strong influence on both the surface morphology and structural properties of the alloy graded buffers. The basic result is that Be-doping improves material properties while the Si degrades them. Part of the work in this thesis is to further study the doping effect in buffers with different alloy grading profiles and grading slopes in order to further optimize the design of alloy graded buffers. Another part of the work is to investigate other methods for TD blocking. By combing a conventional metamorphic buffer with other TD blocking techniques, the metamorphic growth is capable of producing high quality virtue substrates for optoelectronics devices based on cheap commercial substrates.
2 Strain relaxation in heterostructures

2.1 Lattice mismatch and strain

When a thin crystal film is epitaxially grown on a substrate, the lattice of the atoms in the epi-layer tends to align with those in the substrate if the film thickness is much smaller than that of the substrate (typically 300 µm). In the ideal case, the two lattices will align perfectly in the lateral direction and thus the lattice of the epi-layer is forced to deform in both lateral and vertical directions leading to strain in the epi-layer.

Lattice mismatch is one of the key issues to be considered when designing and growing heterostructures. It represents the difference in lattice constants between the epi-layer and the substrate and is defined as:

\[ f = \frac{a_e - a_s}{a_s} \]  

(2-1)

where, \( a_s \) and \( a_e \) are the relaxed lattice constants of the substrate and the epi-layer, respectively. It is sometimes confusing when reading from different literatures that the lattice mismatch may also be expressed as \( f = \frac{a_s - a_e}{a_s} \), \( f = \frac{a_s - a_e}{a_e} \), \( f = \frac{a_e - a_s}{a_e} \) or \( f = \frac{2a_e - a_s}{a_e + a_e} \). The absolute value of these definitions is approximately the same in most cases and the chosen definition must be consistent in any elastic theory used to study critical thickness and strain relaxation. Based on Eq. (2-1), the in-plane strain in a fully strained epi-layer is

\[ \varepsilon_\parallel = -f \]  

(2-2)

The strain in the epi-layer can be classified as two different types: compressive strain and tensile strain. Compressive strain happens when the lattice constant of the epi-layer is larger than that of the substrate, for instance InGaAs grown on GaAs. As shown in Fig. 2-1 (a), the lattice of the epi-layer is biaxially compressed to match that of the substrate in the lateral direction while elongated in the vertical direction. Tensile strain occurs in the opposite case, which is shown in Fig. 2-1 (b).

Strain plays an important role in semiconductor heterostructure devices. It provides another dimension to tailor the band structure and carrier transport. Strain is accumulated when the structure is growing thick, and sometimes causes structures to relax when it is overwhelmingly strong. In devices containing high lattice mismatch, strain relaxation is a severe harm for it can generate different types of defects which could act as carrier traps and degrade device performances. However, strain relaxation can also be utilized. The most significant example is the self-assembled QDs which are formed by nucleation and coalescence of 3D “islands” via Stranski-Krastanov [65] growth mode. QDs have been successfully used in many kinds of devices such as solar cells [66], light emitting diodes [67], diode lasers [68], etc. Another example is metamorphic growth, the main topic of this thesis.
In metamorphic buffers, strain relaxation is required mostly by formation of misfit dislocations (MDs).

In pseudomorphic devices, it is important to know how to avoid strain relaxation while in the other cases, how to relax strain in a controlled manner with as low defect density as possible is the main consideration. Therefore, it is necessary to understand the mechanism of strain relaxation and how to manipulate it.

2.2 Ways of strain relaxation

Strain in heterostructures can be relaxed in many different ways such as formation of 3D islands, formation and propagation of dislocations, cracks, and coherent elastic deformation, etc. In common III-V semiconductor devices, dislocations and 3D islands are the two ways of the most importance. All the different relaxation mechanisms are related and compete with each other. It is important to control the strain relaxation in different circumstances.

2.2.1 Formation of 3D islands

Strain can be relaxed by means of increasing surface area if the increase of the surface energy is smaller than the relief of the strain energy. This happens when the lattice mismatch is large.

Fig. 2-2 (a) shows an example of an epi-layer growing on a substrate with a smaller lattice constant. The formation of the 3D island increases the surface area, and provides extra freedoms for the atoms in the island to stretch and thus relaxes the strain.
Figure 2-2. (a) Schematic and (b) simulation by finite element method (FEM) of coherent strain relaxation in a compressively-strained In$_{0.5}$Ga$_{0.5}$As island 3D island on a GaAs substrate. The color in (b) indicates the value of the in-plane strain. The deformation is 10 times exaggerated.

The strain relaxation in 3D islands is not uniform. Fig. 2-2(b) shows simulation of the in-plane strain for a lens shaped In$_{0.5}$Ga$_{0.5}$As island grown on GaAs. It can be seen that the top part of the island is most relaxed while the edge of the island is highly strained which is consistent with the experiments [69]. Therefore, the strain can’t be fully relaxed in this way, and the relaxation is dependent on the geometry of the islands [70]. If the size of the island is large enough, the residual strain in the island will be further relaxed by formation of MDs [71].

For In$_x$Ga$_{1-x}$As grown on a GaAs substrate, the critical In composition for onset of formation of 3D islands is around 25-30% which has lattice mismatch of about 2% [12]. Coherent 3D islands without dislocations can only be formed at very high lattice mismatch [69], e.g. InAs QDs grown on a GaAs substrate.

### 2.2.2 Misfit dislocations

For lattice mismatched heterostructures with relative small lattice mismatch (<2%), strain tends to be relaxed by formation of misfit dislocations. Dislocation is a type of line defect in crystal lattice, where the periodicity of the lattice is broken. In heteroepitaxy, the thin epi-layer grows pseudomorphically until reaching a critical thickness at which the chemical bonds between the atoms will rearrange under the stress and lower the strain energy. Fig. 2-3 shows an example of a MD generated in a compressively strained epi-layer in which one row of the bonds are missing at the interface, allowing for the lattice of the epi-layer to slightly stretch towards its original size and thus releasing part of the strain.
Although only a small portion of the lattice mismatch can be relaxed by a single MD, formation of a network of orthogonal misfit dislocations is a very effective way of strain relaxation, because the MD density can be very high. For example, for a 400 nm thick In$_{0.15}$Ga$_{0.85}$As layer grown on a GaAs substrate (about 1% lattice mismatch), the MD density could be at around $1 \times 10^{11}$ cm$^{-2}$, and the relaxation rate is about 95%. If the epi-layer grows thicker, the strain can be almost fully relaxed.

Practically, a dislocation is hardly as simple as it is illustrated in Fig. 2-3. In diamond and zincblende (001) heteroepitaxial layers, most of the MDs are of 60° type [72] which is a mixed type of the two basic types of dislocations: edge and screw dislocations [73]. Therefore, it is important to understand this type of dislocations that will discussed in detail in Section 2.3.

2.2.3 Cracks

Cracks only happen in tensile-strained epi-layers and often replace the formation of MDs. When the tensile strain energy accumulated in a pseudomorphic layer is strong enough, the lattice of the epi-layer may shrink back laterally and leaves vacancy and new surfaces between the two parts of the crystal. Crack is a common problem in III-nitride materials [74] but also for other III-V materials for example when InGaAs grown on InP [74, 75]. Fig. 2-4 shows an example of a crack formed in a GaAsN buffer grown on GaAs [38].
2.2.4 Coherent elastic deformation

Strain relaxation through elastic deformation could become significant in nano-scale structures like nanowires. Small structures have a larger surface to volume ratio, thus a larger freedom for elastic deformation than in bulk structures. Fig. 2-5 shows an example of the lateral residual strain from a 500 nm long InAs nanowire with a radius of 30 nm grown on a GaAs substrate simulated by FEM. As seen, the nanowire expands laterally and contracts vertically. The majority upper part of the nanowire is almost strain free. This kind of strain relaxation can be so efficient that, if the diameter of a nanowire is sufficiently small, it can be grown infinitely long without any MDs [77].

Figure 2-5. In-plane strain distribution of a relaxed 30 nm radius InAs nanowire grown on GaAs simulated by FEM. The black frame is the shape without relaxation. The deformation is 10 times exaggerated. The color indicates the value of the in-plane strain.
2.3 Dislocations in zincblende crystals

In zincblende (001) heteroepitaxial layers, most of the MDs are 60° type dislocations [72]. Therefore, it is important to understand more about this type of dislocations especially for the InGaAs/GaAs system which is our main interest in this thesis.

Normally, MDs are harmless because they are confined at the interface and far away from the active region of devices. However, the TDs can thread through the whole structure, including the active region, and terminate at the surface. Therefore it is essential to suppress TDs. The glide of TDs and interactions between MDs and TDs play the key role on the TD reduction.

2.3.1 Formation of dislocation half loops

There are several ways of generating MDs such as bending of existing TDs from the substrate, nucleation and gliding of dislocation half loops and dislocation multiplication, etc [2]. Nowadays, commercial GaAs wafers can have an etch pit density down to $10^3$ cm$^{-2}$ or lower. The bending of existing TDs from the substrate is therefore not enough to relax the strain. The multiplication of dislocations is unlikely to happen at the initial strain relaxation. Therefore, we believe that the dominant strain relaxation mechanism in InGaAs epi-layers grown on GaAs should be the heterogeneous nucleation of dislocation half loops on the surface.

The dislocation half loops first nucleate at the growth front, then glide toward the interface and thus relax part of the strain from the surface through the epi-layer. This process is illustrated in Fig. 2-6. The gliding of the dislocation half loops will eventually stops at the interface between the epi-layer and the substrate to form a MD segment and two TDs if the epi-layer is uniform, or at the position where strain force is balanced by the dislocation line tension and the Peierls–Nabarro friction force in an alloy graded buffer [78]. The two TDs can still glide laterally until meeting strong impedances. Experimentally, it is not very easy to observe a whole dislocation half loop. Normally MDs and TDs appear as separate segments in TEM photos. Fig. 2-7 shows a TEM image of how the MDs and TDs look like in InGaAs.

Figure 2-6. Illustration of the formation and gliding of a dislocation half loop in a uniform epi-layer.
2.3.2 Glide and interactions of 60° dislocations

60° dislocation is the dominant type of dislocations generated in diamond and zincblende (001) structures. For 60° dislocations, the Burgers vector (marked “b” in Fig. 2-8) has a 60° angle with respect to the dislocation line in the (111) crystal plane which is the gliding plane for the dislocation. Fig. 2-8 shows a schematic of both segments of a MD and a TD three dimensionally.

In a uniformly strained layer, initial dislocations are often nucleated on the growth surface and glide towards the interface, forming a half-loop. The bottom part of a dislocation half loop will stay at the interface and is defined as a MD. However, the TD segments are still free to glide as shown in Fig. 2-8 and thus increasing the MD segment. For InGaAs grown on a GaAs (001) substrate, the MDs lie in the [110] and the [110] directions (called α and β dislocations, respectively) [50, 51], forming a grid of dislocation lines at the interface. Fig. 2-9 [80] shows a cross-section TEM photo of a MD grid. The MDs cause strain non-uniformity at the growth front, which induces preferential deposition of the impinging Ga and In atoms and thus thickness and alloy fluctuations [81]. As a result, cross-hatch surface morphology, which partly reflects the grid of MDs below, is formed. A typical AFM image of such a cross-hatch pattern is shown in Fig. 2-10.
Figure 2-8. Illustration of a $60^\circ$ dislocation in zincblende crystals.

Figure 2-9. A MD grid at the interface of $\text{In}_{0.027}\text{Ga}_{0.973}\text{As}/\text{GaAs}$ revealed by bright field planar-view TEM. Reproduced from [80] by permission of the author T. Wosinski. (a) indicates a TD. Two types of MD intersections without (b) and with interaction (c) are indicated.
Only MDs help relax strain. In order to reduce the TD density, the average length of MD segments should be as long as possible. Gliding of TDs increases the length of the MD segments so it would be wonderful if all the TDs can glide all the way to the edge of the sample. However, only a small portion of the TDs can glide to the edge and most of them are stopped after interacting with other MDs or TDs, or pinned by point defects in the crystal. When two MDs or TDs meet, there are several possible ways of interactions and Fig. 2-9 shows a few examples. The most interesting case is that when two TDs with anti-parallel Burgers vectors meet they will annihilate, leaving a MD.

Take the same example again, for a 400 nm thick In$_{0.15}$Ga$_{0.85}$As layer grown on a GaAs substrate (about 1% lattice mismatch), with a 95% relaxation rate, the MD density is around $1 \times 10^{11}$ cm$^{-2}$ while the TD density in the same sample is only around $1 \times 10^7$ cm$^{-2}$, indicating a significant TD reduction process.

### 2.3.3 Formation of edge dislocations

If 3D islands are formed and grow large enough, pure edge MDs can be created at the boundaries of the islands [36, 54]. This type of MDs is more efficient for strain relaxation and don’t contain TD segments. This mechanism is very favorable in GaSb/GaAs (001) system. Strain can be relaxed by formation of so called “interfacial MD arrays” with a very low TD density [55, 56]. However, in the InGaAs/GaAs system the pure edge MDs would coexist together with 60° dislocations and act as very strong impedance on the glide of 60° TDs leading to a high TD density [86,87]. Even worse, when the 3D islands coalesce, pure edge type TDs can be generated threading to the surface [2, 54]. Fig. 2-11 shows a TEM image of such TDs in In$_{0.3}$Ga$_{0.7}$As on GaAs. These edge type TDs can hardly be bent by strain or glide.
laterally as 60° TDs. Therefore, as long as they are formed, it is very difficult to get rid of them. When the In composition of InGaAs is more than 30%, formation of 3D islands is energetically favorable. Consequently, such TDs are commonly found in high In composition InGaAs/GaAs structures. It is therefore important to avoid interfaces with large mismatch when designing heterostructures. Instead, using several small steps or continuous grading for large mismatch can help solve the problem.

Figure 2-11. An XTEM image of In$_{0.3}$Ga$_{0.7}$As on a GaAs substrate showing edge type TDs.
3 Alloy-graded metamorphic buffer layers and doping effect

Use of an alloy graded buffer is one of the most successful metamorphic growth schemes and has been extensively investigated for several material combinations under different growth conditions [61, 62, 63, 64, 65, 66]. By continuously changing the alloy composition in the buffer layer, dislocations can be effectively confined in the bottom part of the buffer layer leaving a nearly dislocation free and fully strained top layer which acts as a virtual substrate with a desired lattice constant.

Doping has been utilized for more than half a century in semiconductor electronic devices [89]. For metamorphic transistors where metal contacts are deposited on the front surface and in-plane electron transport is employed, doping in metamorphic buffer is irrelevant. For metamorphic optoelectronic devices where back-contacts on conductive substrates are often used, it is necessary to dope the metamorphic buffer to lead the current through the device. We found that different types of dopants have a significant effect on structural properties and surface morphology for alloy graded InGaAs metamorphic buffers grown on GaAs [90]. This effect can be controlled and utilized to improve the quality of metamorphic structures.

There will be some discussions regarding grading profiles in the following context. Three grading profiles studied in the thesis are shown in Fig. 3-1. Since the beam flux depends exponentially on the source temperature, the actual alloy profile following a linear source temperature grading (LTG, red curve) is a super-linear curve with a slow increase of the alloy composition initially and a fast increase at the end. The second is a truly linear alloy grading (LAG, magenta curve) produced by a carefully designed source temperature ramping profile to compensate the exponential dependence. The last one is essentially a mirror image of the LTG (M-LTG, blue curve) profile with respect to the LAG showing a sub-linear curve.

![Figure 3-1. Three alloy grading profiles of InGaAs on GaAs studied in the thesis.](image-url)
3.1 Strain relaxation in alloy graded buffer layers

Continuous grading of alloy composition changes the strain relaxation process and dislocation kinetics compared with the case of using a uniform layer with large lattice mismatch. The most significant difference is that the generated MDs have a spatial distribution in the buffer rather than being confined only at the interface. The major mechanisms of the TD reduction in metamorphic structures are bending of the TDs to form MDs and gliding of the TDs leading to the eventual annihilation of TDs with opposite Burgers vectors [68, 69]. Therefore, it is essential to provide favorable conditions for the dislocation gliding and thus increase the chance of the TD annihilation. Most discussions below will be based on our own experiments. All the metamorphic buffers are grown at 380 ºC read by the thermocouple using MBE. Use of a low growth temperature can suppress surface diffusion of adatoms to achieve a relatively smooth growth front.

3.1.1 “Dislocation-free” region and residual strain

Fig. 3-2 shows an XTEM image of a LAG In$_x$Ga$_{1-x}$As buffer with $x=0$–0.42. A clear boundary (marked by the broken line) can be found in the image leaving a nearly “dislocation-free” region above it. This phenomenon was predicted by J. Tersoff [93]. In his model, the equilibrium distribution of dislocations and residual strain in an alloy graded buffer were calculated by minimizing the total energy (strain energy plus dislocation energy). Theoretically, in equilibrium, the part below this boundary is fully relaxed while the upper “dislocation-free” region is fully strained. With increasing the alloy grading rate (thus also of the lattice mismatch), the thickness of the “dislocation-free” region decreases while the residual strain in the upper part of the buffer increases. Taking the LAG profile as an example, the thickness, $h$, can be expressed by

$$ h = \frac{\sqrt{2\lambda}}{bc\epsilon'} $$

and the residual strain, $\epsilon$, is

$$ \bar{\epsilon} = \frac{\sqrt{2\lambda\epsilon'}}{bc} $$

where $\lambda$ is the dislocation energy per unit length, $b$ is the misfit component of the Burgers vector of the dislocation, $c$ is an appropriate elastic constant for biaxial strain and $\epsilon'$ is the grading slope of the lattice mismatch. For a fixed material system, $\lambda$, $b$ and $c$ can be treated as constants. So the thickness of the “dislocation-free” region and the residual strain are dependent only on the grading slope.

The measured thickness of the “dislocation-free” region is always smaller than the theoretical calculation because the strain below the boundary is only partially relaxed due to the dislocation interactions. The difference ranges from 10% to 40% from our experiments depending on the degree of dislocation interactions.
L. B. Freund found that there exists a minimum distance between a MD and the surface of the sample that allows the TD segments to overcome the impeding force of another perpendicular MD [94]. Therefore a thicker clean upper region is more favorable for the glide of TDs. Moreover, during the growth, newly nucleated dislocation half loops can glide downwards without impediments in the “dislocation-free” region. The thick “dislocation-free” region enables the half loops and existing TDs to glide for a long distance before being pinned, leaving longer segments of MDs. This is consistent with TEM observations: a sample with longer average MD segments often has a lower TD density. A thick “dislocation-free” region requires a small grading slope. On the other hand, the driving force for 60° type TDs to glide was found to be proportional to the strain field they experience [81]. A larger grading slope can give larger residual strain and subsequently larger driving force on the TDs. Combining the two factors discussed above, i.e. the thickness of the “dislocation-free” region and the driving force for TDs to glide, an optimal grading slope is expected.

![Figure 3-2. An XTEM image of a LAG In$_x$Ga$_{1-x}$As buffer with $x=0$–0.42.](image)

It is interesting to note that the role of the residual strain on TDs is different when a graded buffer is grown by MOCVD at high temperatures. A large strain field facilitates strong phase separation, resulting in great compositional variation that is a strong impediment for the glide of TDs [34]. This is not the case in MBE grown samples.
3.1.2 Step-like strain relaxation

Another phenomenon found in Fig. 3-2 is that the MDs are formed at discrete levels, which indicates a step-like strain relaxation process even though the alloy grading is continuous. The Tersoff model is based on equilibrium assumptions and can’t explain this phenomenon. We propose the following model. In the beginning of the growth, the epi-layer grows pseudomorphically until the thickness reaches a critical value and the dislocation half loops begin to form. The dislocation half loops glide toward the interface and thus relax part of the strain from the surface through the epi-layer. During the gliding process, the residual strain, which is equal to the difference between the lattice mismatch (position dependent) and the degree of strain relaxation (constant), decreases and so does the strain force that drives the dislocation gliding. The strain force is eventually balanced by the dislocation line tension and the Peierls-Nabarro friction force [78]. The gliding is then stopped and MDs are formed. No MDs will be generated in the region where the strain force is smaller than the friction force. Now, the strain in the upper part of the layer becomes much smaller than before the relaxation. The growth continues, and new strain accumulates again. When it reaches the critical thickness, similar relaxation happens again. New MDs will be generated at the places where the new force balance is established as discussed above. Thus, the strain is relaxed discretely. If the gliding of TDs is impeded by some reasons, e.g. the MDs in the perpendicular direction or crystal defects, the length of MDs can be short and it is difficult to see the step-like distribution of MDs.

Fig. 3-3 shows another example. The In source temperature is linearly graded in this sample leading to an exponentially graded In composition shown in the right side of the figure. It can be seen that in the beginning, the grading slope is small, so it requires a large thickness to initiate the first strain relaxation. When the grading slope becomes steeper, the space between the two neighbor MD layers turns to be smaller. This experimental finding supports our model above.

Figure 3-3. An XTEM image of an LTG In$_x$Ga$_{1-x}$As layer with $x=0$–$0.42$. The right figure shows the In grading profile.
3.2 In segregation

Surface segregation of group III atoms in III-V ternary compounds is a well known fact [95]. For the common In containing III-As compounds, the surface is always found to be In rich. This phenomenon is usually called In segregation [96,97,98,99]. The amount of In atoms and their diffusion length on an In$_x$Ga$_{1-x}$As graded buffer are two important factors determining the surface morphology and roughness or even some of the structural properties.

3.2.1 Theoretical model

J. M. Muraki et al proposed a model to simulate the In segregation process in uniform III-V ternary compounds based on an iterative method [95]. We extend this model to simulate the segregation in alloy graded In$_x$Ga$_{1-x}$As buffers.

We assume the In segregation occurs on the growing surface and involves exchange of atoms only in the first two atomic mono-layers. According to Muraki, a segregation rate, $\eta$, is defined as the percentage of atoms segregated to the surface from the underneath mono-layer. $\eta$ is basically a constant with a typical value around 0.8 for In segregation in InGaAs. The In atoms on the growing surface come from two sources: the segregated In atoms from the underneath mono-layer and the newly deposited In atoms which is

$$ x_i = i \frac{x_0}{N} $$

for the $i$-th layer, where $N$ is the total number of atomic layers in the graded buffer and $x_0$ is the final In concentration. It can be derived that the total amount of In atoms on the surface in unit of mono-layers, $C^{(N)}$, is then:

$$ C^{(N)} = \frac{\eta^{N+1} - (N + 1)\eta + N}{(1 - \eta)^2} \frac{x_0}{\eta} $$

Normally $N$ is a very large number and $\eta$ is always smaller than “1”, so $\eta^{N+1} \to 0$ and $\frac{1}{N} \to 0$. Then

$$ C^{(N)} \approx \frac{\eta}{1 - \eta} x_0 $$

Therefore, the amount of segregated In atoms on top of an LAG buffer is only decided by the final In composition. If we define $\alpha$ as the In grading slope, then the In composition at a distance of $h$ from the substrate is

$$ x(h) = \alpha h $$

and Eq. (3-5) can be expressed as
\[ C(h) = \frac{\alpha \eta}{1 - \eta} h \]  

(3-7)

Although only the In segregation in an LAG profile is derived here, our model can also be applied to calculate In segregation in other grading profiles.

3.2.2 Edge type TD formation caused by In segregation

In the M-LTG profile as shown in Fig. 3-1, the grading slope in the beginning is very large and then decreases gradually leading to a fast In segregation process according to Eq. (3-7) when growing the lower part of the buffer. The In segregation causes an In rich surface which has a large lattice mismatch with respect to the layers beneath and eventually resulting in the formation of 3D islands. The 3D islands will grow larger and coalesce during the subsequent growth, forming edge type TDs which are sessile and can’t be eliminated as described in Section 0.

Fig. 3-4 shows an XTEM image of an M-LTG In\textsubscript{x}Ga\textsubscript{1-x}As buffer with \( x = 0 \sim 0.42 \). It can be found that edge type TDs are formed in the middle part of the buffer and thread to the surface. Although there is also a large grading slope at the end of the LTG profile, the formation of edge type TDs can only be found in the M-LTG profiles in our experiments. The formation of 3D islands is determined by the amount of In on the surface and the lattice mismatch between the surface and the layers underneath. In the initial growth of the M-LTG sample, In is fast segregated to the growth front due to the large grading slope, and the lattice mismatch between the In rich surface and the buffer underneath is large. The 3D islands are eventually formed. While in the LTG sample, although a large amount of In will be segregated at the end of growth, the lattice mismatch between the In rich surface and the relaxed InGaAs buffer is relatively small and is not enough to trigger the formation of 3D islands. Therefore, it is crucial to avoid large grading slope in the beginning of the graded buffer growth.

Figure 3-4. An XTEM image of an M-LTG In\textsubscript{x}Ga\textsubscript{1-x}As buffer with \( x = 0 \sim 0.42 \).
3.2.3 Doping effect on In segregation

We still take the M-LAG profile as an example. Fig. 3-5 shows both the surface morphology and the dislocation distribution of the undoped, the Be-doped ($p$-type) and the Si-doped ($n$-type) samples.

For the undoped sample (a), there are both 3D islands and a cross-hatch pattern on the surface; there are almost no 3D islands but only the cross-hatch pattern for the Be-doped sample (b); and there are both the cross-hatch pattern and very strong 3D islands on the Si-doped sample (c). The sequence of the root-mean-square (RMS) surface roughness value follows: (b)<(a)<(c). As discussed above, the 3D islands on the surface are directly related to the amount of In atoms on the sample surface and their diffusion length. From the TEM images we observe edge type TDs in both the undoped and the Si-doped samples while there is no TDs found in the Be-doped one. The edge type TDs are indications of the coalescence process of 3D islands.

These results strongly suggest that the Be-doping can suppress the In segregation and thus smoothen the growth front and avoid formation of the edge type TDs, while the Si-doping has obviously an opposite effect that it enhances the In segregation leading to both formation of edge type TDs and large surface roughness.
Figure 3-5. Surface morphology obtained by 10×10 μm² AFM scan (left) and XTEM images (right) of the undoped (a), the Be-doped (b) and the Si-doped (c) M-LTG InₓGa₁₋ₓAs buffers with x=0-0.42. The numbers at the lower-right corner of the AFM images are the RMS roughness values in nanometer.
3.3 Doping effect on dislocation kinetics

Doping has strong effects not only on the surface morphology but also on the dislocation kinetics in alloy graded buffers, and directly affects the TD density.

Fig. 3-6 compares the doping effect in samples with an LAG buffer. Together with the XTEM images in Fig. 3-5, it can be observed that for the Be-doped samples, the “dislocation-free” region is basically free of TDs, the boundary of the “dislocation-free” region is well defended, the MD segments are long and smooth and the step-like MD distribution is clear. The situation for the Si-doped sample is totally opposite. It is difficult to find flat MDs and the crystal lattice is strongly distorted in some parts of the buffer. Nearly no “dislocation-free” region can be found and there are many TDs penetrating to the surface.

![XTEM images of the undoped (a), the Be-doped (b) and the Si-doped (c) LAG InₓGa₁₋ₓAs buffers with x=0~0.42.](image)

Based on the experimental observations we can conclude that the Be-doping generally favors the formation and glide of 60° type TDs resulting long MD segments and a very low TD density on top of the buffer layer while the Si-doping facilitates formation of pure edge type TDs and shows strong impedance on dislocation mobility leading to a chaotic dislocation distribution and a very high TD density in the “dislocation-free” region.

The generality of the doping effect exists in all alloy grading profiles studied in this thesis while the degree is found to be dependent on the grading profile as well as the slope. The
difference between the undoped, the Be-doped and the Si-doped samples is less exhibited when an LAG profile with a moderate slope is used.

3.4 Design of alloy-graded buffers for optoelectronic devices

When considering a real optoelectronic device like laser or photodetector, current injection turns out to be an issue. Taking InGaAs/GaAs edge emitting lasers for instance, the most common design is to grow the whole structure on an $n$-type substrate. This is because the $n$-type GaAs substrates show high structural quality, good electric and thermal conductivity. When it comes to metamorphic growth, the buffer layer must also be $n$-type doped. Using an LAG profile with a moderate slope can mitigate the problems related to the Si-doping to a large extent [59].

The high quality Be-doped buffer could be chosen together with a $p$-type substrate, and then the current runs in the opposite direction compared with a conventional semiconductor laser. The problem of this design could be from the relatively low quality of commercial $p$-type substrates and more severely the Joule heating in both the substrate and the buffer layer. The resistivity of $p$-type substrates and buffers is commonly much higher than that of the $n$-type counterparts. The Joule heating can significantly affect the temperature stability and lifetime of the devices.

Another possibility to utilize the advantage of the Be-doped buffer is to design a co-planar contact scheme for current injection on a semi-insulating substrate [57]. In this design, the heat problem is mostly solved because the current does not run through the substrate and the $p$-type buffer, while the non-uniform distribution of current density could cause some problems such as local heating due to the current crowding effect.
4 Threading dislocation blocking

Another method to reduce the TD density in lattice mismatched heterostructures is to block the TDs after a relaxed layer has been grown. Commonly, a thick and relaxed uniform buffer layer is first grown on a substrate, followed by a TD blocking structure, for example multiple QD layers or a strained superlattice (SL). These TD blocking methods alone are normally not efficient enough. However it is possible to combine these methods with the optimized metamorphic buffers to further reduce the TD density.

4.1 TD blocking through interactions with strain fields

TDs can have strong interactions with the strain field they experience [100] and possibly change the propagating directions [11]. Therefore, intentional introduction of strained structures can help reduce the TD densities. There are two main methods based on this mechanism: strained SL and multiple QD layers. The basic idea of both methods is utilizing the excess strain field to bend the TDs.

In the strained SL case, the alternate compressive and tensile strain relative to the relaxed layer below enables to push the TDs back and forth, thus increasing the chance of TD annihilation. Fig. 4-1 schematically shows that two TDs are bent by a strain compensated SL and annihilate. This method has been proven to be effective in InGaAs on GaAs [101], GaAs on Si [102] and InP on Si [103].

![Figure 4-1. Schematic of TD blocking by a strain compensated SL](image-url)
Z. Mi et al. used multiple layers of self-organized InAs QDs as a TD filter above a GaAs buffer and demonstrated QD lasers grown on Si substrate [84, 85]. The local strain field imposed by InAs QDs on GaAs is much larger than that produced by a strained SL. When a TD meets a QD, it can be bent to form a MD segment below the QD as shown in Fig. 4-2. When it glides out of the QD region, it would propagate in the same direction or climb up again in the cap layer. The mechanism is still not fully understood yet. Even if the MD segment turns to be a TD segment again in the cap layer, it can meet another QD in the next QD layer and be bent again. Therefore the possibility for TDs to glide to the edge of the sample or annihilate with other TDs increases with increasing the number of QD layers. The TD blocking by QDs has also been demonstrated in GaN on sapphire substrates [105].

Figure 4-2. Schematic of TD bending by a QD

When the QD filter is intended to be combined with an InGaAs metamorphic buffer, some technical problems arise. The relative rough surface of the metamorphic buffer and the smaller lattice mismatch between InAs and relaxed InGaAs compared with that of InAs on GaAs lead to very different conditions for the formation of the self-organized InAs QDs. The QDs will form at a much larger critical thickness than that on GaAs, and tend to have a larger lateral size which makes them to coalesce and form new dislocations (often pure edge type). Fig. 4-3 shows an XTEM image of multiple QD layers grown on an alloy grade buffer. A large amount of edge type TDs can be observed due to the coalescence of QDs.
4.2 TD blocking by buried dielectric structures

Q. Li et al. demonstrated that use of self-assembled monolayers of silica microspheres can significantly reduce the TD density in GaN epilayers grown on a sapphire [106]. It was found from TEM images that the TDs can be directly blocked by the silica microspheres or bent as showing in Fig. 4-4, resulting in two orders of magnitude of the TD reduction.

Figure 4-4. Schematic of TD blocking by silica in GaN grown on a sapphire substrate.
A similar TD blocking effect in epitaxial lateral overgrowth (ELOG) of InP on Si was utilized by Y. Sun et al. [107,108,109,110]. In ELOG, after growth of an InP seed layer on a Si substrate, a dielectric mask of silica or Si$_3$N$_4$ is deposited. Then the growth of InP only takes place in the openings of the mask. The TD density is very high in the first InP seed layer on Si. These TDs are of the 60° type and have a certain angle to the wall of the openings in the mask. Part of the TDs can thereby be blocked by the mask as shown in Fig. 4-5. If the mask is thick enough, all the TDs can be blocked.

![Figure 4-5. Schematic of TD blocking in the ELOG method.](image)

### 4.3 TD blocking by dilute nitride

J. Schöne et al. found that incorporation of nitrogen into tensile-strained GaAsP has a strong effect on strain relaxation, dislocation formation and motion [38]. We have tried to incorporate nitrogen in metamorphic InGaAs buffers and demonstrated TD blocking resulting in enhancement of photoluminescence (PL) intensity of metamorphic QWs.

The structure of the samples is shown in Fig. 4-6. By inserting N into an In$_{0.15}$Ga$_{0.85}$As buffer to form an In$_{0.15}$Ga$_{0.85}$As/ In$_{0.15}$Ga$_{0.85}$N$_{0.012}$As$_{0.988}$ SL in the TD blocking region, a 3.7 times enhancement of PL intensity from the QW is observed (shown in Fig. 4-7). This indicates a strong TD blocking effect by the N. N was also incorporated in different parts of a strain compensated GaAs/In$_{0.3}$A$_{0.7}$As SL. The strain compensated SL alone increases the PL intensity for about 2.5 times compared with the reference sample. When N is incorporated, a maximum of 5.4 times PL enhancement can be obtained. The origin of the TD blocking effect is found from both the weak strain effect and the strong lattice hardening effect.
Figure 4-6. An XTEM image showing a typical sample structure containing a dilute nitride TD blocking region.

Figure 4-7. PL spectra of the reference sample (Ref) and the sample with a dilute nitride SL (N1).
5 MBE growth and characterization techniques

Material growth by MBE and sample characterization for surface, structural and optical properties compose most of the experimental work in this thesis. MBE growth and some of the characterization techniques are introduced below with particular emphasize laid on the aspects closely related to the metamorphic materials.

5.1 MBE growth

“Molecular beam epitaxy (MBE) is a term used to denote the epitaxial growth of compound semiconductor films by a process involving the reaction of one or more thermal molecular beams with a crystalline surface under ultra-high vacuum conditions.” This is the definition of MBE by its inventors John R. Arthur and Alfred Y. Cho [111]. Nowadays, MBE has become one of the most advanced and widely applied epitaxial techniques. The ultra high vacuum (with a typical background pressure in $10^{-11}$ torr range) in the growth chamber enables the atoms evaporated from the heated sources to impinge to the substrate without collisions. The low growth rate (commonly around 1 monolayer/s) allows the films to grow epitaxially with a precise thickness control up to the sub-monolayer level.

Fig. 5-1 and Fig. 5-2 show a photo and a schematic layout of our EPI 930 model MBE system, respectively. The sources in this system contain pure metals in either solid or liquid form except for the RF nitrogen source utilizing pure nitrogen gas (6N grade). When the effusion cells are heated, a beam of atoms of the source materials are incident onto the substrate. For growth of III-arsenide compounds, arsenic is always available during the growth with its flux controlled by a needle valve. The growth rate is determined by the flux of the group III atoms. The beam of group III atoms can be switched on and off by mechanical shutters providing a precision of sub-monolayer in epi-layer thickness. The beam flux is determined by the effusion cell temperature. The ultra-high vacuum within the growth chamber is maintained by several different high capacity pumps and liquid nitrogen cooled cryo-shrouds. The cryo-shrouds between the effusion cells can eliminate thermal cross-talk and the other one surrounding the substrate holder acts mainly as impurity traps. The substrate holder is heated and can be rotated at a speed up to 300 revolution-per-minute to produce uniform doping, alloy compositions and layer thickness across the wafer.
The substrate temperature or growth temperature is one of the vital parameters determining the material quality. It is measured by both a thermocouple and a pyrometer. The pyrometer can directly measure the temperature of the sample surface with an accuracy of ±5 °C as
shown in Fig. 5-2. However it can only measure temperatures above 450 °C. The thermocouple can measure lower temperatures and the growth temperature of our metamorphic buffers at about 380 °C is measured by a thermocouple. The drawback is that the measured temperature is a combining effect of the substrate heater, the sample holder, the substrate and deposited structure, and the pyrometer window, which can differ significantly from the real growth temperature on the sample surface.

One of the advantages of MBE over other epitaxial technologies is that the ultra-high vacuum enables the in-situ characterization by using reflective high-energy electron diffraction (RHEED). RHEED can be used to check the surface reconstruction process and calibrate the growth rate. A more detailed discussion of RHEED will be in Section 5.2.2.

5.2 Surface characterization

Surface morphology of MBE-grown samples is an important indicator of the material quality. For metamorphic samples, the surface roughness is one of the two main challenges affecting the device quality. Here we discuss two surface characterization techniques: RHEED is used to in-situ monitor the surface morphology and AFM is to measure the surface morphology and roughness after growth.

5.2.1 Atomic force microscopy (AFM)

AFM is one of the most powerful tools to measure the surface morphology at the sub-nanometer resolution. A small tip with a typical radius of 20 nm on a cantilever is used to probe the surface. In our measurements we use the tapping mode, in which the tip is driven by a piezoelectric element to oscillate at a frequency near the cantilever’s resonant frequency. The Van der Waals force acting on the tip can decrease the amplitude of the oscillation when the tip is close to the sample surface. The distance of the cantilever above the surface is adjusted to keep the same oscillation amplitude during the scanning. Thus, the surface topography is reconstructed by the movement of the cantilever.

The equipment used in this work is a Digital Instruments Dimension 3000 Scanning Probe Microscope. AFM is one of the working modes. The highest vertical resolution is 0.1 nm. Fig. 5-3 is an AFM image of MBE grown GaSb surface showing clear atomic steps.
Both the surface morphology and the roughness are very important for metamorphic samples. Fig. 5-4 shows some typical surface morphology of metamorphic buffers.

Figure 5-4. Different types of surface morphologies of metamorphic buffers measured by AFM: (a) a cross-hatch pattern in 10×10 μm² scale; (b), (c) and (d) are big round mounts, cross-hatch and wire-like 3D dots, respectively, in 1×1 μm² scale.
5.2.2 Reflective high-energy electron diffraction (RHEED)

In a RHEED measurement, a beam of high energy electrons (10 to 100 keV) are incident on the sample surface at a glazing angle of 1 to 2° [2]. The electrons do not penetrate deep into the sample at such an angle. The diffraction is essentially only from the 2D lattice on the surface.

During the MBE growth, RHEED can be used to monitor the surface reconstruction process by observing the diffraction patterns. As shown in Fig. 5-5 (a), the diffraction pattern of a perfect surface is a group of parallel streaks. The case (b) shows the RHEED pattern when 3D islands are formed on the surface. The change from a streaky pattern to a spotty pattern is a clear signature of the formation of QDs when growing InAs on GaAs. For a rough surface, the pattern is often a mixture of streaks and dots.

Figure 5-5. RHEED diffraction patterns of a perfect smooth (a) and a rough surface with 3D islands (b).

RHEED can also be used to calibrate the growth rate in MBE. When measuring a specular beam spot of the diffraction pattern, its intensity will oscillate during the film growth. Fig. 5-6 schematically shows such a process. When the surface is covered by a fraction of a monolayer, part of the diffracted electrons will be scattered leading to a decrease of the intensity received by the detector. The amount of scattered electrons is proportional to the coverage of the surface by the adatoms. When a full monolayer is deposited, the intensity will go back to the maximum. Therefore the period of this oscillation corresponds to the time to grow one monolayer of the material, and the growth rate can be calculated subsequently. Practically, the amplitude of the oscillation decays with the film thickness due to the surface roughening [113], but this does not affect the periodicity.
Figure 5-6. Schematic of RHEED intensity oscillation.
5.3 Structural characterization

5.3.1 Transmission electron microscopy (TEM)

TEM is a characterization technique allowing direct vision of the sample structure. Layers with different compositions, interfaces and defects can be seen by different contrast in the images.

Electrons are accelerated to a high energy, typically 200 keV, and focused by electromagnetic lenses onto a specimen. Some of the electrons are scattered by collisions with atoms in the crystal lattice when passing through the sample. The diffraction pattern is an array of bright spots corresponding to the reciprocal lattice as shown in Fig. 5-7. By inserting an aperture in the diffraction plane, a particular diffracted beam can be selected to form an image. If the beam transmitted directly through the sample is chosen, a bright-field image can be obtained. Otherwise, by selecting one of the diffracted beam spots, a dark-field image is achieved. In a bright field image, the regular crystal lattice appears as a bright background while the defects, such as dislocations and impurities, are darker due to stronger scattering of the electrons. Fig. 5-8 shows an example of a bright field cross-sectional TEM image.

![Figure 5-7. Electron diffraction pattern from a metamorphic structure observed in TEM.](image)

TEM is intensively used for the characterization of metamorphic samples. Dislocations and their distribution can be clearly revealed. We can estimate the TD density by counting the number of TDs in large scale XTEM images. Limited by the visual field of a TEM image, this method can be reliable only when the TD density is higher than $10^7 / \text{cm}^2$.
Since the electrons can’t penetrate too deep into a crystal, the specimen should be made very thin, typically below 200 nm, in order to allow electron transmission. Therefore, preparation of the specimen is crucial for obtaining high quality images and is very time consuming. Fig. 5-9 shows the major preparation steps in which a focused ion-beam (FIB) source is employed to cut a slice of material.
5.3.2 X-ray diffraction (XRD)

XRD is a very useful tool for determining the structural properties. It is a non-destructive method with high precision and less time consuming compared with TEM. The basic underlying physics is the Brag diffraction. Fig. 5-10 shows the geometry of an XRD measurement.

Before a real measurement, optimization of the three angles must be implemented. The first one is $\omega$ which is the angle between the incident X-ray beam and the sample surface. The second one is $\phi$ which is the angle between the in-plane crystal direction and the axis of the equipment. The last one, $\psi$, is the tilting angle of the sample surface to the sample holder. The $\omega$-value is theoretically determined when a crystal plane is chosen. It can deviate up to 1° caused by the crystal misorientation in a real measurement. The other two angles should be 0° if the sample is perfectly mounted. These angles are very sensitive to diffraction peak positions and intensity and must be carefully optimized. The procedure is first to find out the rough position of $\omega$ and then optimize $\phi$ and $\psi$ one by one. They are not independent and an iterative optimization procedure is necessary.

Rocking curve is the most common measurement for characterization of the metamorphic samples. This is done by carrying out a $\omega$-2$\theta$ scan. The 2$\theta$ is the angle between the incident and the diffracted beams and the $\chi$ is the offset between $\omega$ and $\theta$. In the $\omega$-2$\theta$ scan, $\omega$ and 2$\theta$ change simultaneously while the $\chi$ is kept constant.

A typical rocking curve of a metamorphic structure is shown in Fig. 5-11. The different peak positions indicate different lattice constants. For a pseudomorphic layer, one rocking curve of a symmetric (004) is sufficient to obtain all the information since the lateral lattice constant is the same as that of the substrate. For a relaxed structure, by measuring a series of scans on

![Figure 5-10. The geometry for the (115) plane asymmetric X-ray diffraction [114].](image-url)
asymmetric planes, commonly the (115) and the (115) planes, both the lateral and the vertical lattice constants can be obtained. The fully relaxed lattice constant can then be calculated from these two values based on elastic theories. If we know the elements of the layer, for example In$_x$Ga$_{1-x}$As, then the compositions of the elements can be determined by Vegard’s law [115].

![Figure 5-11. A typical (004) rocking curve of a metamorphic structure.](image)

The above analysis is valid only for thick layers. For thin layers, theoretical fitting based on dynamic theory is necessary to extract information on thickness and alloy composition. The precision varies depending on structures and is very high for short-period SLs. As shown in Fig. 5-12 for a GaSb/AlGaSb SL, even the high order interference fringes can be matched, leading to a precision up to 0.05 nm in thickness and 0.1% in element composition. For a partially relaxed structure, fitting is not easy to implement unless the relaxation rate is known.

Reciprocal space mapping by XRD is another very powerful method by which all the information regarding strain and relaxation can be obtained. However this kind of measurement is very time consuming.
5.4 Photoluminescence (PL)

PL is one of the most widely used experimental techniques for the characterization of optical property of semiconductor structures. Excited by a focused laser beam with a larger photon energy than the material bandgap, electrons and holes are generated. Then they can relax, diffuse and eventually recombine either by emission of a photon or generation of heat. Through the study of the emission spectrum, a wealth of information can be obtained such as the bandgap energy, energy confinement, defect levels, carrier lifetimes and so on. For the study of metamorphic materials, the optical property of a QW structure above a metamorphic buffer can act as an efficient indicator for the structure quality of the buffers.

Fig. 5-13 shows the experimental setup. The sample is excited by an Ar ion laser with a wavelength of 514.5 nm. The spontaneous emission is then collected and focused into a monochromator for wavelength dispersion. The PL intensity at each wavelength is measured by a liquid nitrogen cooled Ge detector. A phase-locked loop implemented by a chopper and a lock-in amplifier is utilized to improve the signal-to-noise ratio.
The most important parameters of a PL spectrum from a metamorphic QW are the peak wavelength, peak intensity and full-width-at-half-maximum (FWHM). If an identical QW structure is grown on different metamorphic buffers, the variation of peak wavelength can indicate a strain difference in the QW. The PL intensity is a strong indicator of the TD density. Dislocations act as carrier traps in QWs, where electrons and holes combine very fast through a non-radiative channel. Therefore QWs with a high TD density will show weak PL intensities. The FWHM is dependent on the interface roughness and alloy disorder. Fig. 5-14 shows an example of PL spectra from two identical QWs grown on two different metamorphic buffers.

Figure 5-14. An example of PL spectra of two identical QWs grown on two different metamorphic buffers. The blue dashed spectrum is of the QW grown on a uniform $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ buffer and the red one is on a strain compensated GaAs/$\text{In}_{0.3}\text{Ga}_{0.7}\text{As}$ SL. Both of the structures are grown on GaAs substrates.
6 Summary of appended papers

Paper I

The role of $p$- and $n$-type doping on the relaxation of graded composition InGaAs buffers grown by MBE was investigated. It is found that $p$-type Be-doping can improve material properties, resulting in smaller surface roughness and lower threading dislocation density, while $n$-type Si-doping has an opposite effect. The effect is strongly dependent on the grading profile, with the linear grading showing the small differences.

Paper II

We investigate the effects of doping and grading slope on the surface and structure property of linearly alloy graded InGaAs buffers. It is found that the doping effect is strongly dependent on the grading slope. A moderate In grading slope is preferable for the strain relaxation and the minimization of the negative effect of Si-doping. Physical mechanisms are proposed to explain the experimental observations.

Paper III

The effect of threading dislocation blocking by incorporating nitrogen in metamorphic InGaAs buffers grown on GaAs substrates is demonstrated. This has resulted in 3.7 or 5.4 times improvement of photoluminescence intensity from the metamorphic quantum wells when using dilute nitride superlattice alone or adding nitrogen in a strain compensated GaAs/In0.3Al0.7As superlattice, respectively. The origin of the threading dislocation blocking by dilute nitride is found to be from both the weak strain effect and the strong lattice hardening effect.
References


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Papers I - III
Optimization of Metamorphic Materials on GaAs Grown by MBE

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