Materials Issues with the Integration of Lattice-Mismatched In\textsubscript{x}Ga\textsubscript{1-x}As Devices on GaAs

by

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Submitted to the Department of Materials Science and Engineering in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Electronic Materials

at the

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ABSTRACT

The ability to grow high quality In$_x$Ga$_{1-x}$As compositionally graded buffers would facilitate the manufacture of commercial lattice-mismatched devices, including 1.3 μm wavelength emitting lasers and high speed transistors, on GaAs substrates.

In this study, In$_x$Ga$_{1-x}$As light emitting diode (LED) structures incorporating compositionally graded buffers were grown on GaAs substrates by atmospheric organometallic vapor phase epitaxy and molecular beam epitaxy. The microstructure of compositionally graded In$_x$Ga$_{1-x}$As structures is found to be driven by the presence and morphology of high energy boundaries which bound regions with different surface reconstruction during epitaxy. The domain structure of the surface is influenced by the compositionally graded buffer which forces the domains and subsequent boundaries to lie along <110> type directions. It is found that the surface morphology of the structures, the degree of relaxation afforded by the graded buffer, and the defect density strongly depend on the growth temperature and nature of the high energy boundaries. In the temperature regime where the boundaries are the most pronounced, the surface roughens drastically and the threading dislocation density is high. Only growth at high growth temperatures allows for relaxed, low defect density, compositionally graded structures. It should be noted that in the regime where boundaries are pronounced, the microstructure shows features which have been reported as signatures of phase separation in III-V alloys. Calculations show that extreme surface roughness could lead to phase separation. However, there was no direct observation of phase separation during the course of this study and its effects (if it occurred) were secondary. Interestingly, LEDs with high defect densities can have good device characteristics, indicating that the boundary/domain structure may enhance device performance.

Thesis Supervisor: Eugene A. Fitzgerald
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Chapter I

Motivation for Heteroepitaxy and Introduction to Important Materials Issues

This section states the relevance of the research presented in this thesis and gives a background on the key materials issues addressed while researching the integration of lattice-mismatched In$_x$Ga$_{1-x}$As devices on GaAs substrates.
A. Motivation for Lattice-Mismatched Heteroepitaxy

Heteroepitaxy has played an important role in the development of high performance semiconductor devices, some of which include: field-effect devices\textsuperscript{1}, heterostructure bipolar transistors\textsuperscript{2}, lasers\textsuperscript{3}, and solar cells.\textsuperscript{4} The advances in this field have provided promise to the possibility of integrating III-V compound optoelectronics with silicon microelectronics, a highly sought after goal.\textsuperscript{5,6,7}

An intermediate step on the road to monolithic integration of III-V compound semiconductors with silicon microelectronics would be the fabrication of long wavelength In\textsubscript{x}Ga\textsubscript{1-x}As optoelectronics on GaAs substrates.\textsuperscript{8,9,10} Currently, optoelectronic devices which emit light at wavelengths used for fiber optic telecommunications are fabricated on InP substrates. The ability to grow and fabricate devices for these applications on GaAs substrates would potentially lead to higher device yield and lower cost, as GaAs substrates are less expensive (the cost of InP substrates is $51/\text{in}^2$ as compared to GaAs substrates which cost $25/\text{in}^2$) and less defective. In addition, GaAs wafers can be grown to larger diameters, and GaAs devices are more pervasive in microelectronics applications, allowing for greater production capability/capacity and direct integration with GaAs microelectronics. Despite these advantages, there is still a considerable barrier to implementation of such devices on GaAs. The key issue to be resolved is the lattice-mismatch (i.e., difference in lattice constant) between InAs and GaAs. The research presented in this thesis addressed the materials science issues related to overcoming the problems encountered with lattice-mismatched In\textsubscript{x}Ga\textsubscript{1-x}As heteroepitaxy on GaAs substrates.

The goal of the work described herein was to demonstrate reliable, strongly luminescent In\textsubscript{x}Ga\textsubscript{1-x}As light emitting diodes (LEDs) on GaAs emitting at a wavelength of 1.3 \(\mu\text{m}\), the wavelength at which chromatic dispersion is at a minimum in optical fibers. The demonstration of reliable 1.3 \(\mu\text{m}\) LED (a minority carrier device) operation on GaAs would potentially allow for a suite of emission wavelengths up to the emission
wavelength of InAs (3.44 μm) and also enable novel, high speed and high power, majority carrier devices which are less sensitive to material quality.

**B. Dislocations, Phase Separation, and Ordering**

The implementation of lattice-mismatched devices relies on the minimization and isolation of defects, such as dislocations\(^1\), stacking faults\(^2\), and anti-phase boundaries\(^3\), from the active regions of the device. This criterion is critical to the performance, reproducibility, and reliability of the lattice-mismatched devices in general. In particular, for integrating lattice-mismatched In\(_x\)Ga\(_{1-x}\)As devices on GaAs, threading dislocations are cause for concern and their numbers have to be minimized for device applications. Whereas, phase separation and atomic ordering, often encountered in III-V compound semiconductor epitaxy, may not contribute to defect densities, they may change the characteristics of a material and lead to deviations from the original device design. The following subsections give an overview of dislocations, phase separation, and ordering as they play a role in the implementation of lattice-mismatched In\(_x\)Ga\(_{1-x}\)As devices on GaAs.

1. **Overview of Dislocations**

The body of knowledge accumulated about dislocations and their properties is enormous and can not be given its due attention in this section. However, it is worthwhile to discuss some dislocation characteristics. Much of the discussion in this section is excerpted from the books by Hull\(^4\), Friedel\(^5\), and Ghandhi.\(^6\)

a) **Definition of a Dislocation**

A dislocation is a line defect in what would otherwise be considered a perfect crystal. It is an extra half-plane of atoms terminated by a row of vacancies which forms the line defect or dislocation line. A dislocation is characterized by the crystallographic direction of the dislocation line and its Burgers vector which quantifies the disruption of the crystal.
The direction of the Burgers vector with respect to the dislocation line identifies the type of dislocation. The simplest example of a dislocation is the edge dislocation, in which the Burgers vector is perpendicular to the dislocation line. Alternatively, if the Burgers vector is parallel to the dislocation line, the dislocation is a screw dislocation. Dislocations can have a mixed character between edge and screw type. It is important to note that a dislocation may change its line direction in a crystal, changing the character of the dislocation, but the direction of the Burgers vector does not change.

b) **Origin of Dislocations**

Although an equilibrium concentration exists for vacancies in a crystal, dislocations are not in thermodynamic equilibrium in a crystal, since their energy is high and their entropy is relatively low. Dislocations form at high stress levels, but an activation barrier to their nucleation exists due to the line energy of the dislocation. Typically, dislocations are heterogeneously nucleated in a crystal during solidification at stress concentrations caused by thermal gradients. For example, GaAs bulk crystals grown from the melt typically have a dislocation density on the order of $10^3$-$10^4$/cm$^2$. Dislocations can also form through the multiplication of existing dislocations or through the condensation of excess point defects in a crystal to form dislocation loops.

c) **Dislocation Motion**

Dislocations can move through a crystal via two mechanisms, slip (or glide) and climb. During lattice-mismatch epitaxy, dislocation slip is the primary concern and will be addressed in greater detail. Dislocation climb can be an issue for materials systems during device operation and will be discussed briefly.

Dislocation slip is a plastic deformation process that occurs when a crystal experiences a shear stress that moves a dislocation within the plane defined by the dislocation line and its Burgers vector. This plane is referred to as the slip plane and usually belongs to the set of close packed planes. The slip direction is the direction in the slip plane with the
greatest density of atoms. The combination of a slip plane and a slip direction defines a slip system.

Dislocation climb occurs due to the movement of atoms, or alternatively vacancies, which displace the dislocation line from the slip plane. Typically, this is a thermally activated process which requires high temperatures because diffusion of atoms is involved. However, dislocation climb in III-V compound semiconductors is of interest because motion of point defects may be enhanced by other processes at low temperatures.17,18

d) Dislocations and Electrical Properties

The understanding of dislocations is important for device applications because they alter the electrical properties of a material. Dislocations are known to form states in the bandgap of elemental semiconductors and semiconductor alloys such as Si19, SiGe19, and InGaAs.21 In addition to altering the band structure of a material, dislocations can provide low energy diffusion paths during dopant diffusion, forming “conducting wires” that can short-circuit a device. In optoelectronic applications, dislocations may be non-radiative recombination centers which lower the efficiency of optoelectronic devices.22,23 Lastly, dislocations can lower the mobility of holes and electrons through carrier scattering, reducing the operating speed of majority carrier devices.24

e) Dislocations in III-V Compounds

InAs and GaAs are III-V compound semiconductors which exhibit the zincblende crystal structure shown in Figure I-1. The zincblende structure can be described as two interpenetrating face-centered cubic sublattices, each containing a different atom. This results in a stacking sequence in the <111> direction of alternating planes of cations, on (111)A planes, and anions, on (111)B planes.
The primary slip system in the zincblende structure is $<110>\{111\}$. The predominant dislocation in the zincblende structure and In$_x$Ga$_{1-x}$As/GaAs heteroepitaxy is the $60^\circ$ dislocation\textsuperscript{ii}, so-called because the Burgers vector is inclined $60^\circ$ with respect to the dislocation line.\textsuperscript{25} A $60^\circ$ dislocation is actually an extended dislocation and can dissociate into two partial dislocations, referred to as Schockley partials. The dissociation of the Burgers vector of the partial dislocations from the $60^\circ$ dislocation can be expressed as follows:

$$\frac{a}{2}[110] \rightarrow \frac{a}{6}[211] + \frac{a}{6}[12\bar{1}]$$  \hspace{1cm} \text{Eq. I.1}

\textsuperscript{1} Pictures Courtesy of Professor Rob Toreki, Univ. of Kentucky, http://www.chem.uky.edu

\textsuperscript{ii} $90^\circ$ dislocations can also be found in In$_x$Ga$_{1-x}$As/GaAs heteroepitaxy under high lattice-mismatch conditions. However, high lattice-mismatch conditions at one interface are generally undesirable and avoided during heteroepitaxy.
Figure I-2 illustrates a 60° dislocation and its dissociation into partial dislocations. The two partial dislocations bound a stacking fault between them. The dislocations tend to repel one another due to elastic interactions, however minimization of stacking fault energy favors attraction of the dislocations. An equilibrium separation between the partial dislocations is reached, and the two partials tend to move as one unit.

Since (111) planes in the zincblende structure are chemically inequivalent, two different dislocation core structures can be present. Dislocations can terminate on the group III sublattice (α dislocations) or on the group V sublattice (β dislocations). The dislocation nucleation rates and velocities differ for each set of planes. This difference manifests itself during III-V compound epitaxy as an asymmetry in dislocation density in the two <110> directions perpendicular to the growth direction (see Appendix A).

f) Threading vs. Misfit Dislocations

A significant property of dislocations is that a dislocation line can not end inside a crystal and must terminate at a surface or form a closed loop. This property has important consequences during device epitaxy.
Figure I-3: Diagram Demonstrating Threading vs. Misfit Dislocations

Figure I-3 illustrates a typical dislocation half-loop in a single crystal epitaxial film. The dislocation line segment at the interface between the substrate and the film is referred to as the misfit dislocation and is the only part of the half-loop which relieves strain. The two segments that propagate to the surface are termed the threading dislocation segments. Depending on the particular device structure, either misfit or threading dislocations need to be minimized. This point will be discussed in the next chapter, and the distinction between threading dislocations and misfit dislocations should be noted.

2. Phase Separation in III-V Compounds

Phase separation is the dissolution of one phase into two separate phases. Phase separation or the presence of a miscibility gap is represented on a binary phase diagram as shown in Figure I-4. The reaction can be represented as $\alpha' + \alpha'' \leftrightarrow \alpha$. However, there are two mechanisms through which phase separation can occur in bulk crystal. Within the region bound by the dashed line and the solid line, phase separation occurs via nucleation and growth. In this region, the metastable phase undergoes compositional changes which are large in extent, but spread over a small volume. Inside the region enclosed by the dashed line (referred to as the spinodal), spinodal decomposition is the phase separation mechanism.\(^{26}\) Within this region, the compositional fluctuations are small, but they are spread out over a large volume. In compound semiconductor epitaxy, spinodal decomposition is the mechanism of the greatest concern. The phase stability of semiconductor solid solutions has been an area of active study due to the implications for epitaxy of device structures.
The following sections discuss some of the modeling techniques and experimental observations used to identify and predict phase separation\(^{\text{iii}}\) in III-V compound semiconductors.

\(\text{a) Ideal and Regular Solutions}\)

The temperature and composition dependence for phase separation can be calculated by considering two thermodynamic parameters, the entropy and enthalpy of mixing between the two end-members. Typically, the two terms oppose one another and a criterion for phase separation can be determined by deciding the dominant term at a given temperature.

The ideal entropy of mixing is given by

\[
\Delta S_{\text{mix}} = -R[x_A \ln x_A + x_B \ln x_B]
\]

Eq. I.2

where \(x_A\) and \(x_B\) are the mole fractions of the respective end-members. For an ideal solution, the entropy of mixing is always positive and favors the formation of a solid

\(^{\text{iii}}\) Phase separation sometimes is referred to as alloy clustering or alloy segregation.
solution of the end-members. Materials systems without a miscibility gap can be modeled closely by considering only the entropy of mixing and are considered ideal solutions. Si$_x$Ge$_{1-x}$ is an example of a important semiconductor solid solution that is nearly ideal.\textsuperscript{27}

The enthalpy of mixing is the term which usually favors the separation of a single phase into two separate phases. Unlike the entropy of mixing, which does not consider materials properties, the enthalpy of mixing is strongly dependent on the chemical interactions of the end-members. The crystal structures, valence band configurations, and atomic sizes are among the parameters which must be considered when determining whether the enthalpy of mixing will be a large positive quantity and offset the entropy of mixing. In general, the more dissimilar the two end-members, the more likely a miscibility gap will appear in the phase diagram. In some materials systems, the enthalpy of mixing can expressed by a one parameter model, termed the regular solution model, as follows

$$\Delta H_{\text{mix}} = \Omega x_A x_B$$  \hspace{1cm} \text{Eq. I.3}

where $\Omega$ is the interaction parameter which expresses whether the cohesive energies of the solution are more favorable than that of the end-members alone. $\Omega$ is typically determined experimentally, however, there have been efforts to determine the enthalpy of mixing theoretically to predict phase separation in III-V compounds. Some of the results and techniques used for predicting phase separation will be outlined in following sections.

\textit{b) Origin of Enthalpy of Mixing and The Virtual Crystal Approximation}

The enthalpy of mixing in ternary and quaternary III-V compound semiconductor solutions is assumed to come from strain due to the size mismatch of the atoms in solution.\textsuperscript{28} This strain leads to deviations from the approximation that semiconductor solid solutions are "virtual" crystals.
The crystal structures of solid solutions are typically assumed to obey Vegard’s Law which states that the lattice parameter of the solid solution can be linearly interpolated from the lattice parameters of the end-members. The virtual crystal approximation additionally assumes each site in the lattice is occupied by an average atom. Average atoms imply that the cation-anion nearest neighbor distance is always $a_o \sqrt{3}/4$, where $a_o$ is the lattice parameter of the solid solution, and the covalent radii of the different cations/anions are the same. Vegard’s Law is usually valid, however, the covalent radii of the different cations/anions are typically not the same.\[iv\] Since average atoms do not exist, the positions of the atoms deviate from their expected positions in the lattice (i.e., the bond lengths are not what are expected). $In_{x}Ga_{1-x}As$ solid solutions, for example, have lowest energy positions for In and Ga which allow only slight deviations in covalent radii from InAs and GaAs.\[29\] So there is significant contribution to the enthalpy of mixing in a III-V compound solid solution from the angular change of covalent bonds, as opposed to just bond length adjustments.

c) **Modeling of Phase Separation in III-V Compounds**

The literature regarding the modeling of phase separation in III-V compounds is quite confusing and at times contradictory, as different models can give values for the enthalpy of mixing within the range of experimentally determined values. One fairly often referenced technique will be discussed to give some insight into the discrepancies.

As previously mentioned, attempts have been made at modeling III-V compound solutions with various techniques.\[30,31,32,33\] Stringfellow modeled ternary and quaternary phase diagrams with what is referred to as the delta lattice parameter (DLP) model.\[34\] It is an attempt based on modeling enthalpy of mixing with the Phillips-Van Vechten model of bonding in semiconductors.\[35\] Phillips and Vechten based their model on the fact that bonding is stringently defined in tetrahedrally coordinated structures. So, by determining

---

\[iv\] Al$_x$Ga$_{1-x}$As alloys behave close to this assumption because the covalent radii for Al and Ga are nearly identical.
Table 1: Interaction Parameter Values Determined Experimentally and with the Delta Lattice Parameter Model

<table>
<thead>
<tr>
<th>Materials System</th>
<th>Ω (experimental) kJ/mole</th>
<th>Ω (DLP model) kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlAs-GaAs</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>AlAs-InAs</td>
<td>10.48</td>
<td>9.93</td>
</tr>
<tr>
<td>GaAs-InAs</td>
<td>11.79</td>
<td>10.52</td>
</tr>
<tr>
<td>GaSb-InSb</td>
<td>6.18</td>
<td>7.73</td>
</tr>
<tr>
<td>Ge-Si</td>
<td>5.03</td>
<td>4.97</td>
</tr>
</tbody>
</table>

correction factors for ionic and metallic bonding characteristics of different compounds with the same coordination number, they found that the heat of formation could be fit by a model with experimentally determined constants. Based on their work Stringfellow found the enthalpy of atomization, ΔH^m, for III-V compounds can be expressed as \( K a_{o}^{-2.5} \) with \( K \), a prefactor equal to 4.812 J/mole. The enthalpy of mixing can then be taken as the difference between the enthalpy of atomization of the end-members and the solid solution as follows

\[
ΔH^M = K[(1 - x)a_1^{-2.5} + xa_2^{-2.5} - a_{o}^{-2.5}] \quad \text{Eq. I.4}
\]

with \( a_1 \) and \( a_2 \) being the lattice parameters of the end-members and \( x \), the mole fraction of end-member with lattice parameter \( a_2 \). The interaction parameter, \( Ω \), is defined at \( x = \frac{1}{2} \) and, with some approximations, can be expressed as

\[
Ω ≡ 4.375KΔa^2/\bar{a}^{-4.5} \quad \text{Eq. I.5}
\]

Chapter I- Motivation for Heteroepitaxy and Introduction to Important Materials Issues
where $\Delta a = a_1 - a_2$ and $\bar{a} = (a_1 + a_2)/2$. Table I shows experimental values of $\Omega$ and those calculated by the DLP. The predicted values closely match the experimental values.

Unaccounted for in Stringfellow's early calculations was an additional strain factor, the coherency strain, which results upon phase separation. By including the coherency strain energy in the phase stability criterion, Stringfellow determined the coherent spinodal and found that many III-V compound ternary and quaternary alloys (including In$_x$Ga$_{1-x}$As) were be stable and not prone to phase separate.$^{36}$

Considering that phase separation in the bulk is not favorable for III-V compounds, it has been assumed that phase separation during III-V epitaxy is surface driven.$^{37}$ This would explain why phase separation has been reported in systems such as Al$_x$Ga$_{1-x}$As, where no phase separation should occur.$^{38}$

d) Observation of Phase Separation in III-V Compounds

Phase separation in semiconductors is observable with transmission electron microscopy (TEM) and has been reported in several heteroepitaxial systems. Although satellite spots in the transmission electron diffraction pattern have sometimes been attributed to phase separation$^{39,40,41}$, certain types of contrast in the TEM images of III-V alloys are usually considered the signature of phase separation.

There are two distinct contrast modulations in the TEM images which occur over different length scales. One is a fine scale tweed-like contrast which occurs over a scale of approximately 10 nm. The other feature is a wavy contrast which occurs over a scale of about 100 nm. The features are typically aligned in $<100>$ in-plane directions because those directions are elastically soft in the zincblende structure (i.e., the linear atomic spacing in the $<100>$ directions is greatest). However, they have also been reported in other crystallographic directions.$^{42,43}$ Figure I-5 is a TEM image of features commonly associated with phase separation in III-V compound alloys.
The origin of the two features has been the source of controversy. Majahan\textsuperscript{44} reviewed various theories for the contrast and concluded the following:

1) The fine scale contrast is the result of actual phase separation during growth

2) The large scale contrast is a consequence of the strain due to the fine scale phase separation.

Glas\textsuperscript{45} reviewed TEM and x-ray microprobe analysis of the same features observed in phase separated structures. The origin of the coarse modulation was also taken to be strain; however in contrast to Mahajan's conclusions, x-ray microprobe analysis showed the compositional fluctuations to be on the same scale. Supporting Mahajan's analysis, Glas pointed out that the fine scale contrast was due to strain, but there was no evidence of compositional inhomogeneity on that scale. Glas further pointed out that even a homogeneous alloy could show fine scale contrast due to statistical fluctuations of atomic distributions or the mixed sublattice. The results of this thesis show that phase separation may be occurring; however, it plays a secondary role in evolution of the microstructures observed by others.
e) **Phase Separation Engineering**

Phase separation during device epitaxy has been shown to effect device quality and characteristics, although not necessarily for the worse. The results presented in this thesis show that growth conditions where phase separation may be favored promote poor surface morphology and high dislocation density. It has also been speculated that phase separation improves the reliability and performance of optical devices. Since the onset of phase separation is not necessarily predictable, most processes strive to eliminate it. The phase-separated regime of a phase diagram has an upper-bound in temperature because of the greater entropy of mixing contribution at higher temperatures, so epitaxial growth at higher temperatures reduces the likelihood of phase separation. In addition, since phase separation is not stable in the bulk, annealing of the epitaxial layers has been shown to cancel the features observed in TEM. Zn incorporation into III-V alloys has also been found to promote mixing on the group III sublattice and eliminate the signatures of phase separation.

3. **Ordering in III-V Compounds**

Atomic ordering is the preferential positioning of atoms in a lattice, as opposed to a random distribution. Ordering in III-V compounds during epitaxy has been an area of intense research. The effects of ordering are not visible in the research presented in this thesis. However, some of the traits of ordering are worth mentioning because the identification and cause of the two distinct processes (phase separation and ordering) are sometimes areas of confusion.

a) **Origin of Ordering**

The enthalpy of mixing as discussed in the previous section is also a factor when discussing ordering. Interestingly, the criterion for ordering is completely the opposite for that of phase separation. Ordering implies that the intimate incorporation of the two constituents is favored over immiscibility, resulting in a negative enthalpy of mixing. Thus, ordering has been assumed to be less favorable than phase separation since the
enthalpy of mixing in III-V compounds was known to be positive. However, such considerations have been put aside since ordering has been observed in a variety of semiconductor systems.\textsuperscript{49,50,51,52}

As with phase separation, consideration of surface driven effects has led to theories for the evolution of ordering. Zunger\textsuperscript{53} reviewed some of the theories and effects of ordering. Basically, even though ordered phases in the bulk are not favored, certain ordered variants minimize strain at the surface during deposition. CuPt ordering, for example, which is often observed in III-V epitaxy, has the highest formation energy of any high symmetry ordered structure in the bulk, but upon considering surface thermodynamics it is the lowest energy structure in many instances. Despite the thermodynamic driving force, growth conditions are very important to determining the extent of ordering in a structure. Higher temperature\textsuperscript{54}, increased substrate offcut\textsuperscript{55}, very high growth rates (>12 \(\mu m/hr\))\textsuperscript{56} and lower V/III ratios\textsuperscript{57} tend to decrease the extent of ordering.\textsuperscript{*}

\textit{b) Observation of Ordering in III-V Compounds}

TEM observation gives direct evidence of ordering in III-V compound alloys. Although there is contrast in the images of ordered materials, the transmission electron diffraction (TED) patterns give indisputable evidence as satellite spots are clearly visible in ordered structures. Norman, \textit{et al}.\textsuperscript{58} summarized the TEM findings and origins of ordering in III-V semiconductor alloys. The different ordered patterns which exist in III-V compound materials are:

1) CuAu I, ordering occurs on \{110\} and \{100\} planes.

2) CuPt, ordering occurs on \{111\} planes.

3) Chalcopyrite, ordering occurs on \{210\} planes.

\textsuperscript{*} V/III ratio is a term used in organometallic vapor phase epitaxy (OMVPE) and will be discussed in a later chapter.

\textit{Chapter I- Motivation for Heteroepitaxy and Introduction to Important Materials Issues}
c) Effects of Ordering on Device Characteristics

Ordering, as in the case of phase separation, leads to changes in the electronic structure of a material, altering its device characteristics. Most notably, ordering lowers the bandgap of a material.39

C. Summary

In this chapter the motivation for the research presented in this thesis was discussed. There are strong advantages to replacing devices currently grown on InP substrates with comparable devices on GaAs. Furthermore, the demonstration of low defect density, 1.3 μm LEDs on GaAs would be an important stepping stone towards the ultimate goal of monolithic integration of III-V compounds with Si microelectronics.

Dislocations, phase separation, and ordering were reviewed in this section. The important characteristics of dislocations and their effects on semiconductor devices was stressed. The distinction and relationship between threading vs. misfit dislocation segments has also been introduced. Phase separation and ordering in III-V compound alloys were reviewed, stressing the opposing driving forces of the two processes, yet showing both to be surface driven and unstable in the bulk.
Chapter II

Review of In$_x$Ga$_{1-x}$As/GaAs Heteroepitaxy

In this chapter, the key issues regarding successful integration of lattice-mismatched In$_x$Ga$_{1-x}$As on GaAs are reviewed. Methods for controlling threading dislocation density are discussed and published results and models are summarized.
A. Critical Thickness

Most materials systems (epitaxial layer/substrate) used for commercial heterostructure devices are closely lattice-matched (e.g. AlGaAs/GaAs, InGaAsP/InP). The sole reason for this criterion is the desire to avoid defects which accumulate due to the lattice-mismatch induced strain. When the lattice parameters of the film and substrate differ, the epitaxial layer is grown until a certain critical thickness is reached. At this thickness, it is energetically favorable for misfit dislocations to be introduced at the interface to relieve strain energy. Thus, the ability to grow a strained layer on a substrate is determined by an energy balance between strain energy and dislocation line energy. Matthews, et al. determined the criterion for critical thickness based on this energy balance. The critical thickness and associated parameters are given by the following (the parameters are labeled for In$_x$Ga$_{1-x}$As and GaAs):

\[
h_{cso} = \frac{D(1 - \nu \cos^2 \theta)(b/b_{ef})(\ln(\frac{h}{b}) + 1)}{2Yf} \quad \text{Eq. II.1}
\]

\[
D = \frac{G_{GaAs}G_{InGaAs}b}{\pi(G_{GaAs} + G_{InGaAs})(1 - \nu)} \quad \text{Eq. II.2}
\]

\[
b = \frac{\sqrt{2}}{2} a_{InGaAs} \quad \text{Eq. II.3}
\]

\[
\nu = \frac{C_{12}}{C_{12} + C_{11}} \quad \text{Eq. II.4}
\]

\[
Y = C_{11} + C_{12} - 2\frac{C_{11}^2}{C_{11}} \quad \text{Eq. II.5}
\]

\* A force balance on an existing threading dislocation is equivalent to examining the energy balance.
\[ f = \frac{a_{\text{InGaAs}} - a_{\text{GaAs}}}{a_{\text{InGaAs}}} \]  
Eq. II.6

where \( \nu \) is Poisson's ratio, \( b \) is the Burgers vector, \( a \) represents the lattice parameter, \( Y \) is the Young's modulus, and \( f \) is the misfit factor.

If 60° dislocations are assumed and the approximation for crystal anisotropy is used in the definition of \( G \), the shear modulus, the expressions for critical thickness \( (h_{c60}) \) and for the shear modulus for the In\(_x\)Ga\(_{1-x}\)As/GaAs system become:

\[ h_{c60} = \frac{D(1 - \nu \cos^2 \theta)(\ln \left( \frac{h_{c60}}{b} \right) + 1)}{Yf} \]  
Eq. II.7

\[ G = C_{44} - \frac{1}{3}(2C_{44} + C_{12} - C_{11}) \]  
Eq. II.8

\( \theta \) equals 60° since 60° dislocations are assumed. If 90° dislocations (edge dislocations) were assumed, the expression in the denominator of Eq. (7) would be \( 2Yf \) and \( \theta = 90° \).

Figure II-1 shows the critical thickness in the In\(_x\)Ga\(_{1-x}\)As system for 60° and 90° dislocations. The critical thickness for 90° dislocations is less than that of 60° dislocations, as they are more efficient at relieving strain (i.e., the entire Burgers vector component is in-plane and relieves strain). However, they require considerably more energy to glide than 60° dislocations.

In practice, epitaxial layers can be grown past the critical thickness without the introduction of misfit dislocations due to kinetic limitations. However, in these cases thermal budgets for further processing of the devices must be carefully planned.
B. **Strain Relaxation in In$_x$Ga$_{1-x}$As Heteroepitaxy**

The understanding of single layer relaxation processes in In$_x$Ga$_{1-x}$As/GaAs heteroepitaxy have profound implications for lattice-mismatched applications. This section discusses the modeling and observation of relaxation in single layer In$_x$Ga$_{1-x}$As/GaAs systems.

1. **Modeling In$_x$Ga$_{1-x}$As Single Layer Relaxation**

The In$_x$Ga$_{1-x}$As/GaAs heteroepitaxial system has frequently been used to study pseudomorphic films and relaxation processes.$^{64,65,66}$ The data show that the In$_x$Ga$_{1-x}$As/GaAs system behaves closely to models predicted by Matthews, except at higher mismatch where the critical thickness is less than predicted. However, the critical thickness model only predicts the onset of plastic deformation (i.e., misfit dislocation introduction) and processes past the initiation point can be just as important.
Three regimes of epilayer relaxation exist: 1) the thickness below the critical thickness, 2) the initial stage of relaxation when misfit dislocations are favored, and 3) the regime where the relaxation process slows down. Krishnamoorthy, et al.\textsuperscript{67} found the following expressions quantify the relaxation process during the last two stages of In\textsubscript{x}Ga\textsubscript{1-x}As relaxation:

1) $\%relaxation = 2.0 \pm 0.1 \left( \frac{d}{h_c} - 1 \right)$ when $h_c \leq d \leq 30h_c$

2) $\%relaxation = 0.020 \pm 0.005 \left( \frac{d}{h_c} - 1 \right) + 66 \pm 1$ when $30h_c \leq d \leq 450h_c$

Dunstan, et al.\textsuperscript{68} found the actual strain ($\varepsilon$) in the epilayer as function of thickness ($d$), once the relaxation process starts\textsuperscript{vii}, to be given by $\varepsilon(d) = k \frac{b}{d}$. $k$ is a proportionality constant which is about 3 for the In\textsubscript{x}Ga\textsubscript{1-x}As/GaAs system.\textsuperscript{viii}

Krishnamoorthy's and Dunstan's expressions show that in the third regime, sometimes referred to as the work hardening regime, relaxation is very slow. This finding has implications for the design of multilayer mismatched structures and will be discussed.

2. Aspects of Strain Relief in In\textsubscript{x}Ga\textsubscript{1-x}As

Although In\textsubscript{x}Ga\textsubscript{1-x}As/GaAs strain relaxation follows equilibrium strain relaxation models, the microscopic origins of strain release are difficult to identify in some relaxation regimes.\textsuperscript{69,70,71,72,73} Strain relaxation can occur through two mechanisms: 1) dislocation nucleation and glide and 2) surface roughening. In addition, secondary effects due to the

\textsuperscript{vii} The expression does not take into account the original misfit factor, so the onset of relaxation is not predicted by this expression.

\textsuperscript{viii} $kb$ is at times combined into one number, 0.83 nm for $60^\circ$ dislocations.

Chapter II- Review of In\textsubscript{x}Ga\textsubscript{1-x}As/GaAs Heteroeptaxy
presence of misfit dislocations can lead to surface roughening and a tilting of the epitaxial layer with respect to the substrate.

Since strain relaxation is known to be kinetically limited, the nucleation of misfit dislocations has been investigated. Under high mismatch conditions ($x_{In} > 0.4$) and three-dimensional growth, homogeneous nucleation of dislocations has been reported.\textsuperscript{74} However, under lower mismatch conditions heterogeneous nucleation is more likely in In$_{x}$Ga$_{1-x}$As, as the experimentally determined nucleation energies ($\approx 1.4$ eV) are much lower than theoretical values ($\approx 90$ eV).\textsuperscript{75}

Of great concern during the relaxation process is the surface roughening which occurs due to interfacial strains from misfit dislocations at the mismatched interface.\textsuperscript{76,77} Under some conditions, the troughs formed by surface roughening will act as nucleation sources for dislocations in In$_{x}$Ga$_{1-x}$As.\textsuperscript{78}

\subsection*{C. Nearly Lattice-Matched In$_{x}$Ga$_{1-x}$As/GaAs Applications}

The key to implementation of nearly lattice-matched device structures is the growth of a pseudomorphic layer below the critical thickness, thereby avoiding the introduction of misfit dislocations. In low mismatch systems the critical thickness is large, and devices can be fabricated. However, very high mismatch systems do not allow for pseudomorphic growth of sufficient thicknesses for practical device applications. For example, as seen in Figure II-1 the critical thickness for the In$_{x}$Ga$_{1-x}$As/GaAs system for $x_{In} > 0.3$ is about 30 Å. Thus critical thickness excludes highly mismatched systems from many applications.

The In$_{x}$Ga$_{1-x}$As/GaAs materials system has considerable technological importance for nearly lattice-matched applications. With the growth of pseudomorphic layers this materials system has been used for high electron mobility transistors and optoelectronic applications where the emission wavelength was less than 1 µm ($x_{In} < 0.20$).\textsuperscript{79} The In$_{0.2}$Ga$_{0.8}$As/GaAs materials system is used for 980 nm pump lasers for erbium doped...
fiber amplifiers, and this application employs a strained $\text{In}_x\text{Ga}_{1-x}\text{As}$ layer. However, for 1.3 $\mu$m emission a much larger indium content ($x_{in}>0.30$), pseudomorphic layer must be incorporated directly on GaAs. This type of structure would be difficult to fabricate, since misfit dislocations may be introduced and act as nonradiative recombination centers that degrade LED performance, specifically the LED efficiency and possibly long term reliability.

Referring to Figure II-2, the classic lattice-parameter vs. bandgap diagram, it can be seen that the semiconductor solid solutions which are closely lattice-matched to GaAs have energy gaps ranging from 0.85 eV to 1.2 eV. The corresponding emission wavelengths are from 0.89 $\mu$m to 0.59 $\mu$m. This implies that no solid solution can be lattice-matched to GaAs and emit light at 1.3 $\mu$m. Thus, demonstration of such a device operating reliably on GaAs would suggest the feasibility of lattice-mismatched $\text{In}_x\text{Ga}_{1-x}\text{As}$ devices on GaAs.

D. Defect Engineering for Lattice-Mismatched $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ Applications

From the previous section, it is clear that obtaining 1.3 $\mu$m emission from an epitaxial $\text{In}_x\text{Ga}_{1-x}\text{As}$ layer on GaAs requires a defect engineering approach. Unlike nearly lattice-matched applications where misfit dislocations are the cause of concern, in order for lattice-mismatched $\text{In}_x\text{Ga}_{1-x}\text{As}$ to be viable device material, the threading dislocation density (TDD) has to be minimized. There are two aspects to the TDD problem: 1) reduction of the TDD and 2) accurate determination of the TDD. Both are challenging
and important to proper device design. It must be stated that although the TDD would ideally be zero for lattice-mismatched applications, misfit dislocations are actually required to engineer the substrate lattice constant for subsequent device layer growth.

1. Efficient Strain Relief

The total misfit dislocation density needed for a given amount relaxation is predetermined by the overall lattice-mismatch and the magnitude of the Burgers vector. The only question that remains is the number of sources which will be needed for the amount of relaxation desired. Since each nucleation event produces two threading

*Figure II-2: Lattice Parameter vs. Bandgap Diagram*
dislocation segments, lattice-mismatched applications mandate the use of the fewest number of nucleation sources to relieve a given amount of strain. This criterion is often referred to as efficient strain relief. Figure II-3 illustrates the difference between efficient and inefficient strain relief.

Efficient strain relief can be facilitated with two conditions: 1) nucleation of dislocations must be minimized and 2) the strain each dislocation relieves must be maximized. This implies that dislocations which nucleate must be allowed to glide over long lengths and relieve as much strain as possible.

2. Compositionally Graded Buffers

Buffer layers are generally used to engineer a desired lattice constant and bury the misfit dislocations far from the device region. A buffer layer may simply be a uniform composition layer which is meant to separate the active device region from the defects which accumulate at the epilayer/substrate interface. However, such a layer, although easy to implement, typically can not achieve the desired TDD (~10⁶/cm²) for minority carrier device applications within a reasonable thickness, nor can it achieve the amount of relaxation required to engineer the lattice constant precisely. In order for a buffer layer to achieve both goals controllably, it must relieve strain efficiently as mentioned in
the previous section. It has been shown that compositionally graded buffers relieve strain efficiently and allow for a low TDD.\textsuperscript{54,85,86}

Compositionally graded buffers are effective at reducing the TDD because they promote the propagation of dislocations by limiting deleterious dislocation interactions. This feature of compositionally graded buffers can have two positive effects on the TDD. Dislocation propagation maximizes the strain relief of each nucleation event, thereby limiting the number of nucleation events needed. In addition, if dislocations can propagate over long lengths they may encounter other dislocations with opposite sign Burgers vectors and annihilate. Dislocation annihilation has been proposed as the primary effect of lowering the TDD\textsuperscript{87}; however, the limitation of dislocation nucleation and interaction is the first priority. Two factors contribute to the minimization of dislocation interaction in compositionally graded buffers. First, the minimum energy position for dislocations lies in regions of the film with no other dislocations. This is because each subsequent layer with different composition introduces a strain which allows dislocation motion in a new plane, whereas a uniform buffer layer restricts dislocation motion to one plane. Dislocations can thereby glide without impediment (i.e., no dislocation entanglement or work hardening). Secondly, strain is not allowed to accumulate as the system never sees but a portion of the overall mismatch at each interface. This in turn inhibits nucleation of new dislocations and each nucleated source is reused to relieve strain in the subsequent layers. Figure II-4 schematically shows how a graded buffer relieves strain efficiently.

It should be noted that compositionally graded structures are subject to design parameters, which ultimately determine the TDD and amount of strain relaxation, and the use of graded structures alone does not guarantee a low TDD. Slow grading rates (i.e., making smaller steps in composition/strain) and high growth temperatures provide lower
TDD and better device quality. The slower grading rates do not allow for significant accumulation of strain and the higher growth temperatures allow for higher dislocation mobility (i.e., dislocations can relieve the strain more quickly).

\[ \text{a) Theoretical Strain Relaxation of In}_{x}\text{Ga}_{1-x}\text{As Graded Buffers} \]

There are some similarities, yet important differences, between the results of modeling relaxation in a compositionally graded layer of In\(_x\)Ga\(_{1-x}\)As and the results of modeling relaxation in a single/uniform layer of In\(_x\)Ga\(_{1-x}\)As. In addition, the expected relaxation characteristics of a compositionally graded buffer has a dramatic effect on the expected TDD. The following subsections discuss the modeling of the relaxation process in In\(_x\)Ga\(_{1-x}\)As compositionally graded buffers and the implications for the TDD in structures with compositionally graded buffers.

\[ \text{\textsuperscript{a} Nucleation of dislocations is also thermally activated, so there is a tradeoff with dislocation glide. However, if the grading rate is slow enough, the nucleation of dislocations is minimized.} \]

---

Chapter II: Review of In\(_x\)Ga\(_{1-x}\)As/GaAs Heteroepitaxy
Fitzgerald, et al.\textsuperscript{3} initially formulated the equilibrium strain relief models for compositionally graded buffers and those expressions are identified and used in the results section of this thesis. Tersoff\textsuperscript{4} also examined the equilibrium theory of compositionally graded buffers and compared the results to that of single layer equilibrium models. Again, just as for the critical thickness, the expressions were formulated by considering the strain energy vs. dislocation line energy balance.

Defining $\varepsilon'$, the grading rate ($\frac{d\varepsilon}{dz}$), and $z_c$, the thickness beyond which misfit dislocations are not energetically favored, the equilibrium misfit dislocation spacing, $\rho(z)$, is given by

$$\rho(z) = \frac{\varepsilon'(z)}{b_{eff}}, \quad 0 \leq z \leq z_c$$

Eq. II.9

If the grading profile is assumed to be linear (i.e., constant) $z_c$ is given by

$$z_c = d - (2\lambda / c\varepsilon')^{\frac{1}{2}}$$

Eq. II.10

where $d$, is the total thickness of the film, $\lambda$, is the energy per unit line length of the dislocation, and $c$, the appropriate elastic constant for biaxial strain. There are two important points to take from Eq. II.9 and Eq. II.10. First, as the grading rate decreases the misfit dislocation spacing decreases, thereby minimizing dislocation interaction as originally proposed. Second, rearranging the expressions in Eq. II.10 to show $d-z_c$,

$$d - z_c = (2\lambda \varepsilon' / bc)^{\frac{1}{2}}$$

Eq. II.10.1

the expression taken to the $\frac{1}{2}$ power in parenthesis is the critical thickness at the top of the graded buffer. Thus, there is always a constant residual strain ($\varepsilon_r$) for a given $d$, as opposed to the case of a single layer experiencing relaxation where $\varepsilon_r$ decreases as $1/d$. The residual strain in a linearly graded buffer can be expressed as follows

$$\varepsilon_r = d\varepsilon' - z_c \varepsilon' = (2\lambda \varepsilon' / bc)^{\frac{1}{2}}$$

Eq. II.10.2
Lord, *et al.* examined compositional grading of In$_x$Ga$_{1-x}$As on GaAs with different grading rates. At a growth temperature of 450 °C, different grading rates produced buffer layers with a 3000 Å region free of misfit dislocations. Molina, *et al.* examined In$_x$Ga$_{1-x}$As linearly graded buffers with very high grading rates (30% In/μm) grown at 500 °C and found a similar value for the dislocation free region on top of the graded buffer. They compared the results to Tersoff's calculated equilibrium values and the findings can be summarized as follows:

1. The actual height beyond which the linearly graded buffers were dislocation-free, $z_c$, was less than predicted (i.e., the critical thickness was greater than predicted).

2. The dislocation density for each layer ($\rho$) was slightly smaller than calculated.

3. $z_c$ was not equivalent in the two <110> directions indicating an asymmetry in strain relaxation.

The asymmetric strain relaxation is attributable to different dislocation core structures as discussed in Chapter I. The other disparities from the equilibrium model were slight and could be explained by the fact that 22-38% of the dislocations were edge dislocations and not 60° dislocations. Since nucleation of edge dislocations is highly unlikely, this suggests that misfit dislocations interact in the graded buffer. This can be expected because the misfit dislocation density in compositionally graded buffers is high and segments of dislocation lines deep in the graded buffer may react to form edge segments. However, it is important to note that dislocation interactions in the graded buffer do not inhibit the motion of the threading segments, demonstrated by the fact that reported TDDs in the nominal $x_{ln}=0.22$ graded buffers were less than $10^4$/cm$^2$.

As opposed to equilibrium energy balance calculations, Dunstan and co-workers expanded their geometrical theory for strain relaxation in a single layer to multilayer structures. The expression is of the same form with an experimental relaxation constant,
$K$, which is the same as the $kb$ product determined for single layer under relaxation, 0.83 nm. The expressions for $z_e$ and $\varepsilon_e$ are as follows

$$z_e = [2K/\varepsilon']^{\frac{1}{2}} \quad \text{Eq. II.11}$$

$$\varepsilon_e = [2Kn]^\frac{1}{2} \quad \text{Eq. II.12}$$

Sacedón, et al.\textsuperscript{93} examined the correlations between the equilibrium model, Dunstan's model, and experimental data for In$_x$Ga$_{1-x}$As graded buffers. Basically, the results were the same and upon taking into account the number of edge dislocations, the misfit dislocation density was close to that predicted by the models. Overall, the models were found to predict relaxation in In$_x$Ga$_{1-x}$As linearly graded buffers quite accurately.

González and co-workers\textsuperscript{94} reported that nearly all individual layers of a compositionally graded buffer lie in the work hardening regime for single layer relaxation (i.e., the relaxation process reaches this stage more quickly because sources from previous layers are already present). Based on their results, they presented a model based on work-hardening for the relaxation in In$_x$Ga$_{1-x}$As compositionally graded buffers. The average misfit dislocation density at a given interface ($\rho_{w-H}$) for a compositionally graded buffer is given by

$$\rho_{w-H} = 0.42 \times 10^4 + 3.8 \times 10^7 f \text{ cm}^{-1} \quad \text{Eq. II.13}$$

where $f$ is the misfit factor. It should be noted that the structures they examined were step graded (not linearly graded) and the growth conditions were not discussed or varied.

\textit{b) Aspects of Strain Relief in In$_x$Ga$_{1-x}$As Graded Buffers}

The mechanisms of strain relief in graded layers, as in single layers, are plastic deformation and surface roughening. Kavanagh, et al.\textsuperscript{95} reported that at low temperatures the strain relaxation in In$_x$Ga$_{1-x}$As compositionally graded is nearly complete and symmetric, while at higher growth temperatures this is not the case. At higher growth
temperatures, strain relaxation is asymmetric because strain relaxation in the [1\(\bar{1}\)0] direction is inhibited. This asymmetric strain relaxation leads to a severe surface roughening preferentially in the [110] direction. In all cases it was also reported that the epilayer develops a tilt with respect to the substrate, and that substrate offcut is a factor in the magnitude of tilt. Eberl, et al.\textsuperscript{96} found that an initial jump in indium composition (optimally \(x_{\text{in}}=0.18\)) and then a subsequent grade in composition leads to a decrease in the surface roughness, a decrease in epilayer tilt, the best device quality material. The results in this thesis show that Kavanagh’s high temperature results are likely due to boundaries between domains of different surface reconstruction influenced by dislocations in the graded buffer.

3. **Substrate Patterning**

Since dislocations can terminate at the surface of a crystal, substrate patterning can reduce the threading dislocation density. Substrate patterning involves the reduction and isolation of growth area. This isolates heterogeneous nucleation sites and reduces the lengths that threading dislocations must travel to glide off the edge of the sample.\textsuperscript{97} Beam, et al.\textsuperscript{98} found this technique to work well for structures with compositionally graded In\(_n\)Ga\(_{1-x}\)As buffer layers on GaAs. Lattice-mismatched structures can be designed specifically to exert forces on threading dislocations to glide them to the growth area edges.\textsuperscript{99}

An interesting offshoot of traditional substrate lateral overgrowth techniques is the selective epitaxial lateral overgrowth technique.\textsuperscript{100,101} In this technique a substrate is masked with SiO\(_2\) and then holes, or seed areas, are opened in the SiO\(_2\). As growth proceeds out of the seed layer, the film grows laterally onto the SiO\(_2\) mask resulting in a low TDD in the seed layer. The most successful example of this process is the work done at Nichia Chemical in the development of blue lasers with the heteroepitaxy of GaN on sapphire, a highly lattice-mismatched system (15%).\textsuperscript{102}
4. Effects of Materials Properties

Despite the engineering methods which can be implemented in lattice-mismatched heteroepitaxy, some aspects of the materials system aid or hinder the results of the techniques used. For instance, In$_x$Al$_{1-x}$As buffer layers can be substituted for In$_x$Ga$_{1-x}$As buffer layers since the lattice constants are nearly identical. A study comparing the two materials systems shows that In$_x$Ga$_{1-x}$As buffer layers are more effective at relieving strain than In$_x$Al$_{1-x}$As, but epilayer tilting is more inhibited by In$_x$Al$_{1-x}$As buffer layers.$^{103}$

Dislocation velocity is an important parameter in determining how quickly dislocations can relieve strain in graded buffers and is empirically given by

$$v = v_0 \tau_{ef}^n \exp\left(-\frac{Q}{kT}\right)$$  

Eq. II.14

where $v_0$ is a constant, $\tau_{ef}$ is the effective stress on the dislocation, $Q$ is the activation energy for glide, $k$ is Boltzmann's constant, and $T$ is temperature. The effect of the material system is incorporated by $v$ and $Q$. Dislocation motion is dependent on the bond strength of a material and the growth temperature relative to the melting point. III-V compounds are generally weaker than their group IV counterparts and are grown at temperatures much closer to their melting points. Generally, dislocation glide is more favored in III-V compounds than in group IV semiconductors. Further, within a III-V compound, $\alpha$ dislocations typically have a higher velocity than $\beta$ dislocations.

Dislocation nucleation and motion are also influenced by dopants and alloying.$^{104,105,106}$ The critical stress for dislocation generation mechanisms for $\alpha$ dislocations in GaAs is increased with the addition of indium and silicon in small amounts, with the effect of indium being greater. In addition, silicon lowers the velocity of $\alpha$ and $\beta$ dislocations by two orders of magnitude. Indium does not affect dislocation velocity significantly, however, when dislocations are at rest they can getter the indium and become locked. This effect is greater for $\alpha$ dislocations than $\beta$ dislocations.
5. Measurement of TDD

Several techniques have been used to determine the TDD in materials systems. Ideally, the techniques used to measure the TDD should have good defect resolution over a large range of magnifications. A low magnification technique is important to ensure a representative TDD in materials containing a low density of defects.

a) Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a useful technique for observing samples with a high TDD. Examining a sample either in cross-section (X-TEM) or plan-view (PV-TEM) allows direct observation of dislocations; however, TEM is a high magnification technique and does not allow for accurate measurement of samples with a low TDD. If no threading dislocations are observed with X-TEM, it can only be concluded that the TDD is less than $10^8$-$10^9$/cm$^2$. When no threading dislocations are observed with PV-TEM the TDD can be assumed to be less that $10^7$/cm$^2$, although statistical measurements improve with more viewed area. Figure II-5 shows an X-TEM image of an In$_x$Ga$_{1-x}$As structure with a compositionally graded buffer which has a TDD in the cap layer below the detection limit. Note that the misfit dislocation density in the grade buffer is high enough to be viewed by X-TEM.
b) **Electron Beam Induced Current**

Electron beam induced current (EBIC) is a low magnification scanning electron microscope (SEM) technique which can be used to spatially map a specimen and determine the TDD.\textsuperscript{107} To use EBIC the sample must have an internal field, usually introduced by a p-n junction or Schottky contact. The electron beam creates electron-hole pairs in the sample which can be measured as an external current if the generated carriers lie within the junction or one diffusion length of the junction. If there is a dislocation (or any other defect) in the vicinity of the generated carriers (i.e., in the vicinity of the scanning electron beam), the carriers are trapped and recombine via the defect level and the measured current decreases. This decrease in the induced current can be seen as a dark region in a spatial map of the current collection. EBIC has been very
successful when studying materials systems/devices whose carriers have long diffusion lengths ($10^3$ cm), such as $\text{Ge}_x\text{Si}_{1-x}/\text{Si}$. Materials such as $\text{InAs}$ and $\text{GaAs}$, which have direct bandgap transitions, have much smaller diffusion lengths. The studies during the course of this research found it difficult to obtain sufficient contrast for threading dislocation imaging of III-V compounds. Figure II-6 shows an EBIC analysis of the same structure shown in Figure II-5, exhibiting contrast variations which are not from the threading dislocations. Instead, this contrast is related to the classic cross-hatched pattern observed in structures with compositionally graded buffers.

\textit{c) Cathodoluminescence}

Cathodoluminescence (CL), like EBIC, is a low magnification defect imaging technique which uses the electron beam of the SEM as an excitation source for electron-hole pairs. The radiative recombination of the electron-hole pairs can be collected and the relative intensity can be mapped spatially.\textsuperscript{10a} Threading dislocations and other defects may act as non-radiative recombination centers and can be detected by a decrease in light intensity.
when the electron beam is nearby. Thus, a defect appears as a “dark” region on a spatial map. Usage of CL is generally limited to materials which have significant radiative recombination due to direct gap transitions. SEM stages which can cool samples to liquid helium temperatures allow materials with indirect bandgap transitions to be imaged. In this study, CL, just as EBIC, could not accurately determine the TDD density because no direct observation of single threading dislocations was recorded. Thick layers above the graded buffer can be used to create enough material for CL identification of TDD, but the required thickness is impractical for most structures (3-4 μm).

d) Chemical Etching

Defect revealing etchants have been developed to expose dislocations in materials. These etchants take advantage of the fact that regions with dislocations have different bonding characteristics, allowing etchants to remove material from these regions at a different rate. Selective chemical etching is a low magnification technique which is good for determining the TDD for materials with a low defect density, however, the method is destructive. In addition there are no specific etchants which have been researched for the InGaAs/GaAs system, so some trial and error is typically necessary. Figure II-7 shows the same In0.5Ga0.5As sample as shown in the X-TEM and EBIC images, which was chemically etched with a HF:CrO3:H2O solution. The TDD for this sample was determined to be 2 x 10⁷/cm².
E. Summary

In this chapter, the applications and study of In$_x$Ga$_{1-x}$As/GaAs heteroepitaxy were reviewed. For nearly lattice-matched applications, strained In$_x$Ga$_{1-x}$As layers below the critical thickness, inhibiting the introduction of misfit dislocations, are implemented in the active device regions. Lattice-mismatched systems, however, require misfit dislocations and threading dislocations are the cause for concern.

Research and theories involving compositionally graded In$_x$Ga$_{1-x}$As buffers were reviewed. Theory and experiment support the use of compositional grading to reduce the TDD, although the amount of strain relaxation and crystallographic tilt of the epilayers are subject to design parameters. Alternate methods for reducing the TDD were also discussed, although only compositional grading was explored in this thesis.
The difficulties of determining the TDD in In$_x$Ga$_{1-x}$As layers were discussed. At the moment, TEM with appreciable statistics is the most accurate method of determining the TDD.
Chapter III

III-V Compound Epitaxy and Overview of OMVPE

This chapter gives an overview of the main epitaxial growth techniques used for the research presented in this thesis. The theory of organometallic vapor phase epitaxy (OMVPE) and the relevant growth calibration data compiled during the course of this study are surveyed.
A. Growth Techniques Used for III-V Compound Epitaxy

There are several techniques for III-V compound epitaxy, each having its unique advantages and limitations. Table II lists the different epitaxial growth techniques used commonly for III-V compound epitaxy along with some of their positive aspects and disparaging features. Organometallic vapor phase epitaxy (OMVPE) and molecular beam epitaxy (MBE) were the two epitaxial growth techniques used for the research presented in this thesis.⁴

<table>
<thead>
<tr>
<th>Growth Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Phase Epitaxy (LPE)</td>
<td>Extremely Pure Material</td>
<td>Poor Thickness Uniformity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Difficult to Make Abrupt Interfaces</td>
</tr>
<tr>
<td>Molecular Beam Epitaxy (MBE)</td>
<td>Excellent Control of Interfaces</td>
<td>Slow Growth Rates</td>
</tr>
<tr>
<td></td>
<td>in-situ Diagnostics</td>
<td>High Vacuum Process</td>
</tr>
<tr>
<td>Hydride Vapor Phase Epitaxy</td>
<td>Very High Growth Rates</td>
<td>No Aluminum</td>
</tr>
<tr>
<td>(HVPE)</td>
<td>In-situ Etching of Substrates</td>
<td>Poor Process Control</td>
</tr>
<tr>
<td>Organometallic Vapor Phase</td>
<td>Flexible Process</td>
<td>Expensive Reactants</td>
</tr>
<tr>
<td>Epitaxy (OMVPE)</td>
<td>High Purity</td>
<td>Complicated Process</td>
</tr>
</tbody>
</table>

⁴ Organometallic and metalorganic are commonly interchanged along with vapor phase epitaxy and chemical vapor deposition. So the acronyms OMVPE, MOVPE, OMCVD, and MOCVD all refer to the same epitaxial growth technique.
B. Some Notes on MBE

The MBE growth process involves the evaporation of elemental species onto a heated substrate. Under high vacuum conditions \(10^{-10} \text{ torr}\) and a sufficient substrate temperature, the impinging atoms will migrate on the substrate surface until they attach to lattice sites.

MBE sources are very pure (99.99999%) and are typically heated in miniature furnaces called effusion cells (in the case of Si sources, electron beam evaporation can be used). The evaporation rate of the elemental species is controlled by the temperature of the effusion cells, and shutters at the entry point into the chamber allow for switching of elemental species for heterostructures and solid solutions. The substrates are mounted on molybdenum blocks or ring holders which rotate to allow for uniform thickness across the wafer/substrate, and the temperature of the substrate during growth is monitored by a thermocouple or optical pyrometer. Deviations from the traditional MBE process include the use of gaseous sources for group V elements and metal-organic precursors for the group III elements. Typically the epitaxial processes which implement these deviations are referred to as gas source MBE (GS-MBE) and metal-organic MBE (MOMBE).

There are very attractive features for using MBE in specific scientific studies and some commercial applications. The two primary features which make MBE an essential growth tool for some applications are:

1) The growth rate and growth temperature can be decoupled since the growth rate is controlled by the evaporation rate of the adatoms which is determined by the temperature of the effusion cell, not the substrate temperature.

2) The availability of *in-situ* diagnostics, reflective high energy electron diffraction (RHEED) for example, allow for monitoring of the growth processes, such as surface morphology and surface reconstruction.
The first advantage is that growth kinetics can be controlled independently from the growth rate. This allows for the growth of structures which are not in equilibrium and cannot be achieved via other epitaxial techniques. The \textit{in-situ} diagnostics provide crucial scientific data for the initial stages of growth and subsequent stages of heteroepitaxy. \textit{In-situ} characterization of epitaxial growth is not as easily implemented in other growth processes and is highly advantageous for the growth of high quality heterostructures.

Due to its advantages, MBE is implemented in several commercial applications including Al$_x$Ga$_{1-x}$As/GaAs lasers and microwave device components. However, as shown in Table II, MBE does not lend itself to high volume manufacturing or applications which implement compositionally graded buffers since the low growth rates mandate long growth sequences. OMVPE is a more practical growth tool for applications which require compositionally graded buffers since the growth rates are much higher.

\section{Overview of OMVPE}

OMVPE has distinct advantages for device applications which require compositionally graded buffers. In addition to high growth rates, the flexibility of OMVPE allows for a suite of III-V and II-VI solid solutions for heteroepitaxial applications. However, the flexibility of the process (i.e., number of design parameters) also makes OMVPE a very complicated epitaxial technique. In fact, many aspects of the process are not entirely understood.

The following sections discuss the essential elements of OMVPE for III-V compound epitaxy and present some of the calibration data for the OMVPE reactor used in this thesis. Much of the theoretical description of OMVPE is taken from the book by Stringfellow.\textsuperscript{112}

\section{OMVPE Basics}

OMVPE is typically conducted at relatively high pressures, 0.1-1.0 atm, in cold-walled reactors to avoid deposition on surfaces other than the substrate. The mass transport of
the precursor species is conducted via vapor phase constituents under the presence of a carrier gas, such as H₂ or N₂.

GaAs can be grown with trimethyglyllium (TMG) as the group III precursor and arsine (AsH₃) as the group V precursor. The reaction of the species can be expressed as follows:

\[(CH₃)₃Ga(g) + AsH₃(g) \rightarrow GaAs(s) + 3CH₄(g)\]

This equilibrium reaction is actually quite simplified as several intermediate steps must occur before GaAs is incorporated on the surface. A more complete description of the process involves the diffusion of TMG and arsine through the gas boundary layer at the surface of the film. The reactants must then decompose prior to allowing Ga and As to migrate to their appropriate lattice sites. Although the reaction path has been extensively studied, some aspects are not fully understood yet.¹¹³,¹¹⁴,¹¹⁵

For III-V compound epitaxy, it is generally found that the group III species is depleted at the surface and the group V element is present in excess. Since group V partial pressures are much greater than that of the group III, the excess group V presence is necessary to avoid volatilization of group V species from the sublattice. These features have consequences on the growth rate and the epitaxial quality of III-V compounds and solid solutions grown by OMVPE.

2. **Growth Rate Dependencies with OMVPE**

OMVPE features three regimes of growth rate \( (r_g) \) temperature dependence:

1) kinetically limited regime (I), where growth rate is highly dependent on temperature; the rate limiting step is the cracking of the precursors.

2) mass transport limited regime (II), showing a weak temperature dependence; the rate limiting step is diffusion across the gas boundary layer.
3) thermodynamically controlled regime (III), noted by a decrease in growth rate with increasing temperature; higher temperatures drive an exothermic reaction back towards the reactants.\

The three regimes are shown schematically in Figure III-1.

Calibration data for growth of GaAs in our OMVPE system is shown in Figure III-2. The growth rate starts to become independent of temperature at approximately 600 °C. Most epitaxial structures are grown in the mass transport limited regime and the bulk of the growth data presented in this thesis was gathered under mass transport limited conditions. As noted earlier, the group III species is depleted at the surface and the group V species is in excess during III-V compound epitaxy with OMVPE. This has the following consequences on the growth rate:

1) Group V flow rate has practically no effect on the growth rate of III-V compounds.

2) With the ratio of different group III precursors in the gas phase fixed, increasing the total group III flow rate increases the growth rate of a film.

" The decrease in growth rate in this temperature regime has also been attributed to depletion of reactants on reactor walls upstream from the substrate.
Figure III-1: Typical Temperature Dependence on Growth Rate with OMVPE

Figure III-2: Growth Rate vs. 1/Temperature for GaAs in Our OMVPE Reactor

Chapter III- III-V Compound Epitaxy and Overview of OMVPE
3. **Solid Solutions and Epitaxy of In\textsubscript{x}Ga\textsubscript{1-x}As**

The growth rates and composition of III-V solid solutions grown with OMVPE are dependent on the total flow of group III species, the relative flows of the different precursors, and the comparative cracking efficiencies of the precursors.

For solid solutions with multiple constituents on the group III sublattice, such as In\textsubscript{x}Ga\textsubscript{1-x}As, the composition of the epitaxial film is typically linearly dependent on the ratio of the flow rates of the constituents under mass transport limited conditions.\footnote{For mixing on the group V sublattice, the dependence is not linear as the incorporation rate of group V precursors are very different. It is very difficult to get a InAs\textsubscript{x}P\textsubscript{1-x} film with high P content.} The figure of merit for the relative incorporation of a species \(A\) in solid solution with \(B\) is the distribution coefficient, \(k_A\), given by

\[
 k_A = \frac{x_A}{p_A/(p_A + p_B^*)}
\]

Eq. III.1

where \(x_A\) is the mole fraction of species \(A\) in the film and \(p_A^*\) is the partial pressure of species \(A\) in the gas stream (\(p_B^*\) is the same for constituent \(B\)). The partial pressures are proportional to the flow rates, and therefore can be replaced with the flow rates of the respective precursors. For most III-V solid solutions with mixing on the group III sublattice, \(k\) is unity, implying that the diffusion coefficients of the group III species are identical. Figure III-3 is a plot of the composition of In\textsubscript{x}Ga\textsubscript{1-x}As epitaxial films versus the fraction of trimethylindium (TMI) in total group III precursor flow grown at 700 °C. The plot shows that the incorporation of indium into In\textsubscript{x}Ga\textsubscript{1-x}As films in our reactor is not linear (i.e., it is not entirely mass transport limited).

Examining the composition data for several nominal \(x_{In}=0.06\) graded buffers, \(k\) is found to differ with temperature (see Table III). This trend and the data in Figure III-3 demonstrates the different cracking efficiencies of TMI and TMG. TMI cracks more...
readily at lower temperatures allowing for higher indium content films at lower temperatures.\textsuperscript{116}

The difference in cracking efficiencies also manifests itself in the form of different growth rates at different temperatures for the same total group III flow and ratio. Figure III-4 shows the growth rate of $\text{In}_x\text{Ga}_{1-x}\text{As}$ as a function of temperature for an average group III flow rate of 0.23 secm with an average TMI fraction of 0.063.

It should be noted that the determination of calibration curves for lattice-mismatched epitaxy is not trivial. Measurement of composition with x-ray diffraction requires that both residual strain and epilayer tilt be extracted.\textsuperscript{117,118} Other methods, such as Rutherford Backscattering Spectroscopy (RBS) and quantitative energy dispersive spectroscopy (EDS), do not rely on the strain state of the system and give excellent compositional data. However, they do not provide some of the other essential data needed for characterization.
Table III: Incorporation Coefficient as a Function of Temperature

<table>
<thead>
<tr>
<th>Growth Temperature (°C)</th>
<th>$k_{la}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.77</td>
</tr>
<tr>
<td>550</td>
<td>0.64</td>
</tr>
<tr>
<td>600$^{iii}$</td>
<td>0.47</td>
</tr>
<tr>
<td>650</td>
<td>0.61</td>
</tr>
<tr>
<td>700</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Figure III-4: Growth Rate of $In_xGa_{1-x}As$ vs. Growth Temperature

$^{iii}$ This point at 600 °C was regrown and characterized, confirming the same results.

Chapter III- III-V Compound Epitaxy and Overview of OMVPE
of lattice-mismatched epilayers. The work in this thesis relied on x-ray diffraction and luminescence data (i.e., emission wavelength) to determine compositional calibration curves. Although these methods require greater diligence to determine accurate compositional calibration data and are more susceptible to errors, the completeness of data retrieved far outweighed any detractions. On that note, the compositional calibration data on In$_x$Ga$_{1-x}$As with $x_{In} < 0.40$ is quite accurate with errors in indium fraction content on the order of ±0.04. Compositions with higher fractions of indium were beyond the scope of the calibration data required for this research and would have to be further examined.

For a more accurate calibration (composition or growth rate) of atmospheric OMVPE grown In$_x$Ga$_{1-x}$As, a complete survey of growth rate and compositional uniformity across a sample would have to be undertaken. Also, unstable TMI delivery rates are a common problem with OMVPE and would have to be monitored.\textsuperscript{119}

4. **Doping with OMVPE**

The incorporation of dopants by OMVPE is an important consideration for device structures. Typically, the incorporation of dopants can be considered to occur in two regimes. In the case where the dopant vapor pressure is low (i.e., the vapor pressure of the dopant at the surface, $p^*_D$, is much less than that in the gas phase, $p^*_D$) the fraction of dopant in the solid solution, $x_D$, is given by

$$x_D = \frac{p^*_D}{p_m^*} \quad \text{Eq. III.2}$$

where $p_m^*$ is the total partial pressure of the group III sources. In the other regime where the vapor pressure of the dopant is high ($p^*_D \approx p^*_D$), the solid fraction of the dopant is expressed as

$$x_D = kp^*_D \quad \text{Eq. III.3}$$
with \( k \), the distribution coefficient. As with the expression in the previous section, the partial pressures in the gas phase can be taken as proportional to the flow rates. The two dopants implemented in our OMVPE reactor are silane (SiH\(_4\)) for n-type doping and dimethylzinc (DMZ) for p-type doping. Typically, SiH\(_4\) doping\(^5\) behaves within the regime of Eq. III.2, while DMZ incorporation is represented by Eq. III.3. Figure III-5 illustrates the doping of GaAs in our OMVPE reactor for a range of gas flows of silane and DMZ with the TMG flow fixed at 0.21 sccm. Note that the dopant concentrations were taken with secondary ion mass spectroscopy (SIMS) and do not necessarily reflect actual carrier concentrations.

There are two significant points to be made regarding doping with Si and Zn. Zn is a fast diffuser in III-V compounds, creating gradual p-n junctions or displacing the junction

*Figure III-5: Doping Concentrations of Zinc and Silicon in GaAs Grown at 650 °C*
from its intended position.\textsuperscript{iv} Si is well behaved with respect to diffusing in III-V's; however, it incorporates readily with increasing temperature and at high concentrations can nucleate dislocation loops. Figure III-6 shows an X-TEM image of a GaAs buffer with dislocation loops caused by high Si doping at 650 °C. The SiH\(_4\) and TMG flow rates for the sample shown in the figure were 0.040 sccm and 0.21 sccm, respectively.

\textit{Figure III-6: X-TEM Sample Showing Dislocation Loops in GaAs Due to Excessive Si Doping}

\textsuperscript{iv} There are only two points for Zn in Figure III-5 because the steps in doping concentration were smeared out by the diffusion of Zn.

Chapter III- III-V Compound Epitaxy and Overview of OMVPE
5. **High Quality Epitaxial Films and the V/III Ratio**

Since the group V elements in III-V compounds are highly volatile and can deplete from the crystal at high temperatures, the group V partial pressure is always in excess of what is needed for film growth. The ratio between the total group V flow rates and the total group III flow rates is commonly quoted in the literature as the V/III ratio. Strictly defined, the V/III ratio is the ratio of the partial pressures of the group III and group V sources at the interface and not in the gas phase. The expression for V/III ratio is given by

\[
\frac{p_V^i}{p_{\text{III}}^i} = \frac{K_{\text{III}V}}{a_{\text{III}V}} (p_V^*)^2
\]

Eq. III.4

where \( K \) and \( a \) are the equilibrium constant for the reaction forming the III-V compound/solution of interest and activity of the same compound/solution, respectively. Note that the true V/III ratio is dependent on the group V flow rate squared and is not dependent on the group III flow rate.

Despite the discrepancies and misunderstanding of the V/III ratio, it is commonly understood that the group V flow rate must be at least 10 times than of the group III flow rate to prevent depletion of the group V species from the substrate or epitaxial film. Excessive depletion of the group V elements causes the formation of droplets of group III elements on the surface.

**D. Experimental Section**

Although results with OMVPE are consistent within the literature, actual growth conditions change depending on the reactor design and flow conditions. The following sections discuss the OMVPE reactor used in this study, along with typical growth conditions used during device epitaxy.
1. **Thomas Swan Atmospheric Reactor**

The OMVPE system brought on-line for the research presented in this thesis was a Thomas Swan Atmospheric Research Reactor. A schematic of the gas flow sequence of the system is shown in Figure III-7. The delivery of the source gases was controlled by mass flow controllers (MFCs), rated for 100 or 200 sccm flow, except for the carrier gas and vent line MFCs, rated for 10000 sccm. The dilution stages and bubblers can be supplied with $\text{H}_2$ or $\text{N}_2$ for the delivery and/or dilution of the precursors.

![Figure III-7: Gas Flow Diagram of Thomas Swan Reactor](image)

Chapter III- III-V Compound Epitaxy and Overview of OMVPE
The quartz growth chamber is cold-walled and only accommodates pieces of substrate material with an average dimension of 1.5 cm x 2.0 cm. The small volume eases quartz cleaning and decreases gas cost (high purity N₂ and H₂, one of which is always flowing). The substrates were placed on a graphite susceptor and a thermocouple embedded in the susceptor was used to monitor the temperature of the substrate. A halogen lamp underneath the quartz tube heats the susceptor during epitaxy with the power to the lamp controlled by a Eurotherm temperature controller. Figure III-8 is an illustration of the growth chamber.

2. **Precursors and Typical Growth Conditions**

The group III, group V, and doping sources, along with their typical flow rates are listed in Table IV. The flow rates of the group V sources and SiH₄ are straightforward, as they are gaseous sources. The group III precursors and DMZ are liquid sources which are
Table IV: OMVPE Sources and Typical Growth Settings

<table>
<thead>
<tr>
<th>Reactant/ Precursor</th>
<th>Vapor Pressure Curve, $f(T)$</th>
<th>Bubbler Temperature</th>
<th>Vapor Pressure</th>
<th>Typical Flow Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsine (AsH₃)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>67</td>
</tr>
<tr>
<td>Phosphine (PH₃)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>138</td>
</tr>
<tr>
<td>1% SiH₄ in H₂</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.005</td>
</tr>
<tr>
<td>Dimethylzinc (DMZ)</td>
<td>$\log(p) = 7.802 - \frac{1560}{T(K)}$</td>
<td>-10</td>
<td>123.3</td>
<td>0.01</td>
</tr>
<tr>
<td>Trimethylgallium (TMG)</td>
<td>$\log(p) = 8.07 - \frac{1703}{T(K)}$</td>
<td>2</td>
<td>76.0</td>
<td>0.21</td>
</tr>
<tr>
<td>Trimethylindium (TMI)</td>
<td>$\log(p) = 10.52 - \frac{3014}{T(K)}$</td>
<td>25</td>
<td>2.6</td>
<td>0.09</td>
</tr>
<tr>
<td>Trimethylaluminum (TMA)</td>
<td>$\log(p) = 8.224 - \frac{2135}{T(K)}$</td>
<td>17</td>
<td>7.0</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The flow rate, $f$, of an organometallic source out the bubbler is given by

$$f = f_b \times \frac{p_{\text{MO}}}{p_T}$$

Eq. III.5

---

** The tabled value of SiH₄ flow rate is the actual flow rate of SiH₄, already considering the dilution of the source.

*** TMI is typically a solid source, but erratic delivery rates of indium led to the development of solution TMI.
with \( f_b \), the flow of the carrier gas through the bubbler; \( P_{OM} \), the partial pressure of the organometallic source; and \( p_n \), the total pressure over the bubbler. For a double dilution line, the output flow from the buffer is given by

\[
\dot{f} = \frac{f_b \times \frac{P_{OM}}{P_r}}{f_b + f_{dl}} \times f_{out}
\]

Eq. III.6

with \( f_{dl} \), the flow of carrier gas through the dilution line, and \( f_{out} \), the flow coming through the output mass flow controller (MFC). Note that if the dilution line flow is zero and the output flow is the same as the bubbler flow, the expression is the same as for a organometallic source with no dilution. A word of caution about double dilution lines, as the output flow is not restricted to one path. A pressure controller maintains the pressure above the bubbler and can allow flow to an alternate path besides the output flow MFC. If the sum of the flow rates through the bubbler and dilution line is not enough to support the flow through the output line and the prescribed pressure over the bubbler, the pressure over the bubbler will drop. For our OMVPE system, the pressure over all the bubblers was typically 1200 torr.

3. Preparation of Substrates and Common Growth Procedures

Since our OMVPE reactor can not support full wafers, the GaAs wafers purchased from AXT were typically cleaved or die-sawed for subsequent growth. For cleaved pieces no cleaning procedures were necessary as the wafers were epi-ready. When wafers were die-sawed, they were typically coated with photoresist prior to dicing in order to avoid significant particle accumulation on the surface. The photoresist was stripped with acetone and the wafer pieces were then etched to remove contaminants left behind by the acetone and photoresist. Several etching solutions are used to prepare GaAs substrates for epitaxy.\(^{120}\) The etching solution predominantly used for our studies was 1:1:20
\( \text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O} \) The actual growth sequences differed depending on the design of the experiment or heterostructure, however, there were some general procedures which applied to all growth runs. All growths were carried out under a \( \text{H}_2 \) carrier flow of 5000 sccm, although some advantages to using \( \text{N}_2 \) and greater flow rates have been reported elsewhere when considering the thermal profile across the substrate.\(^{121}\) To initiate each growth sequence, the substrate was taken up to 200-300 °C for 5 minutes to evaporate any water or other volatile contaminants on the surface. Subsequently, the substrate was heated to 650 °C for thermal desorption of the oxide on GaAs for 5 minutes in an \( \text{AsH}_3 \) flow of 67 sccm. A GaAs buffer layer was then grown for at least 5 minutes (\( \approx 3000 \) Å) prior to heteroepitaxy.

**E. Summary**

In this chapter the main advantages regarding the use of MBE for heteroepitaxy were outlined. However, it was also pointed out that the growth rates attainable with MBE are not optimal for applications with graded buffers which require thick layers. OMVPE is considered a better alternative for compositionally graded buffers due to the high growth rates which can be attained. The basic operation of OMVPE, the calibration data obtained in our reactor, and our experimental growth procedures/parameters were summarized.

\(^{121}\) The ratios of the solution had to be varied depending on where on the wafer the piece was taken from and whether it part of a 2" or 3" GaAs wafer. This is due to increased defect delineation on substrate material closer to the edge of the wafer and on larger wafers.
Chapter IV

$\text{In}_x\text{Ga}_{1-x}\text{As LED Structures Grown by MBE}$

This chapter presents the materials characterization results obtained from examining 1.3 μm LED structures grown by molecular beam epitaxy (MBE). Much of the work was published in the Volume 83 of the Journal of Applied Physics, p. 592 (1998).

In this study, 1.1-1.3 μm light-emitting diode (LED) structures with $\text{In}_x\text{Ga}_{1-x}\text{As}$ compositionally graded buffers were grown on GaAs substrates by MBE and characterized using microstructure and discrete device characterization techniques. The growth temperature and design of the graded buffer greatly affect the luminescence of the active device region above the graded buffer. These effects were most prominent in quantum well LEDs. In quantum well devices, bright luminescent bands in the $<110>$ directions are revealed under cathodoluminescence and the number of bands and their intensity depend on grading rate.
A. Introduction

Optoelectronic devices which emit at wavelengths for fiber optic telecommunications applications (1.3 and 1.55 μm) are fabricated on InP. The ability to grow and fabricate devices for these applications on GaAs substrates would potentially lead to higher device yield and lower cost, and offer potential for integration with GaAs electronics, which in turn would allow for a higher device density at a lower cost. Such a technology could have an impact on the economic feasibility of fiber to the home applications, where the cost of emitters, detectors, and hybrid electronics are a factor for ubiquitous deployment. Since no solid solution lattice-matched to GaAs can emit light at the wavelengths of interest, the challenge is to overcome the lattice-mismatch which must be addressed for such device applications.8,122

Compositionally graded buffers in the Ge$_{x}$Si$_{1-x}$/Si, In$_{x}$Ga$_{1-x}$As/GaAs, and GaAs$_{x}$P$_{1-x}$/GaAs materials systems have been effective in accommodating lattice-mismatch (i.e. relieving strain efficiently) while allowing high quality device characteristics from regions above the graded buffer.5,6,84,91,123,124 The effects of the graded buffer on light emitting diode (LED) active regions due to surface roughness, carrier transport properties, and trap levels, have not been fully investigated. We expect the relaxed graded buffer to influence LED emission characteristics based on studies examining effects on other device properties.125,126

B. Experimental Procedures

The samples were grown by solid-source molecular beam epitaxy (MBE) on n+ GaAs substrates at the Max Planck Institute in Stuttgart, Germany. The LED design implemented a single strained quantum well acting as the emitting region (referred to as the QW LED design). Figure IV-1 is a schematic of the general QW LED structure. The microstructure of the samples was examined by cross-sectional and plan-view transmission electron microscopy (X-TEM and PV-TEM) with a JEOL 200CX operating
at 200 kV. Emission properties were examined by photoluminescence (PL) measurements at 4 K with a 488 nm He-Ne laser as the excitation source. A JEOL JSM-6400 scanning electron microscope (SEM) with an Oxford Instruments cathodoluminescence (CL) attachment was used to spatially map the luminescence from the samples. A Ge detector model EO-817L from Northcoast was used for both PL and CL experiments.

The particular values of $x_n$ (indium composition) in the quantum well and clad were chosen after modeling the effective bandgap (i.e., emission wavelength) of the active region as a function of strain, indium composition, and quantum confinement. The expression for the effective bandgap of the active region incorporates the following terms:

$$E_g (eV) = 1.42 - 1.615x_n + 0.555x_n^2 + \left[ 2a\left( \frac{C_{11} - C_{12}}{C_{11}} \right) + b\left( \frac{C_{11} + 2C_{12}}{C_{11}} \right) \right] + \frac{\pi^2h^2}{8n_f^2} + \frac{\pi^2h^2}{8n_i^2} \quad \text{Eq. IV.1}$$

The first three terms are the contributions from the natural bandgap of the $\text{In}_{x}\text{Ga}_{1-x}\text{As}$ alloy in the active region. The terms in square braces take into account the effect of strain on the bandgap of the active region in the QW LED, where $a$ is the hydrostatic
deformation potential constant, $b$ is the shear deformation potential constant, and $C_{II}$ and $C_{II}$ are components of the stiffness matrix of the epilayer. Strain, $\varepsilon$, is taken as the misfit,

$$\varepsilon = \frac{a_s - a_o}{a_o}$$  \hspace{1cm} \text{Eq. IV.2}

with $a_s$, the lattice parameter of the substrate, and $a_o$, the lattice parameter of the epilayer. Referring to Eq. IV.1, the sign in front of the second term in square braces is negative if the layer is under tension and positive if it is under compression (for the InGaAs/GaAs system the sign is positive, as the strain is compressive). The strain term can change the size of the bandgap noticeably if the active region is completely strained.\(^{127}\) The last two terms of Eq. IV.1 incorporate the effect of electron and hole confinement due to the quantum well. The effect of the quantization of the energy states in Eq. IV.1 is modeled to first order by the classic particle in a box analysis, where $l$ is taken as the thickness of the quantum well. Since some of the materials properties of the In$_x$Ga$_{1-x}$As ternary alloy are not known for all compositions, we linearly interpolate the properties based on the binary compounds, InAs and GaAs (Table V lists the relevant materials properties of InAs and GaAs used in this study).\(^{128}\) With the critical thickness of the quantum well as a constraint, we fixed the difference in indium composition between the quantum well and adjacent clad layers at 0.10 indium. This constraint is equivalent to fixing the strain in the quantum well. With this constraint in place, we calculated the luminescence wavelength from the quantum well as a function of $x_{in}$ in the quantum well/clad and the thickness of the quantum well (see Appendix D). The results of the calculation are shown as a contour plot in Figure IV-2. There are two distinct regimes on the plot. The first regime is at large thickness, where the emission wavelength is not sensitive to thickness, but this is not feasible since the critical thickness for introducing misfit dislocations is exceeded ($h_c \approx 175$ Å). The second regime at fairly small thickness, where the emission wavelength is an extremely sharp function of quantum well thickness, leads to very demanding growth control. The structures used in this study were designed as a compromise between the two regimes in the thickness range 80-150 Å, in which practical
growth tolerances can be met while maintaining the desired emission wavelength. The indium compositions of the clad ($x_{\text{clad}}$) and quantum well ($x_{\text{QW}}$) were 0.22 and 0.35, respectively, for this study. We chose a 0.13 indium composition difference between the quantum well and clad, since this choice would allow for more carrier confinement and less indium content in the graded buffer (i.e., the thickness of the graded buffer could be decreased).

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Chapter IV- In$_{x}$Ga$_{1-x}$As LED Structures Grown by MBE
Figure IV-2: Results of Model Depicting Emission Characteristics of Quantum Well

Table VI: Growth Parameters Used for Quantum Well LED Structures

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate</td>
<td>350</td>
<td>480</td>
<td>580</td>
<td>580</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grading Rate</td>
<td>22</td>
<td>22</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>%In/μm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To investigate this structure, four different QW LED structures were grown with varying growth temperatures and grading rates (%In/μm) as described in Table VI. There were minor differences in the growth sequences of samples 1 and 2. First, sample 1 had an initial jump in indium composition at the GaAs surface of 11%; however, the overall grading rate was maintained at 22%. Sample 1 also experienced growth interruptions and anneals during the growth of the graded buffer every 500 Å in an attempt to relax the structure completely. During the growth sequence of sample 2, the temperature was dropped to 420 °C for growth of the quantum well and top clad layer to achieve a more 2D-like quantum well structure.

C. Materials Characterization Results

Figure IV-3 shows X-TEM images of sample 1 and sample 3. Both structures had the same grading rate, but were grown at 350 °C and 580 °C, respectively. Both samples show no threading dislocations coming up from the graded buffer, implying a threading dislocation density (TDD) less than 10⁹/cm² (due to the sensitivity limit of X-TEM, we can not speculate on lower TDDs). However, sample 1 differs from sample 3 in that there are steps in the graded buffer free of misfit dislocations, indicating that the graded buffer is not completely relaxed. Sample 3 has no regions in the graded buffer which were free of misfit dislocations, indicating the graded buffer has a greater degree of relaxation than sample 1. Sample 3 also shows regions of strong contrast in the quantum well region. The TEM contrast indicates areas of 3D topography in the layer. The thickness variations have produced regions of high local strain which have nucleated dislocations in the vicinity of the quantum well.129 It should be stressed that these dislocations are not related to the strain relieved by the compositionally graded buffer, and the strain inherent to the quantum well is below the critical strain for dislocations introduced in a 2D layer.
The differences in microstructure between samples 1 and 3 lead to differences in the bulk luminescence properties as well. Figure IV-4 shows the PL spectra of samples 1 and 3 taken at 4 K under identical excitation conditions. The emission wavelengths of the clad and quantum well for sample 1 are shorter than anticipated. Residual strain from the incomplete relaxation of the graded buffer raises the bandgap of the active region. The PL spectrum from sample 3 shows that the emission wavelengths of both the clad and quantum well are at a longer wavelength than that of sample 1. This agrees with the TEM observation that sample 3 had a greater degree of relaxation in the graded buffer. However, the emission of the clad and quantum well are not as sharp for this sample. The inhomogeneous strain seen in the X-TEM images of sample 3 creates variations in the bandgap, producing larger linewidths. Also note that the quantum well peak is much larger relative to the clad peak in sample 3 than the quantum well peak in sample 1. This enhanced quantum well luminescence suggests more effective carrier trapping in sample 3.
Figure IV-4: PL Spectra from (a) Sample 1 and (b) Sample 3
We can use the ratio of the peak heights of the quantum well and the clad emission as a measure of the ability of the quantum well to trap carriers. Figure IV-5 is a plot of this ratio for all samples as a function of excitation power (all data were taken at 4 K). The data show a clear correlation between the ability of the quantum well to trap carriers and the characteristics of the compositionally graded buffer. As the growth temperature of the graded buffer increases or the grading rate decreases, the quantum well becomes more efficient at trapping carriers. At high excitation powers, the ratio starts to plateau and then decrease as states in the well begin to saturate. Note that saturation is achieved with the least amount of power for sample 4, which was grown with the slowest grading rate at the highest growth temperature. It should be noted that the higher capture efficiencies of quantum well structures grown at higher temperature are not due to degradation of the luminescence properties of the clads. Figure IV-6 shows the overall luminescence intensity from all the structures at a laser power of 1.0 W. Note that the clad and the quantum well emission increase with higher growth temperatures.
To better understand the correlation between microstructure and luminescence properties of the quantum well, we used spatially resolved cathodoluminescence (CL). Figure IV-7 shows the CL data from sample 3 taken at 4K with a 25 kV acceleration voltage and a probe current of 150 nA. The CL spectrum [Figure IV-7(a)] shows that the average luminescence intensity from the quantum well was much less than that of the clad layer. Monochromatic CL maps at the emission wavelengths for both the quantum well and clad are shown in Figure IV-7(b). The variation in intensity in the clad is consistent with the classic cross-hatched pattern which develops from the strain fields that emanate from the buried dislocations in the graded buffer.\textsuperscript{130} The map of luminescence from the quantum well, shows that there are sharp bands of emission forming in one $<110>$ direction, and other regions with little or no luminescence. This effect can be quantified by looking at the line intensity profiles [Figure IV-7 (c)] along the lines plotted on the two maps. The intensity profile from the clad shows a consistent variation across the sample. The intensity profile from the quantum well plotted along the same line shows regions of luminescence which are greater than that of the clad despite the fact that the average luminescence from the clad is much greater than that of the quantum well. In addition the brightest regions are off the brightness scale on our map, while the dark regions are at or
Figure IV-7: CL Spectrum (a), CL Maps (b), and Intensity Profiles (c) from Sample A (Growth Temp = 580 °C and Grading Rate = 22% In/μm)
Figure IV-8: CL Spectrum (a), CL Maps (b), and Intensity Profiles (c) from Sample 3 (Growth Temp ~ 580 °C and Grading Rate ~ 22% In/µm)
near the bottom of our scale. The key point is that the luminescence from the quantum well is coming mostly from a few highly efficient emitting regions aligned along a <110> direction.

Figure IV-3 shows the CL data from sample 4 which was grown at the same temperature as sample 3, but at a grading rate less than that of sample 3 (8% In/µm vs. 22% In/µm). The spectrum from sample 4 shows that the average luminescence from the quantum well was much greater than that of the clad. The CL map at the clad emission wavelength showed a similar cross-hatched pattern to that of sample 3 with a similar intensity profile. The CL map of the quantum well emission in sample 4 reveals strong luminescent bands in the <110> direction as seen in sample 3, but the lines are more sharp and greater in number. The intensity profile of the quantum well showed more contrast than the quantum well in sample 3. Again, the majority of the light emanated from these highly emitting regions.

D. Discussion

The materials characterization data shows that the graded buffer is affecting the luminescence from the active device region. The effect is a function of grading rate and growth temperature. Two different hypotheses that explain the luminescence behavior will be discussed.

Strain fields from dislocations in the graded buffer may create spatial variations in the bandgap in the uniform cap and quantum well. Such strain fields from a graded buffer will create regions of varying compressive strains in the uniform cap layer and quantum well region above, thereby varying the bandgap in the quantum well. Thus, those regions of increased bandgap may not trap carriers effectively creating “dark” regions, while regions where the bandgap was not affected would have enhanced trapping efficiency, making those regions “bright.”
To test this hypothesis we modeled the effect of the dislocation strain field on the bandgap of the quantum well. Our model assumes a completely relaxed graded buffer with a random distribution of 60° dislocations. Since the features in our CL map lay predominantly in one <110> direction, our model emulated this anisotropy by considering dislocations in only one <110> direction. Figure IV-9 shows the tetragonal distortion ($\varepsilon_{33}$) from a completely relaxed 22% indium, 1 µm graded buffer (see Appendix E). The strains are very large close to the graded buffer and decay as $1/r$ ($r$ is the distance from the top of the graded buffer).

The bandgap variations of the quantum well due to strains from the graded buffer were calculated using Eq. (IV.1). Using an upperbound approximation, the change in bandgap was linked to the larger strain (absolute value), $\varepsilon_{11}$ or $\varepsilon_{22}$. We compared the bandgap energy for a quantum well modeled 0.5 µm above a 1 µm, 22% indium, graded buffer and above a 3 µm, 22% indium, graded buffer. It is important to note that our model only includes the effect of dislocation strains on a planar quantum well. Other strains induced
by 3D growth (i.e., samples 3 and 4) are not included in this model. Figure IV-10 shows the calculated changes in bandgap at a distance of 0.5 μm away from the graded buffer (this distance was close to our experimental parameters). Over a range of 20 μm the variations in bandgap are 2 meV and are significant at 4 K (kT=0.35 meV). Comparing the variations in bandgap from our model and the quantitative CL profiles from Figure IV-7(c) and Figure IV-8(c), we can see some interesting features which suggest some correlation between the strains from the graded buffer and the emission properties of the quantum well. Examining the CL map line profile from sample 3 (1 μm graded buffer) in Figure IV-7(c), we see that the bright emitting regions are separated by approximately 15-20 μm. Examining the changes in bandgap from our model of a 1 μm thick graded buffer, there are two distinct minima over 20 μm. Furthermore, the CL map line profile from sample 4 (3 μm graded buffer) in Figure IV-8(c) shows approximately 6-8 brightly emitting regions over a range of 20 μm. Our model results show an equivalent number of minima over the same range. From these observations, there is a clear correlation between the number of minima in bandgap energy (or strain) and the number of

![Graph showing changes in bandgap with different buffer thicknesses.](image)

*Figure IV-10: Plot of Model Showing Changes in Bandgap of a Quantum Well 0.5 μm from Graded Buffers with Different Grading Rates (8% In/μm and 22% In/μm)*

Chapter IV- In$_x$Ga$_{1-x}$As LED Structures Grown by MBE
luminescent bands formed in the quantum well. In fact, these minima in bandgap energy may be directly responsible for the enhanced recombination locally in these regions. However, the results from our model cannot account for the trend in the overall luminescence intensity from the quantum well. The PL data in Figure IV-5 show that the quantum well in sample 3 is less efficient at trapping carriers than the quantum well in sample 4, and this trend is corroborated by examining the intensity from the quantum wells in CL spectra from samples 3 and 4 [Figure IV-7(a) and Figure IV-8(a)]. The band offsets were determined to be 137 meV and 125 meV for samples 3 and 4, respectively. If we consider these structures as planar quantum wells, we would expect the quantum well in sample 3 to have greater ability to trap carriers than the quantum well in sample 4, but this is not the case. The strain induced changes in bandgap of the quantum well are only on the order of 2 meV, so the graded buffer cannot be solely responsible for the fact that sample 4 is more efficient at trapping carriers than sample 3. The shorter emission wavelength from sample 4 supports the idea of another confinement effect, as additional spatial confinement leads to a higher transition energy and shorter emission wavelength.

One source of such additional effect, which may explain the trend in trapping efficiency, is the effect of dislocation strain fields on indium adatom migration during epitaxy. We speculate that In atoms have enough surface mobility at high temperature to react with the strain fields from the graded buffer and/or the change in surface morphology created by the strain fields, preferentially attaching to lattice sites depending on the sign and magnitude of the strain. This would lead to indium rich regions where carriers would tend to recombine due to the lower bandgap and vice versa in indium poor regions. Although we could not detect any change in indium composition with energy dispersive spectroscopy (EDS), PV-TEM showed a clear microstructural change only for the samples grown at higher temperature (580 °C). Figure IV-11 shows PV-TEM images of samples 1 and 3 in \( g = <220> \) diffraction conditions. There are no distinct features in the image of sample 1 besides threading dislocations. However, the image of sample 3 shows different contrast features on two distinct scales (PV-TEM images of sample 4 showed similar features). The large scale undulation, which is seen in the direction of the
cross-hatched pattern, occurs over approximately 200 nm, while other fine features which occur on the scale of about 10 nm. The diffraction patterns show no evidence of ordering which has been reported elsewhere in III-V compound epitaxy.\textsuperscript{67,132,133,134,135} We believe that the small scale features are surface rippling at the top of the quantum well. This rippling can explain the high contrast regions seen in the X-TEM images. Such coherent rippling has been observed in the InGaAs/GaAs system and the SiGe/Si system.\textsuperscript{74,136,137} A \textit{g=\langle 004 \rangle} X-TEM image of the QW (not shown) indeed shows a rippled top QW interface for sample 3. Note that these ripples cannot be correlated to the luminescent lines seen in the CL data, since the ripples are at a much finer scale. Thus, the longer wavelength features seen in Fig. 12(b) must be correlated to the luminescent lines. The origin of the longer wavelength variations in nearly lattice-matched cases has been correlated to strain variations.\textsuperscript{44} Note that in the near-lattice-matched cases, the long wavelength variations occur equally in both in-plane \textit{\langle 100 \rangle} directions. Figure IV-11 clearly shows that our variations lie in the \textit{\langle 110 \rangle} directions and that there is a strong preference along one \textit{\langle 110 \rangle} direction. The asymmetry in dislocation density in the [110] and [1-10] directions

![Figure IV-11: PV-TEM Images of Sample 1 and Sample 3](image_url)

Chapter IV- \textit{In}_{x}\textit{Ga}_{1-x}\textit{As LED Structures Grown by MBE}
due to the zincblende structure has been discussed previously.\textsuperscript{138,139,140,141} We believe that asymmetric strain fields produce this long wavelength microstructural change in the \textless 110\textgreater  direction, suggesting that strain is the precipitating factor for the formation of these long-wavelength variations.

\textbf{E. Conclusions}

We conclude that the In\textsubscript{x}Ga\textsubscript{1-x}As growth temperature and grading rate affect the emission intensity and spatial origin of luminescence from a single quantum well 1.3 \textmu m LED design. Specifically, growth at higher temperatures and slower compositional grading rates greatly improve the light emitting properties of the active device region. Spatially resolved luminescence shows that quantum well luminescence is directly affected by the relaxed In\textsubscript{x}Ga\textsubscript{1-x}As buffer, forcing linear regions of spontaneous confinement along \textless 110\textgreater  directions. Two theories were proposed to explain the role of the graded buffer in the luminescence properties of the active region. One theory considered the direct effect of the strain fields from the graded buffer on the bandgap energy of the quantum well. We concluded that although there are spatial variations in bandgap energy due to the strain fields from the graded buffer, the changes in the bandgap alone could not account for all the luminescence data. A second theory focused on stress enhanced diffusion and/or surface morphology as the cause of indium rich region which trapped carriers, explaining the observed luminescence properties more completely. Although no compositional difference could be seen with characteristic x-ray analysis, PV-TEM showed a microstructural variation that occurs on the scale of features observed in CL images.

\textbf{F. Acknowledgments}

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Chapter V

\textit{In}_x\text{Ga}_{1-x}\text{As LED Structures Grown by OMVPE}

In this chapter, the results from \textit{In}_x\text{Ga}_{1-x}\text{As} LED structures grown by OMVPE are presented. Special emphasis is placed on analysis and calculations of \textit{In}_x\text{Ga}_{1-x}\text{As} phase separation during growth. The materials science conclusions from the OMVPE work explain some of the data obtained from the MBE grown \textit{In}_x\text{Ga}_{1-x}\text{As} LED structures discussed in the previous chapter. Some of this work was published in Applied Physics Letters, Volume 72, p. 1608 (1998).

\textit{In}_x\text{Ga}_{1-x}\text{As} structures with compositionally graded buffers were grown by organometallic vapor phase epitaxy (OMVPE) on GaAs substrates and characterized with plan-view and cross-sectional transmission electron microscopy (PV-TEM and X-TEM), atomic force microscopy (AFM), and x-ray diffraction (XRD). The results show that the microstructure of compositionally graded structures is highly dependent on the growth temperature possibly due to a transition in the \textit{In}_x\text{Ga}_{1-x}\text{As} surface reconstruction. The surface reconstruction is altered by dislocation strain fields from the graded buffer. The morphology of boundaries between domains of different surface reconstructions may determine the strain relaxation, defect density, and surface quality of compositionally graded structures. Drastic surface roughening, poor relaxation, and high TDDs are observed at low growth temperatures. Only growth at high temperatures produces relaxed compositionally graded structures with good surface morphologies and low defect densities. Calculations show that phase separation may be favored due to surface roughening, but no compositional modulations were observed experimentally.
A. Introduction

Compositionally graded buffers are implemented in lattice-mismatched heteroepitaxy to maintain a low threading dislocation density and achieve a completely relaxed growth template. Organometallic vapor phase epitaxy (OMVPE) is a well established growth technique capable of growth rates significantly greater than those of molecular beam epitaxy (MBE), therefore OMVPE is a more practical choice for fabricating graded buffers.

B. Experimental

In this study, we examine $\text{In}_x\text{Ga}_{1-x}\text{As}$ graded buffers on GaAs substrates grown by atmospheric OMVPE at different temperatures. The samples were grown in a Thomas Swan atmospheric research reactor on $n^+$ GaAs substrates from AXT. The transmission electron microscopy [plan-view (PV-TEM) and cross-sectional (X-TEM)] was done with a JEOL 2000FX. The x-ray diffraction (XRD) was performed with a Bede D$^3$ triple-axis diffractometer. The atomic force microscopy (AFM) experiments were conducted with a Digital Instruments D3000 Nanoscope.

To explore relaxation in compositionally graded $\text{In}_x\text{Ga}_{1-x}\text{As}$, the initial samples were graded to $x_{in}=0.06$ ($\approx 0.4 \%$ mismatch) at temperatures between 500-700 °C. This small amount of mismatch should allow excellent relaxed layers independent of most growth parameters. In addition, $\text{In}_x\text{Ga}_{1-x}\text{As}$ graded buffers with nominal final indium concentration of $x_{in}=0.33$ were grown at 550 and 700 °C to examine the evolution of the morphologies seen in $x_{in}=0.06$ structures. Only structures grown for device applications were doped. All growths were performed with a 5000 sccm $\text{H}_2$ carrier flow and 67 sccm $\text{AsH}_3$ flow. The TMG flow was fixed at 0.21 sccm throughout the graded buffer growth sequence. Compositional grading was accomplished by stepping the TMI flow rate by approximately 0.005 sccm up to a final flow of 0.031 sccm for the $x_{in}=0.06$ graded buffer and 0.163 sccm for the $x_{in}=0.33$ graded buffer. Other $\text{In}_x\text{Ga}_{1-x}\text{As}$ compositions were
obtained by linearly interpolating TMI flow rates in that range. Sufficient vent times were incorporated after each change in TMI flow setting to ensure the expected composition.

C. Results and Discussions

The following subsections discuss the materials data from the OMVPE graded structures. AFM, XRD, and TEM were the main characterization techniques.

1. AFM Data on OMVPE Structures

A visual inspection of the surface morphology of the nominal $x_{In}=0.06$ structures reveals that surface roughness has a strong dependence on growth temperature, which is surprising for such a low lattice mismatch. AFM surface roughness data taken on 10 $\mu$m x 10 $\mu$m areas of each $x_{In}=0.06$ sample, along with the $x_{In}=0.15$, $x_{In}=0.27$, and $x_{In}=0.33$ structures, is depicted in Figure V-1. The data show that the rms roughness (52 nm) is

![Figure V-1: RMS Roughness for In$_{Ga_{1-x}}$As Structures Grown at Different Temperatures.](image)
significantly greater for the nominal $x_{in}=0.06$ sample grown at 550 °C than for the other $x_{in}=0.06$ structures (10 nm). Despite the low mismatch, the sample grown at 550 °C is not specular. In addition, the surface roughness of the $x_{in}=0.33$ structure grown at 700 °C is less than that of any $x_{in}=0.06$ structures grown at lower temperature. The $x_{in}=0.27$ graded buffer structure grown at 550 °C has an rms roughness 20X than of the $x_{in}=0.33$ graded buffer grown at 700 °C.

2. Relaxation of $x_{in}=0.06$ OMVPE Grown Graded Structures

Key criteria for device applications implementing graded buffers are sufficient strain relief and low threading dislocation density. To determine the degree of strain relaxation and the indium composition of the cap layer, glancing exit (224) reciprocal space maps were gathered for the $x_{in}=0.06$ structures by triple axis XRD. Since the $x_{in}=0.06$ structures were grown on on-axis substrates, the effect of epilayer tilt was neglected (no glancing incidence (224) or (004) reciprocal space maps were acquired to determine tilt). In addition, it should be noted that wafer bowing is neglected in the interpretation of the x-ray measurements, since an $x_{in}=0.06$ structure with minimal thickness (∼ 2 μm) is not expected to cause much wafer bowing. X-TEM was used to measure the thickness, which in combination with the final composition, gave the grading rate. Table VII shows the residual strain in each of the nominal $x_{in}=0.06$ structures as a function of temperature. The structure grown at 500 °C had a noticeably greater residual strain, while no trend is observed among the other samples. However, since the compositions and grading rates differed, the strain relief of the graded buffers was compared after calculating the equilibrium plastic strain rate (strain/thickness) and the overall equilibrium plastic strain. The equilibrium plastic strain rate is given by

$$C_\delta(h) = C_f + \frac{3D \left(1 - \frac{\nu}{4}\right) \ln \left(\frac{2\pi h C_\delta}{e}\right)}{2Yh^2}$$

Eq. V.1
Table VII: Composition, Grading Rates, and X-Ray Data for \( x_{In} = 0.06 \) Structures Grown at Different Temperatures

<table>
<thead>
<tr>
<th>Growth Temp (°C)</th>
<th>% Indium in Graded Buffer</th>
<th>Grading Rate (%In/µm)</th>
<th>Residual ε (x 10^3)</th>
<th>% of Equilibrium ε Relieved</th>
<th>20 FWHM for Cap Layer</th>
<th>ω FWHM for Cap Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>9.81</td>
<td>15.32</td>
<td>-2.15</td>
<td>79</td>
<td>233</td>
<td>505</td>
</tr>
<tr>
<td>550</td>
<td>8.21</td>
<td>11.90</td>
<td>-1.59</td>
<td>85</td>
<td>283</td>
<td>356</td>
</tr>
<tr>
<td>600</td>
<td>6.06</td>
<td>8.81</td>
<td>-1.41</td>
<td>84</td>
<td>151</td>
<td>512</td>
</tr>
<tr>
<td>650</td>
<td>7.76</td>
<td>8.21</td>
<td>-1.28</td>
<td>89</td>
<td>144</td>
<td>415</td>
</tr>
<tr>
<td>700</td>
<td>7.14</td>
<td>7.51</td>
<td>-1.59</td>
<td>79</td>
<td>109</td>
<td>460</td>
</tr>
</tbody>
</table>

where \( C_f \) is the mismatch introduction rate (misfit/thickness), \( Y \) is the Young’s Modulus, \( h \) is the film height and \( D = Gb / [2\pi(1 - \nu)] \) with \( G \), the shear modulus; \( \nu \), Poisson’s ratio; and \( b \), the magnitude of the Burgers vector (60° dislocations are assumed). The expression for the overall equilibrium plastic deformation in a graded buffer is

\[
\delta_{eq}(h) = C_\sigma(h)h
\]

Eq. V.2

The percentage of equilibrium strain relieved (i.e., percent relaxation) is also listed in Table VII. All samples showed a similar degree of relaxation (≈ 80-85%). At such a low mismatch, the differences in strain relief are expected to be small since many of the dislocation blocking mechanisms are not active (i.e., dislocation pileups should not be present). The disparities are more pronounced at higher indium concentrations. The \( x_{In} = 0.27 \) structure (the final TMI setting was for \( x_{In} = 0.33 \), but the actual composition was
determined with XRD) grown at 550 °C was 88% relaxed and the \( x_{in} = 0.33 \) structure grown at 700 °C was 95% relaxed.

3. Suspected Phase Separation of \( \text{In}_{x}\text{Ga}_{1-x}\text{As} \) Graded Structures

This section reports the microstructure observed in the OMVPE grown structures. Some of the microstructures observed show similarities to phase separated microstructures which have been reported by other authors. The analysis described in subsequent sections of this chapter show that phase separation is not likely the cause of the observed features. However, phase separation may occur as a consequence of surface roughening due to other characteristics of the microstructure.

The X-TEM and XRD data show great differences in microstructure between the \( x_{in} = 0.06 \) sample grown at 550 °C and the same structure grown at 700 °C, in agreement with the drastic difference in surface morphology. Figure V-2 shows the X-TEM micrographs of the two structures. Both structures have threading dislocation densities below the X-TEM limit (\(< 10^8/\text{cm}^2\)). Thus, the very poor surface morphology of the 550 °C sample is not due to a very high defect density in the top \( \text{In}_{x}\text{Ga}_{1-x}\text{As} \) layer. The uniform cap layer of the structure grown at 550 °C does show additional semi-circular regions in the top of the film. These features have weak contrast and are not dislocations. As will be discussed later, it is suspected that the contrast is associated with boundaries between domains of surface reconstruction which lie in the plane of the TEM foil (i.e., we are looking at the boundaries from the side, as opposed to top-down).

The x-ray data in Table VII show a significantly greater spread in the \( \theta/2\theta \) (or lattice-parameter) direction for the uniform cap of the 550 °C sample than any of the other samples grown at different temperatures. This spread is be indicative of a variation in lattice constant and is attributed to strain in the epilayer. Note that the sharpest peak in the \( \theta/2\theta \) direction is from the sample grown at 700 °C. The FWHM in the \( \omega \) direction for
Figure V-2: X-TEM Pictures of $x_m = 0.06 \text{In}_0.33 \text{Ga}_{0.67} \text{As}$ Structures Grown at (a) 550 °C and 700 °C (b)

Figure V-3: (004) Reciprocal Space Maps of $\text{In}_0.33 \text{Ga}_{0.67} \text{As}$ Compositionally Graded Structure Grown at 700 °C and $\text{In}_0.33 \text{Ga}_{0.67} \text{As}$ Structure Grown at 550 °C

Chapter V- $\text{In}_x \text{Ga}_{1-x} \text{As}$ LED Structures Grown by OMVPE
the cap in the structure grown at 550 °C was less than that of the other $x_{\text{In}}=0.06$ samples, creating a circular projection of the (224) spot in reciprocal spot, as opposed to the typical elliptical spot for a relaxed heterostructure. The XRD data for higher indium content structures showed similar traits. Figure V-3 shows (004) reciprocal space maps for the $x_{\text{In}}=0.27$ structure grown at 550 °C and the $x_{\text{In}}=0.33$ structure grown at 700 °C. The structure grown at 700 °C has the typical x-ray pattern for a high quality compositionally graded structure with a sharp peak in the $\theta/2\theta$ direction and what is referred to as mosaic spread in the $\omega$ direction due to dislocations in the graded buffer.\textsuperscript{85} The $x_{\text{In}}=0.27$ structure grown at 550 °C has a significant spread in the $\theta/2\theta$ direction like the $x_{\text{In}}=0.06$ structure grown at the same temperature.

In addition to having greater surface roughness and a greater FWHM in the $\theta/2\theta$ direction, the $x_{\text{In}}=0.06$ structure grown at 550 °C shows striking contrast in PV-TEM. Figure V-4 is a PV-TEM image of the $x_{\text{In}}=0.06$ In\textsubscript{x}Ga\textsubscript{1-x}As structure grown at 550 °C showing a wavy contrast in $<110>$ directions (the same direction as the dislocations in the graded buffer) under a $g=<220>$ diffraction condition. The contrast disappears in the perpendicular $g=<220>$ condition. These strain-originating striations are commonly attributed to compositional variations or phase separation. As discussed in the introduction, the striations (i.e., long wavelength undulation) are typically in $<100>$ type directions and there should be no driving force for phase separation at such a low indium content. Features associated with phase separation occurring in a $<110>$ type direction and at a composition of only $x_{\text{In}}=0.06$ indicate that if phase separation is occurring, it is promoted by misfit dislocations in the graded buffer.
4. Modeling of Phase Separation in In$_x$Ga$_{1-x}$As

This section considers the driving force for phase separation in compositionally graded In$_x$Ga$_{1-x}$As structures. The models for phase separation described in this section show that phase separation is possible, but only as a consequence of other features that govern the evolution of the microstructure.

Two possibilities for phase separation at low indium content structures will be presented in this section. In addition, possible sources of the drastic surface roughening observed at 550 °C, which is not due to high threading dislocation density, are addressed.

a) Phase Separation Induced by Dislocation Strain Fields

Since the features associated with phase separation occur in a <110> type direction, it is natural to suspect that dislocation strain fields may be responsible for the phase separation. A possible theory would be that adsorbed atoms at the surface respond to the strain fields from dislocations in the graded buffer and preferentially deposit in regions...
which lower the strain energy of the film, thus producing phase separation. This process will be favored if dislocation-induced phase separation lowers the strain energy enough to offset the other thermodynamic parameters which favor solubility.

The thermodynamic parameters which contribute to the free energy of mixing, $\Delta G_{\text{mix}}$, and determine if an alloy will stay in solution or phase separate are the enthalpy of mixing, $\Delta H_{\text{mix}}$, the entropy of mixing, $\Delta S_{\text{mix}}$, and the temperature, $T$. $\Delta H_{\text{mix}}$ and $\Delta S_{\text{mix}}$ are functions of the overall indium composition, $x_{\text{In}}$. An additional free energy term exists due to the dislocation strain fields. This strain energy, $E(x,y)$, varies spatially with the strain fields of a misfit dislocation array in a graded buffer. The calculation of the $\Delta G_{\text{mix}}$ on a surface above a compositionally graded buffer is shown schematically in Figure V-5. A positive $\Delta G_{\text{mix}}$ anywhere on the surface would favor immiscibility in that region and a negative $\Delta G_{\text{mix}}$ indicates that the solution is stable. The Gibb’s free energy, $\Delta G_{\text{mix}}$, as a function of position, composition, and temperature is given by

$$\Delta G_{\text{mix}}(x_{\text{In}}, x, y, T) = \Delta H_{\text{mix}}(x_{\text{In}}) - T\Delta S_{\text{mix}}(x_{\text{In}}) + \Delta E_{\text{disf}}(x, y)$$  \hspace{1cm} \text{Eq. V.3}$$

![Depositing Atoms](image)

*Figure V-5: Schematic of Model Examining Phase Separation Due to Dislocation Strain Fields*
The enthalpy of mixing can be determined from Stringfellow’s delta lattice parameter model and is given by

\[ \Delta H_{\text{mix}}(x_{In}) = K(x_{In}a_{InAs}^{-2.5} + (1 - x_{In})a_{GaAs}^{-2.5} - a_{In,Ga_{1-x}As}^{-2.5}) \]  

Eq. V.4

with K, a proportionality constant, equal to $5.28 \times 10^7 \text{ J/mole} \cdot \text{Å}^{-2.5}$. For $x_{In}=0.06$, $\Delta H_{\text{mix}}$ is 839 J/mole. The entropy of mixing can be expressed as

\[ \Delta S_{\text{mix}}(x_{In}) = R[x_{In} \ln x_{In} + (1 - x_{In}) \ln(1 - x_{In})] \]  

Eq. V.5

with R, the ideal gas constant, 8.314 J/mole. The $-T\Delta S_{\text{mix}}$ term at 550 °C is then -1553 J/mole. The criterion for phase separation on the surface can then be expressed as $\Delta E_{\text{disl}}>714 \text{ J/mole}$. If this is not the case, the dislocation strain fields are not likely to be directly responsible for phase separation, as phase separation can not relieve enough strain from the dislocation strain fields to make $\Delta G_{\text{mix}}>0$.

The criterion for phase separation due to dislocation strain fields can be further simplified by determining whether the strain energy on the surface approaches 714 J/mole. The $E_{\text{disl}}$ at the surface can be determined by modeling a random array of dislocations in a graded buffer. Summing the components in $\sigma_{ij}$ due to each dislocation at each point on the surface, $\varepsilon_{ij}$'s can be determined subsequently. $E_{\text{disl}}(x,y)$ is then

\[ E_{\text{disl}}(x,y) = \frac{\sum_{ij} \frac{1}{2} \sigma_{ij}(x,y) \bullet \varepsilon_{ij}(x,y)}{N_v} \]  

Eq. V.6

where, $N_v$ is the molar volume for the In$_x$Ga$_{1-x}$As and is only necessary in the expression to convert from strain energy/volume to strain energy/mole. The results of the calculation of $E_{\text{disl}}(x,y)$ for a 5 μm x 5 μm area above an $x_{In}=0.06$, 1 μm graded buffer with a 3000 Å graded layer critical thickness (i.e., the surface is 3000 Å from the misfit dislocation array) is shown in Figure V-6 (see Appendix F). The plot shows that the maximum strain energy due to misfit dislocations in the graded buffer is approximately 150 J/mole.
This is 4X too low to satisfy the criterion for phase separation at any point on the surface. So dislocation strain fields from the compositionally graded buffer are not likely to cause phase separation of In_{0.06}Ga_{0.94}As at 550 °C. It should be noted that the model examines decomposition into the binary compounds, InAs and GaAs. This is a simplification so the model does not consider all paths for phase separation in the system.

b) **Phase Separation Induced by Surface Roughness**

The data show alloy segregation may be occurring along the direction of dislocations in the graded buffer and cannot be caused directly by dislocation strain fields. Another possibility is that the well-known surface cross-hatched pattern, which develops due to dislocation strain fields\(^{142}\), may be responsible for initiating phase separation (i.e., can surface roughness due to the cross-hatched pattern promote phase separation in certain regions of a depositing film?). Regions of a surface which have roughened due to strain relaxation exhibit a larger average lattice parameter due to spreading of the lattice planes while other regions support lower lattice-parameters. The differences in free (strain) energy between a roughened surface and a flat surface can be expressed by considering the difference in strain state experienced by an alloy on a roughened surface as opposed
to a flat surface. Referring to Figure V-7, the strain, $\varepsilon$, is given by $\frac{a_2-a_1}{a_1}$ and can be shown to be $\frac{h-h_0}{h_0}$. With $\frac{h}{h_0}$ defined as $L_{21}$, the difference in strain energy between the two states, $AE_{surf}$, can be expressed as

$$\Delta E_{surf} (L_{21}) = \frac{\frac{1}{2} Y (L_{21} - 1)^2}{N_v}$$

Eq. V.7

with $Y$ the Young’s modulus of the film. Including the 150 J/mole from the dislocation strain fields, the criterion for phase separation of In$_{0.06}$Ga$_{0.94}$As at 550 °C now becomes

$$\frac{\frac{1}{2} Y (L_{21} - 1)^2}{N_v} > 564 \text{ J/mole}$$

Eq. V.8

Inserting the constants and solving for $L$, the difference between $l_2$ and $l_1$ needs to be 1.8% (i.e., $L_{21}$ > 1.018 is enough for phase separation to be favored at 550 °C). Table VIII lists the relative surface roughening needed for phase separation of In$_{0.06}$Ga$_{0.94}$As as a function of temperature. We now compare this roughness to the experimental cross-hatch roughness. Keep in mind that the experimental data are for layers in which phase separation may have already occurred, whereas the model is based on the initiation of

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**Figure V-7**: Schematic of Differences in Lattice Parameter Due to Surface Roughening

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Chapter V- In$_x$Ga$_{1-x}$As LED Structures Grown by OMVPE
Table VIII: Degree of Surface Roughening Needed for Phase Separation of \textit{In}_{0.06}\textit{Ga}_{0.94}\textit{As} at Different Temperatures

<table>
<thead>
<tr>
<th>Growth Temperature (°C)</th>
<th>L_{21}(model)</th>
<th>L_{21}(experiment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>1.016</td>
<td>1.002</td>
</tr>
<tr>
<td>550</td>
<td>1.018</td>
<td>1.041</td>
</tr>
<tr>
<td>600</td>
<td>1.020</td>
<td>1.009</td>
</tr>
<tr>
<td>650</td>
<td>1.021</td>
<td>1.001</td>
</tr>
<tr>
<td>700</td>
<td>1.022</td>
<td>*</td>
</tr>
</tbody>
</table>

phase separation. The surfaces of the compositionally graded buffers with the exception of the structure grown at 700 °C showed consistent cross-hatch wavelengths. The surface length, \( l_2 \), to horizontal distance, \( l_p \), determined by AFM is also tabulated for the compositionally graded buffers. It should be noted that the profiles are based on the surface profiles of graded buffers with uniform cap layers. The uniform cap would lower \( L_{21} \) (i.e., the cap partially smooths the cross-hatched pattern).

There are several important points to be taken from Table VIII. First, the graded buffer grown at 550 °C, which features the greatest spread in lattice parameter, has a value of \( L_{21} \) which satisfies the criterion for phase separation. This result implies that phase separation may be promoted by surface roughening at 550 °C. The sample grown at 500 °C, which has a lower criterion for immiscibility and exhibited less spread in lattice a parameter than the structure grown at 550 °C, did not roughen appreciably. Lower growth temperature limits atom mobility and does not allow for the surface to roughen. Therefore, it is suspected that phase separation may be kinetically limited at low enough temperatures. As predicted, the \( L_{21} \) criterion increases with growth temperature (\( L_{21} \) is approximately 25% greater at 700 °C than 550 °C). So, phase separation should be less
likely at higher temperatures. The experimental data show that there is less spread in lattice parameter at higher temperatures. It can be concluded that any surface instability during epitaxy which promotes roughening can lead to phase separation.

The last important consideration is whether the surface cross-hatch induced by dislocation strain fields can create the variations in surface topology needed to initiate phase separation (i.e., is the surface cross-hatch rough enough?). It is unlikely that the dislocation strain field cross-hatched pattern creates the surface morphology needed to induce phase separation. This suggests that there is another source of strain energy that roughens the surface.

c) Surface Roughening In Compositionally Graded In$_{x}$Ga$_{1-x}$As Structures

A theory for the initiation of phase separation based on surface roughening has been proposed, but two issues need to be resolved: 1) the source of roughening which initially nucleates the phase separation (if it is occurring) and 2) the enhanced surface roughening at 550 °C. This section expands on the evaluation of phase separation past initiation and provides insight into both issues.

When phase separation occurs, coherency strain develops at the boundaries between two compositions. A similar argument, based on the analysis of a surface-induced phase separation model, can be made to show that the coherency strain energy can be relieved by surface roughening at the expense surface energy. Referring back to Figure V-7, consider a film of lattice parameter $a$, experiencing a coherency strain. It can lower its strain energy by roughening (i.e., allowing the lattice planes to spread out) if the decrease in strain energy is more than the increase in surface energy due to the increased line length. The criterion for whether this will occur, with $\Delta \varepsilon$ defined as $\frac{l_2 - l_1}{l_1}$, is

$$-\frac{1}{2} Y \Delta \varepsilon^2 h l_2 + (l_2 - l_1) \gamma < 0$$

Eq. V.9
with \( h \), the maximum height of the film and \( \gamma \), the surface energy per unit area. The units of the expression are energy/unit length. The product, \( hl_2 \), is an overestimate for the cross-sectional area, as the surface is actually curved and not rectangular. The criterion can be weighed by examining the scale of AFM roughening profiles for the \( x_{in}=0.06 \) compositionally graded buffer grown at 550 °C (\( l_2 \approx 850 \) nm, \( l_1 \approx 820 \) nm, and \( h \approx 40 \) nm) and by estimating the surface energy to be that of GaAs, 0.46 J/m².\(^{143} \) The increase in surface energy is \( 1.26 \times 10^{-9} \)/m, while the decrease in strain energy is \( -2.8 \times 10^{-6} \)/m. Clearly, the strain energy relieved overwhelms the added surface energy. Now, the question is whether the strain energy relieved is due to coherency strain between two phases. Examination of the magnitudes of strain involved leads to another conclusion.

Cahn, in his classic paper on spinodal decomposition, showed that for small compositional fluctuations in the form of a cosine function the coherency strain energy/mole is given by

\[
E_{coh} = \frac{A^2 \eta^2 Y}{2(1-\nu)N_v} \quad \text{Eq. V.10}
\]

where \( A \) is the amplitude of the compositional variation (\( Ax_{in} \) in the case of \( \text{In}, \text{Ga}_{1-x} \text{As} \)), \( \eta \) is the strain per unit change in composition which is \( \frac{a_{\text{InAs}} - a_{\text{GaAs}}}{a_o} \), and \( \nu \) is Poisson’s ratio. \( Y \) and \( N_v \) are the Young’s modulus and molar volume, respectively. Note that Cahn’s expression shows that the average strain energy in an infinite solid due to a small compositional change is only dependent on the amplitude of the modulation and not on the wavelength. Therefore, no assumption as to the scale of the phase separation is implied, only that the modulation is periodic. The only free parameter in the expression is the compositional change, and we can calculate the compositional difference needed to initiate the roughening seen experimentally. If the decrease in strain energy/volume (\( -2.8 \times 10^{-6} \)/m \( * l_2 * h \)) relieved by surface roughening in the \( x_{in}=0.06 \) structure grown at 550 °C is exactly the amount of coherency strain energy that is relieved, solving for \( A \) in
Cahn's expression yields an amplitude in composition modulation equal to $\Delta x_{ln} = 0.41$, which would mean that the total compositional fluctuation is $\Delta x_{ln} = 0.82$. Obviously, this too large a composition gradient (by approximately two orders of magnitude) to be consistent with the relatively small lattice parameter spreads determined by XRD. Nevertheless, the experimental data show that drastic surface roughening occurring at 550 °C must occur due to considerable strain energy in the film.

5. **Formation of High Energy Boundary**

It has been established that the surface roughening that occurs at 550 °C is not from the cross-hatched pattern, and even phase separation (i.e., relief of coherency strain energy) could not roughen the surface to the extent observed. What is the source of the extra strain energy in the film which allows for the drastic surface roughening?

From examination of X-TEM pictures of structures grown at 550-650 °C, boundaries form at certain intervals on the surface and roughen of the surface locally. Roughening of this type has been reported previously. Figure V-8 shows the boundaries in structures grown at 550, 600 and 650 °C. The surface clearly roughens in the vicinity of the boundaries. The boundaries show contrast which resembles that of anti-phase boundaries (APB) in some films (Figure V-9), while in other films the boundaries appear to exhibit strong strain contrast and do not appear to be APBs (Figure V-10). An APB is a planar defect consisting of wrong nearest neighbor bonds which can form in a zincblende structure when there is a sublattice displacement such that two domains are rotated by 90°. Polar on non-polar epitaxy (i.e., III-V on group V epitaxy) and ordering in III-V compounds can result in APB formation. In$_x$Ga$_{1-x}$As on GaAs heteroepitaxy is not polar on non-polar epitaxy and no ordering spots could be seen in diffraction patterns observed with TEM. In addition, ordering is not likely at small indium alloy compositions ($x_{ln} = 0.06$). So, the exact nature of the boundaries is unknown, but their effects are clear (i.e., the amount of surface roughening observed indicates a high energy associated with them).
Figure V-8: X-TEM Micrographs of Boundaries in \( x_{\text{In}} = 0.06 \) Structures Grown at (a) 550 °C, (b) 600, and (c) 650 °C
It is proposed that the observed boundaries form due to a surface reconstruction change at 550 °C. At approximately 550-580 °C, the surface of In$_x$Ga$_{1-x}$As undergoes a transition in surface reconstruction due to the high volatility of In. RHEED studies during the growth In$_x$Ga$_{1-x}$As with MBE have shown that, depending on growth conditions, the surface reconstruction can change from a 2 x 4 As terminated surface to a 4 x 2 group III terminated surface.$^{147}$ Although the observed surface reconstruction changes during the epitaxy of In$_x$Ga$_{1-x}$As by MBE can not be correlated directly with the state of the surface during OMVPE growth, it is speculated that there is a mixed surface reconstruction character in the same temperature regime (550-580 °C). In addition, it is suspected that strain fields from misfit dislocations in the graded buffer encourage the orientation of regions (domains) with different surface reconstruction in a $<110>$ type direction. The boundaries between the different domains have a high self-energy and cause the surface to roughen drastically. The surface roughening/phase separation process as a function of temperature can then be described as follows. The boundaries initiate due to the combination of dislocation strain fields and the inherent surface reconstruction transition during the epitaxy of In$_x$Ga$_{1-x}$As at approximately 550 °C. The surface roughens to lower the energy of the boundaries and the criterion for phase separation is satisfied by the enhanced cross-hatched pattern.$^{xviii}$ However, it should be noted that x-ray microprobe analysis of structures that have surfaces satisfying the criterion for phase separation does not show any compositional differences.$^{xix}$ At higher temperatures, it is speculated that the surface has a less mixed surface reconstruction character (i.e., one domain is dominant) and that the boundaries are further apart and fewer in number. In addition, the boundaries which are present deviate from (110) type directions at times. This indicates that at higher temperatures, atoms have sufficient mobility to reconfigure and lower the

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$xviii$ Note that the term enhanced is used to distinguish the surface roughening due to the boundaries from that of the dislocation strain fields alone.

$xix$ It should be said that a more detailed x-ray study may determine that compositional differences are present.

Chapter V- In$_x$Ga$_{1-x}$As LED Structures Grown by OMVPE
Figure V-9: Boundary in $x_n=0.06$ Structure Grown at 650 °C Showing APB-like Contrast

Figure V-10: Boundaries in $x_n=0.27$ Structure Grown at 550 °C Showing Strain Contrast
Figure V-11: AFM Maps of $x_p=0.06$ Structures
energy of the boundaries. As the boundary energy is suppressed at higher temperatures, the surface does not roughen to the amplitude seen at 550 °C. However, it should be noted that the x-ray data in Table VII for the $x_{\text{In}}=0.06$ structures grown at 600 °C and 650 °C show a greater spread in the $\theta/2\theta$ with respect to the same structure grown at 700 °C. This indicates that the boundaries do cause strain, but the extent is less than that at 550 °C. Figure V-11 shows the evolution of the surface morphology for the $x_{\text{In}}=0.06$ structures grown at different temperatures.

As the temperature increases and the indium content increases, a different type of boundary forms during the epitaxy of In$_x$Ga$_{1-x}$As. Figure V-12 shows an X-TEM image of the cap layer from the $x_{\text{In}}=0.33$ structure grown at 700 °C. The boundaries in the cap layer appear in-plane in this structure. Georgakilas, et al.\textsuperscript{148} reported similar striations.

\begin{center}
\textbf{Figure V-12: X-TEM Image Cap Layer of In$_{0.33}$Ga$_{0.67}$As Compositionally Graded Structure Grown at 700 °C}
\end{center}
during the epitaxy of In$_x$Ga$_{1-x}$As on Si. They attributed these 10 nm scale features to be phase separation in the growth direction. No phase separation can be inferred from our analysis. We can point out that the surface roughness associated with this structure is low, indicating that the boundary energy is lower for this structure. The presence of these boundaries at high indium content and their minimal effect on surface roughness infers that the vapor pressure of the indium contributes to the morphology of the boundaries and that the boundaries need not have a high self-energy.

6. Dislocation Interaction with Boundaries

Figure V-13 shows a typical dislocation-boundary interaction observed in an In$_x$Ga$_{1-x}$As compositionally graded buffer structure grown at a nominal temperature of 700 °C. The picture shows threading dislocations which appear to be blocked by a boundary. This structure was a device structure grown on a larger piece than the other structures discussed so far. Furthermore, examination of the surface revealed a temperature gradient induced nonuniformity. The temperature across most of the wafer, including the region in Figure V-13, was most likely lower than 700 °C. Figure V-14 shows a PV-TEM image of the same structure that features strong contrast due to the boundaries shown in Figure V-10. Note that dislocations appear to be blocked at the boundaries in this structure as well, creating dislocation pileups which in turn lead to a high threading dislocation density throughout the structure. However, the results are less conclusive for this sample because the surface was very rough. Samavedam and Fitzgerald showed that surface roughening can block dislocation motion, leading to a high TDD as well.\textsuperscript{126} Mahajan\textsuperscript{149} suggested that In$_x$Ga$_{1-x}$As and quaternary III-V solutions are less likely to degrade in optoelectronic devices because phase separation inhibits the motion of dislocations. The dark-line defect process, which degrades laser lifetime, occurs from a dislocation climb process. If the results shown in this section are correct, one might believe that dislocation climb would be inhibited by such microstructures. However, it is the boundaries which promote surface roughening and impede dislocation motion; there is no direct evidence of phase separation at all.
Figure V-13: PV-TEM Image of a Compositionally Graded Device Structure Grown at 700 °C

Figure V-14: PV-TEM Image of $x_m=0.27$ Structure Grown at 550 °C Showing Dislocations Blocked at Boundaries
Another aspect of boundaries and dislocation motion should be discussed. As the growth temperature increases, the morphology and energy of the boundaries change. Figure V-15 shows a full cross-section of the compositionally graded structure shown in Figure V-12. The threading dislocation density is low, $< 8.5 \times 10^6$/cm$^2$, and this structure was 95-98% relaxed. This illustrates that dislocation glide past the boundaries is very possible at high temperatures. In addition, there appear to be misfit dislocations in the cap layer where the boundaries reside, indicating that the resolved shear stress due to the boundaries may promote dislocation propagation. Thus, not only does increasing the growth temperature improve surface morphology, but it allows the dislocation motion necessary for relaxation of the graded buffer and a low TDD.

![Image: X-TEM Image of $x_{in}=0.33$ Structure Grown at 700 °C]

*Figure V-15: X-TEM Image of $x_{in}=0.33$ Structure Grown at 700 °C*
D. Conclusions

The data suggests that the microstructure of compositionally graded buffers is very dependent on growth temperature, more so than comparable structures in other solid solution systems such as Si$_x$Ge$_{1-x}$. Features associated with phase separation were observed and calculations show that severe surface roughening can induce compositional spreads. However, phase separation was not directly observed and was clearly not the mechanism driving the severe surface roughening seen at 550 °C and the observed microstructures. It is speculated that the surface roughening and corresponding microstructure are due to the formation of boundaries between domains of different surface reconstruction. It is speculated that the dislocation strain fields alter the surface reconstruction during early stages of In$_x$Ga$_{1-x}$As growth, which in turn leads to the boundary formation. The boundaries encourage surface roughening and, at low growth temperatures, can block dislocation motion. The boundaries at higher growth temperatures and at higher indium content have a different morphology and do not inhibit dislocation motion. The results imply that the only window for growth of In$_x$Ga$_{1-x}$As compositionally graded buffers which provides sufficient relaxation, low threading dislocation density, and good surface morphology is at high temperature (≈ 700 °C). It is important to note that MBE can not attain such high growth temperatures due to limited arsenic overpressure.

E. Acknowledgments

We would like to thank Prof. S. Mahajan at Carnegie Mellon University for helpful discussions. Funding for this work was provided by AFOSR SBIR Phase II contract DSI-500 with Discovery Semiconductors. This work made use of MRSEC Shared Facilities supported by the National Science Foundation under Award Number DMR-9400334.
Chapter VI

MBE and OMVPE Grown LED Analysis

This chapter describes In$_x$Ga$_{1-x}$As/GaAs LED structures and their operation. I-V data, electroluminescence, and cathodoluminescence were the techniques used to characterize the LEDs.
A. Device Design

The same conservative LED design was used for both the MBE and OMVPE device structures to study the effects of different materials properties on LED performance. They were not designed to be efficient light emitters and the top contact blocks much of the active region. Figure VI-1 shows a SEM micrograph a typical LED structure. The mesa size ranged from 240 μm to 40 μm. All structures had a p-type cap on the mesa and an n-type clad for the bottom contact. The n+ substrates allowed substrate contact for some measurements.

The LED process was:

1. Wet mesa etch LED structures using 1:1:220,H₂SO₄:H₂O₂:H₂O. The nominal etch rate for InₓGa₁₋ₓAs structures with xₐₓ=0.20-0.30 was 2000 Å/minute.

2. Passivate with plasma enhanced chemical vapor deposition (PECVD) SiO₂. The deposited SiO₂ was typically 2000 Å.

3. Open holes in SiO₂ for top contacts on mesa and bottom contacts.

4. Pattern contact by e-beam metal evaporation and metal lift-off (50 Å Ti and 1200 Å Pt).

5. Rapid thermal anneal (RTA) contacts for 30 seconds at 375 °C.
B. **MBE LED Structures**

Five different LED structures were examined for diode behavior and luminescence characteristics. The bulk of the comparisons were drawn from samples 1, 3, and 4 which were all processed in the same lot. Materials properties of the three structures were described in chapter IV. The differences between the growth sequences of the samples can be reviewed as follows:

- Sample 1- grown at 350 °C with a grading rate of 22% In/μm
- Sample 3- grown at 580 °C with a grading rate of 22% In/μm
- Sample 4- grown at 580 °C with a grading rate of 8% In/μm

1. **I-V Curves**

The I-V curves were taken by probing the top and bottom contacts with a probe station featuring a Hewlett-Packard 4145A parameter analyzer. Figure VI-2 shows typical I-V curves taken from the three samples.
Diode reverse break-down voltages are greater than 8 V for all diodes. However, the diodes behave differently under forward bias. Samples 3 and 4 have excellent turn-on characteristics, with sample 4 having slightly superior characteristics. Sample 1 does not turn on until 3 V. Table IX lists the ideality factors and leakage characteristics of the diodes as a function of diode size. All the results were averaged over 4 diodes from each size range, except the starred (*) selections in the table which were averaged over a lower number of diodes due to lithography problems. The leakage characteristics from sample to sample were approximately the same. Also, the independence of leakage current density on diode size suggests that leakage is dominated by the bulk characteristics of the diodes and that surface leakage is minimal. The samples grown at higher temperature samples had consistent diode behavior throughout the size range. Sample 4 outperformed sample 3 in each size category based on the accumulated statistics. Sample 1 did not have consistent device behavior and had poor forward bias characteristics throughout the size.
Table IX: I-V Data from MBE LED Structures

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>TDD in structure (#/cm²)</th>
<th>240 µm Mesa</th>
<th>200 µm Mesa</th>
<th>120 µm Mesa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>2 x 10⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( J_0 ) at -1V (A/cm²)</td>
<td>-1.26E-4*</td>
<td>-1.63E-4</td>
<td>-9.74E-5</td>
<td></td>
</tr>
<tr>
<td>Ideality Factor</td>
<td>5.93*</td>
<td>24.19</td>
<td>48.00</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>1.4 x 10⁹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( J_0 ) at -1V (A/cm²)</td>
<td>-1.87E-4</td>
<td>-2.69E-4</td>
<td>-1.40E-4</td>
<td></td>
</tr>
<tr>
<td>Ideality Factor</td>
<td>1.77</td>
<td>1.77</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>Sample 4</td>
<td>2.13 x 10⁸</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( J_0 ) at -1V (A/cm²)</td>
<td>-1.22E-4</td>
<td>-1.72E-4</td>
<td>-1.03E-4</td>
<td></td>
</tr>
<tr>
<td>Ideality Factor</td>
<td>1.73</td>
<td>1.74</td>
<td>1.74</td>
<td></td>
</tr>
</tbody>
</table>

range. It should be noted that the large values for the ideality of the diodes from sample 1 indicate another effect, such as a back-to-back diode, superimposed on the p-i-n junction behavior. In addition, the ideality factors were extracted based on the ideal diode equation, which does not consider an intrinsic (i) region, so the ideality factor can not be related directly to recombination current or high level injection.

The key point from the data in Table IX is that the correlation between threading dislocation density and diode characteristics is the inverse of what would be expected.

Chapter VI- MBE and OMVPE Grown LED Analysis
Sample 1 had a much lower threading dislocation density (by at least an order of magnitude) than samples 3 and 4, but had worse device characteristics. This indicates that dislocation density alone does not necessarily determine the best device characteristics for lattice-mismatched In$_x$Ga$_{1-x}$As applications. However, the conditions which usually promote lower TDD (but not in samples 3 and 4), slow grading rate and higher growth temperature, do provide the best device characteristics.

Figure VI-3 shows I-V data from two more LED structures, one with a quantum well (QW LED) and another without a quantum well (PN LED). The QW LED structure growth process was identical to that of sample 4, except that the growth temperature was 350 °C. There was a high threading dislocation density throughout the structure and in the active region (>10$^9$/cm$^2$). The source of this high TDD is unknown. The PN LED structure was an In$_x$Ga$_{1-x}$As PIN junction (x$_{in}$=0.33) grown on top of a compositionally graded buffer with a grading rate of 22% In/μm grown at 420 °C. This LED structure had a threading dislocation density less than 10$^7$/cm$^2$ (determined with X-TEM and PV-TEM). The QW LED has a very high turn-on voltage and a high breakdown voltage,
while the PN LEDs had a conventional I-V curve with a typical turn-on voltage (< 1 V), but a lower breakdown voltage. This may indicate that lower growth temperature correlates to a higher turn-on voltage. There is some uncertainty to this hypothesis because it is unclear whether the high turn-on voltage for the QW LEDs is due to high threading dislocation density. This is because the QW LED structure features threading dislocations coming up from the graded buffer (i.e., they went through the entire junction) unlike samples 3 and 4 which only have a high TDD past the quantum well region (see Chapter IV). It is still worth noting that the threading dislocations do not act to short-circuit the devices in this structure. Whether this is due to the intrinsic properties of dislocations or because conduction down the dislocation cores is impeded by the quantum well discontinuity is not certain. The reason for the lower breakdown voltage for the PN LED structure is unknown. Further analysis of the junction characteristics for each of the structures with techniques such deep level transient spectroscopy (DLTS) would provide more insight into some of the device characteristics observed. It is suspected that point defects are incorporated during growth at lower growth temperatures and degrade device performance.

2. Luminescence

This section reports the electroluminescence data from three of the structures discussed in the previous section:

- The PN LED Structure
- The QW LED Structure
- Sample 3

Despite the model I-V curve and low threading dislocation density, little electroluminescence is observed from the LEDs without a quantum well. A broad radiation spectrum, consistent with heating of the LED, is observed. Figure VI-4
Figure VI-4: EL Data from QW LED Structure

shows the results of the electroluminescence (EL) study on the QW LEDs at two different drive currents. Despite a poor turn-on voltage and high threading dislocation density, these LEDs emitted light near the anticipated wavelength. As the drive current increases, the well saturates and more recombination occurs in the clad layers. Efficiency measurements on the QW LEDs show the external efficiency to be $6.44 \times 10^{-7}$ photons/electron. In comparison, the published efficiency of a commercial 1.3 μm LED with an InGaAsP active region with the output coupled to a fiber optic pigtail is $1.1 \times 10^{-4}$ photons/electron.

The EL from sample 3 is shown in Figure VI-5. The drive current was 10 mA and the peak emission for this structure was at 1.33 μm. Although no direct quantitative comparisons can be made because the structures were tested under different conditions, the quantum well emits much more strongly relative to the clad for the LED made from
sample 3 than the QW LED structure shown in Figure VI-4. Sample 3 had better I-V characteristics and a lower defect density, so it is not surprising that the EL output is greater.

Considering the high threading dislocation density (at least 5 orders of magnitude greater than that found in lattice-matched heterostructures) and the unoptimized geometry of the LEDs that exhibited strong luminescence our devices, we expect that In$_x$Ga$_{1-x}$As LED efficiencies can be greatly improved by lowering the TDD and by designing a better device structure.

C. **OMVPE LED Structures**

Three different OMVPE LED structures were compared for device characteristics. All were graded at the same rate (6% In/µm) with differences as follows:

1. Sample 0217- was grown at 700 °C, and graded up to 33% In with Al$_x$In$_{1-x}$As barriers lattice-matched to the In$_x$Ga$_{1-x}$As. A 33% In quantum well was placed between the
Al$_x$In$_{1-x}$As barriers. The purpose of this structure was to examine the efficiency of the LEDs with larger band offsets.

2. Sample 0225- was grown at 700 °C, and graded to 30% In with 30% In clad layers. A 38% strained quantum well was placed between the clad layers.

3. Sample 0301- was grown at 650 °C, and graded to 30% In with 30% In clad layers. A 38% In strained quantum well was placed between the clad layers. In addition, this sample had the same overall grading rate as the other structures, but the step size was halved (i.e., 0.6% In steps grown for half the time of 1.2% In steps).

Figure VI-6 shows a X-TEM image of structure 0225. It should be noted that these structures were grown on larger and thicker substrates. As a result, a temperature gradient developed across the pieces during growth, as evidenced by a pattern of

![Image](image_url)

*Figure VI-6: X-TEM of 0225 LED Structure*
cloudiness. It is suspected that the nominal growth temperature was less than that measured with the reactor thermocouple.

1. I-V Curves and Materials Data

The I-V data was taken as described for the MBE-grown structures. Due to the temperature gradients, the variation in the I-V data for the OMVPE structures is larger than in the MBE structures. Typical I-V characteristics taken from 200 μm mesa LEDs for the three structures are shown in Figure VI-7. LEDs from 0217 and 0301 feature a large series resistance that flattens the I-V curves. The temperature gradients result in thickness variations across the pieces, thus it was difficult to ensure that all structures were contacted to the n-clad. It is suspected that the mesa etch penetrated to the undoped graded buffer for some of the devices. As with the MBE grown LED structures, the break-down voltages were greater than -8 V.

Despite the variations, it was possible to extract the forward bias and leakage current characteristics of the diodes (see Table X). The starred (*) values indicate averaging

![I-V Characteristics for OMVPE LED Structures](image)

*Figure VI-7: Typical I-V Characteristics for OMVPE LED Structures*
Table X: I-V Data from OMVPE LED Structures

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>240 µm Mesa</th>
<th>200 µm Mesa</th>
<th>120 µm Mesa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0217</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_o$ at -1V (A/cm²)</td>
<td>1.59E-6</td>
<td>1.02E-4</td>
<td>1.03E-6</td>
</tr>
<tr>
<td>Ideality Factor</td>
<td>1.94</td>
<td>2.41</td>
<td>2.01</td>
</tr>
<tr>
<td>0225</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_o$ at -1V (A/cm²)</td>
<td>2.37E-4*</td>
<td>2.03E-4*</td>
<td>1.29E-6*</td>
</tr>
<tr>
<td>Ideality Factor</td>
<td>1.30*</td>
<td>2.42*</td>
<td>1.59*</td>
</tr>
<tr>
<td>0301</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_o$ at -1V (A/cm²)</td>
<td>4.06E-4</td>
<td>2.35E-4</td>
<td>1.88E-4</td>
</tr>
<tr>
<td>Ideality Factor</td>
<td>3.87</td>
<td>2.04</td>
<td>1.58</td>
</tr>
</tbody>
</table>

over fewer than four diodes. Specifically, the 0225 diode data were averaged over two diodes for the 240 µm devices and three diodes for the 200 and 120 µm mesa structures.

Examining the trends in Table X, all the turn-on characteristics were similar, with slightly higher values for the 0301 diodes. The leakage current densities also appeared to be larger for the 0301 structure. All the diode structures exhibit better forward bias characteristics than the diodes grown at low temperature structures with MBE. As mentioned in the analysis of the MBE structures, the ideality factors can not be fit properly to the ideal diode equation.
2. Luminescence

Electroluminescence data was not taken from this set of diodes, but quantitative CL measurements taken from bulk pieces of 0225 and 0301 showed some differences. The structures were examined simultaneously to allow quantitative comparison. Both structures were excited at 600X magnification with 15 kV acceleration voltage and 112 nA probe current. The overall luminescence from sample 0301 (grown at a lower temperature) was less than that of 0225. This may be attributed to the higher TDD in sample 0301 (2.5 x 10⁶/cm² in sample 0301 as opposed to 2.7 x 10⁷/cm² in 0225). However, comparing the relative emission of the quantum well and clad, 0301 appears to have better confinement characteristics, although it may also be that the higher defect density quenches cladding luminescence more strongly than quantum well luminescence in sample 0301. The boundary/surface reconstruction morphology discussed in Chapter V may also provide carrier confinement to produce regions of enhanced luminescence.

![Graph showing luminescence intensity vs. wavelength for 0225 and 0301 structures.](image)

*Figure VI-8: Quantitative CL Data from 0225 and 0301 Structures*
D. Discussions

The quantum well structures featuring the best confinement characteristics were grown in the temperature regime where features associated with phase separation are pronounced. By inspection with an infrared camera while conducting the I-V measurements, the MBE grown diodes grown at 580 °C were determined to have superior light output compared to any of the other structures grown by either technique. As discussed earlier, other authors have suggested that phase separation improves performance of quantum well device structures. However, as previously noted, no phase separation was ever recorded in our examination of the microstructures. Since the microstructure is primarily driven by the high energy boundaries resulting from the mixed surface reconstruction character during In$_x$Ga$_{1-x}$As epitaxy, it is more likely that the domains and boundaries produce regions of enhanced luminescence. Re-examining the CL line profiles (Chapter IV) for the samples 3 and 4, structures grown with MBE at 580 °C, a mechanism for the enhanced performance of these devices can be proposed. Figure VI-9 shows the intensity profiles from the quantum well and clad as a function of position from sample 3. It appears that

![Graph showing CL line profile for Sample 3]

Figure VI-9: CL Line Profile for Sample 3
some of the regions that emit strongly in the quantum well also emit strongly in the clad. A similar pattern is observed in the profile from sample 4. This may indicate that the boundary/domain structure in the clads results in a higher current density in regions where the quantum well is most efficient at confining carriers, thereby enhancing luminescence in these regions.

E. Conclusions

Examination of the device structures indicates that slower grading and higher growth temperature lead to better junction characteristics and more light output for In$_x$Ga$_{1-x}$As diodes. LEDs with high TDD at or near the active region can emit more strongly than less defective structures grown at lower temperature. Testing of several diode structures with high TDDs shows that the dislocations do not short circuit the devices. However, threading dislocations do lower the efficiency of the LEDs. The superior light output of MBE grown structures is proposed to be the result of the surface reconstruction transition during the epitaxy of the quantum well and the clads.
Chapter VII

Conclusions and Future Work

The conclusions for the materials and device work completed in this thesis are outlined in this chapter. In addition, future directions for the continuation of this work are proposed.
A. Conclusions

This section summarizes the findings from the materials and device characterization conducted on the MBE and OMVPE grown In$_x$Ga$_{1-x}$As lattice-mismatched structures studied in this work.

1. Sequence of Findings

This work addressed several materials issues in the development of low defect density 1.3 $\mu$m LEDs. The timeline for progress and findings is represented in Table XI.

Features associated with phase separation or alloy segregation were first observed in the MBE grown In$_x$Ga$_{1-x}$As LED structures. The effect of strain fields from the compositionally graded buffer on the luminescence properties of the quantum wells was examined. The analysis led to the conclusion that a microstructural change, possibly phase separation, was responsible for the enhanced luminescence in these structures. The microstructural change was kinetically limited at lower temperatures.

Growth and characterization of the OMVPE compositionally graded buffers showed that the signatures of phase separation were less pronounced with increasing growth temperature. Thermodynamic calculations showed that surface roughening could promote phase separation. However, the identification of high energy boundaries between domains of different surface reconstruction led to the hypothesis that phase separation, if present, was not the primary cause of the observed microstructures.

The current understanding of surface roughening in the In$_x$Ga$_{1-x}$As compositionally graded buffers is based on the formation of high energy boundaries between regions of different surface reconstructions. The mixed character of the surface reconstruction is due
Table XI: Timeline of Research

<table>
<thead>
<tr>
<th>Timeline</th>
<th>Significant Event/Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>March 1996</td>
<td>MBE grown device structures show lateral confinement characteristics and strong emission despite high TDD. Signatures of phase separation are observed in microstructures.</td>
</tr>
<tr>
<td>May 1996</td>
<td>MBE grown devices are fabricated. LED testing shows that a high TDD quantum well structure has better emission characteristics than a simple PN junction with a lower TDD.</td>
</tr>
<tr>
<td>October 1996</td>
<td>Drastic surface roughening is observed for $x_n=0.06$ compositionally graded structures grown at 550 °C.</td>
</tr>
<tr>
<td>April 1997</td>
<td>Low TDD $x_m=0.33$ In$<em>x$Ga$</em>{1-x}$As compositionally graded structure is grown with peak emission at approximately 1.3 μm. The window for growth of low defect density compositionally graded buffers is established.</td>
</tr>
<tr>
<td>May 1997</td>
<td>Modeling of MBE grown structures shows that the graded buffer can not account for the spatial luminescence pattern shown by the MBE grown structures. Alloy segregation is proposed due to dislocation strain fields.</td>
</tr>
<tr>
<td>Summer 1997</td>
<td>Surface roughness and microstructure versus growth temperature are mapped out for OMVPE grown In$<em>x$Ga$</em>{1-x}$As structures. Phase separation is suspected and determined to decrease with growth temperature.</td>
</tr>
<tr>
<td>February 1998</td>
<td>Modeling of thermodynamic driving force for phase separation due to dislocation strain fields is examined. It is determined that strain fields can not be responsible for phase separation.</td>
</tr>
<tr>
<td>March 1998</td>
<td>It is determined that surface roughening can initiate phase separation. However, the roughening is attributed to boundaries which form due to changes in the surface reconstruction of In$<em>x$Ga$</em>{1-x}$As at 550 °C and phase separation is not determined experimentally.</td>
</tr>
<tr>
<td>March 1998</td>
<td>Dislocation blocking in structures with features associated with phase separation is observed.</td>
</tr>
</tbody>
</table>

...to a reconstruction transition at 550 °C and the effect of dislocation strain fields from misfit dislocations in the graded buffer. Changes of the domain structure at higher growth temperatures explain the observed range of morphologies for In$_x$Ga$_{1-x}$As compositionally graded buffers.

2. **Materials Conclusions**

The material quality of compositionally graded In$_x$Ga$_{1-x}$As is mapped in Figure VII-1. Compositionally graded structures with high relaxation, low TDD, and good surface
morphology are possible at high temperatures (≈700 °C). Growth at low temperature avoids the surface roughening and possible phase separation by limiting kinetics and by moving away from the surface reconstruction transition temperature. However, strain relaxation required to engineer the lattice constant is not obtained. Poor surface morphologies and high defect densities are exhibited in the middle temperature regime where high energy boundaries are pronounced in In$_x$Ga$_{1-x}$As.

3. Device Conclusions

A map of device performance versus growth temperature is shown in Figure VII-2. The results show that, despite the low TDD, the device characteristics of devices grown at low temperatures (< 500 °C) are poor. The poor performance is believed to be due to the accumulation of point defects that degrade both the diode behavior and luminescence of the structures.
Figure VII-2: Device Characteristics vs. Growth Temperature Map

At growth temperatures where high energy boundaries are pronounced, the I-V characteristics of device structures are good and the light output is greater than the structures grown at higher temperatures, despite the fact that structures grown at higher temperatures have lower TDD.

LEDs fabricated out of the best OMVPE material featured good I-V characteristics, however, the luminescence was lower than that of structures grown by MBE in the regime where high energy boundaries are favored. Structures grown by OMVPE do show that a higher TDD lowers the overall luminescence efficiency. Thus, In$_x$Ga$_{1-x}$As compositional grading at higher temperatures is desirable because it reduces TDD, and therefore, increases efficiency.

**B. Future Work**

This section proposes future directions for research to further develop understanding of the microstructures observed in compositionally graded In$_x$Ga$_{1-x}$As structure and to obtain optimal device performance.
1. Proposed Materials Work

The most significant and least explored aspect of the materials research in this study centers around the surface reconstruction change which occurs in compositionally graded In$_x$Ga$_{1-x}$As. The surface reconstruction and step structure can be better understood by examining compositional grading of In$_x$Ga$_{1-x}$As on offcut GaAs substrates. In addition, a study on the effect of V/III ratio on the surface mobility and subsequent domain structure would provide insight into the range of morphologies seen at different growth temperature and In$_x$Ga$_{1-x}$As alloy compositions. A complete study to determine whether spatial compositional variations are actually present in the growth temperature regime where phase separation is suspected would be informative.

Even though a growth temperature window for low TDD in In$_x$Ga$_{1-x}$As compositionally graded structures has been determined, the process is not fully optimized. For instance, the optimum grading rate and growth sequence can be explored further. Efforts which parallel those in the Si$_x$Ge$_{1-x}$ system to lower TDD may realize high gains in material quality. Finally, the mechanism for dislocation blocking in structures which exhibit features associated with phase separation has important consequences for device characteristics. A thorough study of dislocation behavior in structures with boundaries and domains of surface reconstruction might explain the resistance of In$_x$Ga$_{1-x}$As light-emitting structures to dark line defect degradation.

2. Proposed Device Strategy

The most interesting aspects of the device results obtained in this study are the improved luminescence and excellent I-V characteristics from the highly defective devices grown by MBE. Although the TDD has an adverse effect on the emission intensity, an optimal structure would appear to incorporate both a compositionally graded structure grown at high temperature and an optimized boundary/surface domain structure in the active region grown at lower temperature. Specifically, analysis of whether the clad and quantum well require a given domain structure with associated boundaries would aid in

Chapter VII- Conclusions and Future Work
design of high performance structures. With a full set of diode structures, a study of the degradation of structures with high and low threading dislocation density and different domain/boundary morphologies would provide a more definitive understanding of the enhanced performance achieved in such structures.

The ultimate validation of $\text{In}_x\text{Ga}_{1-x}\text{As}$ compositionally graded structures would be the demonstration of a $1.3 \, \mu\text{m}$ laser on GaAs with equal or better characteristics than that of the InGaAsP devices on InP. Improvement of the device design would include multiple quantum wells and the incorporation of higher band offsets in the active region (i.e., better confinement and efficiency). The incorporation of AlInAs or InGaP barrier layers would be the first step in this process.
# Appendix A

**Materials Properties of InAs and GaAs**

<table>
<thead>
<tr>
<th>Material Property</th>
<th>GaAs</th>
<th>InAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>144.6</td>
<td>189.7</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>5.31</td>
<td>5.67</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>1238</td>
<td>943</td>
</tr>
<tr>
<td>E₀ (eV)</td>
<td>1.42</td>
<td>0.36</td>
</tr>
<tr>
<td>a₀ (Å)</td>
<td>5.6419</td>
<td>6.0584</td>
</tr>
<tr>
<td>mₑ⁺ (m₀)</td>
<td>0.067</td>
<td>0.023</td>
</tr>
<tr>
<td>mₘ⁺ (m₀)</td>
<td>0.62</td>
<td>0.60</td>
</tr>
<tr>
<td>C₁₁ (dynes/cm²)</td>
<td>11.88 x 10¹¹</td>
<td>8.33 x 10¹¹</td>
</tr>
<tr>
<td>C₁₂ (dynes/cm²)</td>
<td>5.38 x 10¹¹</td>
<td>4.53 x 10¹¹</td>
</tr>
<tr>
<td>a (eV)</td>
<td>2.7</td>
<td>2.5</td>
</tr>
<tr>
<td>b (eV)</td>
<td>-1.76</td>
<td>-1.8</td>
</tr>
</tbody>
</table>
Crystallographic Orientations

GaAs crystallographic orientations/directions are commonly quoted with two different reference frames. The two reference frames and their implications for crystallographic directions of dislocation lines are defined as follows:

*Surface normal defined in the [100] direction*

- (111) planes with Group III elements terminate at the surface in [01-1] directions.
- α and β dislocations are typically assumed to lie in [01-1] and [011] directions, respectively.

*Surface normal defined in the [001] direction*

- (111) planes with Group III elements terminate at the surface in [1-10] directions.
- α and β dislocations are typically assumed to lie in [1-10] and [110] directions, respectively.
Appendix B

Typical Growth Run Sheet

Growth Run Procedure for Compositionally Graded Device Structure

The procedure includes steps for initiation of growth on Si. If the growth was on GaAs, the procedure prior to InGaAs growth would be the same as outlined in Chapter III.

Substrate: Si wafer

Start 50% N₂ flow into reactor

**Si Cleaning**
1. Take substrate up to 350 °C for 10 minutes, start SiH₄, AsH₃, and TMG to vent in H₂
2. Take substrate up to 550 °C with SiH₄ (100% with no dilution) to reactor for 90 sec
3. Drop temperature to 400 °C and switch all flows to H₂

**GaAs Growth**
1. Flow Arsine to sample for 1 minute
2. Flow TMG sample and grow GaAs for 10 minutes
3. Take substrate up to 650 °C and grow GaAs n-type for 18 minutes (1 μm GaAs total), start TMI to vent at 10% flow

**InGaAs Growth**
1. Take up to 700 °C, drop TMI flow to 2.4%.
2. Grow InGaAs for 8 minutes, n-type
3. Step up TMI to 3.6%
4. Grow InGaAs for 4 minutes, n-type
5. Repeat steps 10 and 11 for 4.8, 6.0, 7.2, 8.4, 9.6, 10.8, 12.0, 13.2, 14.4, 15.6, 16.8, and 18.0%
6. Grow InGaAs Cap for 8 minutes (n)
7. Grow InGaAs Cap for 2 minutes (i)
8. Stop TMI and TMG flows and set TMI to 26.4% for 5 minutes
9. Grow InGaAs Quantum Well for 30 sec
10. Stop TMI and TMG flows and set TMI to 18.0% for 5 minutes
11. Grow InGaAs Cap for 2 minutes (i)
12. Grow InGaAs Cap for 2 minutes (p)

Drop to temperature w/ arsine flowing
Appendix C

Matlab Code for Critical Thickness Calculation

% CRITICAL.M
% This program calculates the critical thickness for an epilayer on a substrate.
% The formula's and expressions are from "Properties of Lattice-Mismatched and Strained Indium Gallium
% Arsenide" edited by Pallab Bhattacharya with the lattice mismatch section written by Eugene Fitzgerald.

% clear all variables
clear

% The values below are for materials properties of the end members of interest.
% Variables ending with 'A' refers to InAs and 'S' refers to GaAs. The units for the lattice parameter are Å
% and the stiffness components are in dynes/cm^2.
AA = 6.0584;
AS = 5.64191;
C11A = 8.329e11;
C12A = 4.526e11;
C44A = 3.959e11;
C11S = 11.88e11;
C12S = 5.38e11;
C44S = 5.94e11;

% The values below are the indium alloy compositions for the overlayer and the substrate.
% If the substrate was GaAs, xIns would be zero for instance.
xIno=0.30
xIns=0.0

% Linear interpolation of materials properties for overlayer and substrate.
C11o=xIno*C11A+(1-xIno)*C11S;
C12o=xIno*C12A+(1-xIno)*C12S;
C44o=xIno*C44A+(1-xIno)*C44S;
C11s=xIns*C11A+(1-xIns)*C11S;
C12s=xIns*C12A+(1-xIns)*C12S;
C44s=xIns*C44A+(1-xIns)*C44S;
Gs=C44s-(2*C44s+C12s-C11s)/2;
Go=C44o-(2*C44o+C12o-C11o)/2;
Y=C11o+C12o-2*C12o^2/C11o;
u=C12o/(C12o+C11o)
A=(xIno*AA)+(1-xIno)*AS;
As=(xIns*AA)+(1-xIns)*AS;

% Definition of constants for critical thickness expressions
b = 2^.5/2*A;
beff=b/2;
D=(Go*Gs*b)/(3.1428*(Go+Gs)*(1-nu));
alph=60/180*3.1428;
f=abs((As-A)/A);
% Initial guess for critical thickness is 50 Å.
hc1=0;
hc2=50;

% Loop to establish critical thickness iteratively until difference between successive guesses is
% less than 1 Å.
while(abs(hc1-hc2)>1)
    hc1=hc2;
    hc2=D*(1-nu*cos(alph)^2)*(log(hc1/b)+1)/(Y*f)
end

% Prints out final value for critical thickness
hc2
% CRITPLOT.M
% This program computes and plots the critical thickness for an
% epilayer on a substrate over a range of composition.

% clear all variables
clear

% The values below are for materials properties of the end members of interest.
% Variables ending with 'A' refers to InAs and 'S' refers to GaAs. The units
% for the lattice parameter are Å and the stiffness components are in dynes/cm².

AA = 6.0584;
AS = 5.64191;
C11A = 8.329e11;
C12A = 4.526e11;
C44A = 3.959e11;
C11S = 11.88e11;
C12S = 5.38e11;
C44S = 5.94e11;

% Define indium fraction in substrate and range of critical thickness plot for epilayer
xInS=0
xInO=[0.03:0.02:0.53];
Num=size(xInO,2)

% Loop to determine critical thickness for epilayer at every indium composition
% assuming 60° and 90° dislocations.

% k is the counter
k=1;
while k<=Num

    k

% Linear interpolation of materials properties for overlayer and substrate
C11o=xInO(k) * C11A + (1-xInO(k)) * C11S;
C12o=xInO(k) * C12A + (1-xInO(k)) * C12S;
C44o=xInO(k) * C44A + (1-xInO(k)) * C44S;
C11s=xInS * C11A + (1-xInS) * C11S;
C12s=xInS * C12A + (1-xInS) * C12S;
C44s=xInS * C44A + (1-xInS) * C44S;
Gs=C44s-(2*C44s+C12s-C11s)/2;
Go=C44o-(2*C44o+C12o-C11o)/2;
Y=C11o+C12o-2*C12o^2/C11o;
nu=C12o/(C12o+C11o);

% Definition of constants for critical thickness expressions
A = (xInO(k)*AA) + (1-xInO(k)) * AS;
As= (xInS*AA) + (1-xInS) * AS;
b = 2^.5/2*A;
beff=b/2;
D=(Go*Gs*b)/(3.1428*(Go+Gs)*(1-nu));
f=abs(As-A)/A;
% Initial guess, hc2, is 500 Å and loop solves for hc2 until consecutive guesses vary by less than 2 Å.

% Loop for 60° dislocations
hc1=0;
hc2=500;
alph=60/180*3.1428;
while (abs(hc1-hc2)>2)
    hc1=hc2;
hc2=D*(1-nu*cos(alph)^2)*(log(hc1/b)+1)/(Y*f);
end
hcs(k)=hc2;

% Loop for 90° dislocations
alph=90/180*3.1428;
hc1=0;
hc2=500;
while (abs(hc1-hc2)>2)
    hc1=hc2;
hc2=D*(1-nu*cos(alph)^2)*(log(hc1/b)+1)/(2*Y*f);
end
hcn(k)=hc2;
k=k+1;
end

% Plots critical thickness for 60° and 90° dislocations
whitebg
plot (xIno,hcs)
hold on
plot (xIno,hcn,'--')
axis ([0.3 0.5 0 100])
hold off

Appendix C
Appendix D

Matlab Code for Calculation of Quantum Well Emission

% INGAAS.M
% This program calculates emission wavelengths for InGaAs-GaAs heterostructures by
% considering In content, strain, and active layer thickness (i.e., quantum effect).

% Sets parameters Wavelength (emission wavelength), Eg (bandgap),
% DE1 (change in bandgap from alloy content), DE2 (change in bandgap
% from strain), and DE3 (change in bandgap from quantum confinement) to null.

Wavelength = []; Eg = []; DE1 = []; DE2 = []; DE3 = [];

% 'i' is the number of points between the compositions of interest to be calculated.
i = 150;

% Xin is the composition of the InGaAs cladding layer and Xac is the
% composition of the InGaAs quantum well.
Xin = linspace (0,9,i);
Xac = Xin + 0.1;

% Thickness is the thickness of the quantum well in meters.
Thickness = linspace (50E-10,500E-10,i);

% Loop To Determine Eg as a function of composition and quantum well thickness
% Note that y is the counter for the number of points in
% the Thickness vector and x is the counter for the number of points
% in the Xin (or Xac) vector. In this case the matrix is square as
% Thickness and Xin have the same length, 'i'. Within the loop three
% functions are called upon: alloy (calculates the bandgap due to alloy
% composition), quantum (calculates the change in bandgap due to the quantum
% confinement effects on the holes and electrons), and strain (calculates
% the change in bandgap due to the strain).

y = 0;
while y < i
    y = y+1;
    x = 0;
    while x < i

Appendix D
\texttt{x = x + 1;}
\texttt{DE1 = alloy (Xac(x));}
\texttt{DE2 = quantum (Xsc(x), Thickness(y));}
\texttt{DE3 = strain (Xin(x), Xac(x));}
\texttt{Eg(x,y) = DE1 + DE2 + DE3;}
\texttt{end}

\texttt{end}

\texttt{\% Converts thickness to \textit{Å} and the bandgap to emission wavelength}
\texttt{ThicknessA = Thickness \times 1e10;}
\texttt{Wavelength = 1.24 ./ Eg;}

\texttt{\% Creates a matrix with the same dimensions as Wavelength with all the values set to 1.3\mu m}
\texttt{\% This serves as a reference plane on the plot of emission wavelength.}
\texttt{Emission = ones(i) \times 1.3;}

\texttt{\% Plots the data and labels the axes}
\texttt{figure (1)}
\texttt{clg}
\texttt{meshc (ThicknessA, Xin, Wavelength)}
\texttt{hold}
\texttt{meshc (ThicknessA, Xin, Emission)}
\texttt{ylabel ('Fraction Indium in Buffer')}
\texttt{xlabel ('Thickness of Active Layer (Angstroms)')}
\texttt{zlabel ('Emission Wavelength (microns)')}
\texttt{title ('Lasing Properties vs. Xin (buffer) and Active Region Thickness')}\texttt{save data1 Xin Thickness Wavelength Emission}

\textbf{Appendix D}
% QUANTUM.M
% This function calculates the bandgap change due to the finite thickness of a quantum well.
% It receives two values, the thickness of the quantum well and the indium content of the well.

function Q = quantum (Xac,thickness)

% Loads materials properties from Materials.m
Materials

% Linearly interpolates effective masses of electrons and holes for quantum well composition
Me = [(Xac*MeA) + (1-Xac)*MeS]*9.11e-31;
Mh = [(Xac*MhA) + (1-Xac)*MhS]*9.11e-31;

% Calculates effective quantization energy on electrons and holes
Qe = (6.63e-34)^2/(8*thickness^2*Me);
Qh = (6.63e-34)^2/(8*thickness^2*Mh);

% Sum energies to get total change in bandgap and converts to eV
Q = (Qe+Qh)/1.6e-19;

% ALLOY.M
% This function calculates the bandgap of the quantum well due to the indium content

function A = alloy (Xac)

% Loads materials properties from materials.m
Materials

% Calculates bandgap of quantum well based on indium composition
Eac = E1 + E2 * (1-Xac) + E3 * (1-Xac)^2;

A = Eac;
% STRAIN.M
% This function calculates the bandgap of the quantum well due to strain. The expressions are
% discussed and referenced in Chapter IV.

function S = strain(Xin,Xac)

% Loads materials properties from Materials.m
Materials

% Linearly interpolates relevant materials properties
Abuf = (Xin*A) + (1-Xin) * AS;
Aac = (Xac*A) + (1-Xac) * AS;
C11 = Xac * (C11A) + (1-Xac) * (C11S);
C12 = Xac * (C12A) + (1-Xac) * (C12S);
a = aA*Xac + (1-Xac)* (aS);
b = bA*Xac + (1-Xac)* (bS);

% Calculates strain in layer and subsequent change in bandgap
f = (Abuf - Aac)/Aac;
S = (2 * a * (C11-C12)/C11 + b * (C11 + 2 * C12)/C11) * f;

% MATERIALS.M
% InAs materials constants, effective masses of electrons and holes (m*), lattice constant (A),
% stiffness coefficients (dynes/cm^2), hydrostatic and shear deformation potentials (eV).
MeA = 0.023
MhA = 0.60
AA = 6.0584;
C11A = 8.329e11;
C12A = 4.526e11;
C44A = 3.959e11;
aA = 2.5;
bA = -1.8;

% GaAs Materials Parameters, same units as above
MeS = 0.067;
MhS = 0.62;
AS = 5.64191;
C11S = 11.88e11;
C12S = 5.38e11;
C44S = 5.94e11;
aS = 2.7;
bS = -1.7;

% Constants to quadratic expression to bandgap (eV)
E1 = 0.36;
E2 = 0.505;
E3 = 0.555;

Appendix D
Appendix E

Matlab Code for Calculation of Strain Field From Graded Buffer Viewed in Cross-Section

```
% BUFSIMXM
% This program computes the strain fields from a compositionally
% graded buffer viewed in cross-section. Note that the reference frame
% indicated above makes the y-direction the growth direction. So \( \varepsilon_y \) is the
% tetragonal distortion with \( \varepsilon_x \) and \( \varepsilon_z \) the in-plane strains.

% Clears all variables
clear

% The values below are for materials properties of the end members of interest.
% Variables ending with 'A' refers to InAs and 'S' refers to GaAs. The units
% for the lattice parameter are \( \text{\AA} \) and the stiffness components are in dynes/cm².
AA = 6.0584;
C11A = 8.329e11;
C12A = 4.526e11;
C44A = 3.959e11;
AS = 5.64191;
C11S = 11.88e11;
C12S = 5.38e11;
C44S = 5.94e11;

% Final indium conc. of graded buffer and percent relaxation
xin=0.22;
percrel=100;
```
% Linear interpolation of materials properties for buffer layer. Note that
% the expression only considers the final indium composition for the buffer layer
C11 = xIn * (C11A) + (1-xIn) * (C11S);
C12 = xIn * (C12A) + (1-xIn) * (C12S);
C44 = xIn * (C44A) + (1-xIn) * (C44S);
G=C44-(2*C44+C12-C11)/2;
Y=C11+C12-2*C12^2/C11;
u=C12/(C12+C11);

% Determine lattice constant and magnitude of Burgers vector components
Abuf = xIn*AA + (1-xIn) * AS;
b = 2^0.5/2*Abuf;
beff = b/2;
bitil = b*2^0.5/2;

% Total lattice mismatch
Mismatch = (AS-Abuf)/Abuf;

% Set graded buffer thickness, total thickness, and x range of interest (all in Å)
tbuffer=10000;
ttotal=20000;
xtotal=200000;

% Determines spacing of dislocations, allowed positions for dislocations, and number of
% points (x,y) for calculation
S = beff(-1*Mismatch*percel/100);
XRange = [0:2000:xtotal];
YRange = [tbuffer:1000:ttotal];
BRange = [0:50:tbuffer];
XPoints = size(XRange,2);
YPoints = size(YRange,2);

% Determines number of dislocations in x-range of interest
Num =round(xtotal/S);

% Loop to generate x and y values of position for each dislocation randomly
% The sign of the screw and tilt components is picked randomly
% The in-plane edge component is fixed to point in one direction. Note that
% the direction of the in-plane edge component is set to make sure that the
% extra half plane for each dislocation is in the substrate.
% Dislocations are only considered in one direction for this model.
% k is a counter
k=1;

while k<=Num
    dx(k) = round(rand*xtotal/50)*50;
    dy(k) = round(rand*(tbuffer-50)/50)*50;

    q = round(rand);
    if q == 0
        bt(k) = -1*bitil;
    else
        bt(k) = bitil;

Appendix E
end
q=round(rand);
if q == 0
    bs(k)=-1*beff;
else
    bs(k)=beff;
end
be(k)=-beff;
k=k+1;
end

% Marker to observe progress of the program
% This helps determine if the simulation will take too long or if it is trapped in an infinite loop.
1

% Creates stress matrices for the at every point
% All values are set to zero initially.
sigxxe=zeros(XPoints,YPoints);
sigyye=zeros(XPoints,YPoints);
sigzze=zeros(XPoints,YPoints);
sigxye=zeros(XPoints,YPoints);
sigxxt=zeros(XPoints,YPoints);
sigyyt=zeros(XPoints,YPoints);
sigzzt=zeros(XPoints,YPoints);
sigxyt=zeros(XPoints,YPoints);
sigxx=zeros(XPoints,YPoints);
sigyy=zeros(XPoints,YPoints);

% Loop to compute the stress at each point above the graded buffer from each dislocation (edge comp)
k=1;
while k<=Num
    x=1;
    while x<=XPoints
        y=1;
        while y<=YPoints
            Prefactor=G*be(k)/2/(1.1428/(XRange(x)-dx(k))^2+(YRange(y)-dy(k))^2);
sigxxe(x,y)=sigxxe(x,y)+(-1*Prefactor*(YRange(y)-dy(k))^2*(XRange(x)-dx(k))^2;
sigxye(x,y)=sigxye(x,y)+(Prefactor*(XRange(x)-dx(k))^2*(YRange(y)-dy(k))^2;
(sigxyt(x,y)=sigxyt(x,y)+(Prefactor*(YRange(y)-dy(k))^2*YRange(x)-dx(k))^2;
sigzze(x,y)=sigzze(x,y)+(-1*Prefactor*G*be(k)*nu/3.1428/(1-
    nu)*YRange(y)/(XRange(x)-dx(k))^2+(YRange(y)-dy(k))^2)];
y=y+1;
    end
    x=x+1;
end
k=k+1;
end;
% Loop to compute the stress at each point above the graded buffer from each dislocation (tilt comp)
2
k=1;
while k<=N
x=1;
while x<=X
y=1;
while y<=Y

Prefactor=G*bt(k)/2/1428/(1-nu)*((XRange(x)-dx(k))^2+(YRange(y)-dy(k))^2);

sigxxt(x,y)=sigxxt(x,y)+(-1*Prefactor*(YRange(y)-dy(k))*(3*(XRange(x)-dx(k))^2+(YRange(y)-dy(k))^2));
sigxyt(x,y)=sigxyt(x,y)+(Prefactor*(XRange(x)-dx(k))*(XRange(x)-dx(k))^2+(YRange(y)-dy(k))^2));
sigytt(x,y)=sigytt(x,y)+(Prefactor*(YRange(y)-dy(k))*(XRange(x)-dx(k))^2+(YRange(y)-dy(k))^2));
sigzzt(x,y)=sigzzt(x,y)+(-1*G*bt(k)*nu/1428/(1-nu)*YRange(y)*(XRange(x)-dx(k))^2+(YRange(y)-dy(k))^2));
y=y+1;
end;
x=x+1;
k=k+1;
end;
% Loop to compute the stress at each point above the graded buffer from each dislocation (screw comp)
3
k=1;
while k<=N
x=1;
while x<=X
y=1;
while y<=Y

Prefactor=G*bs(k)/2/1428/(XRange(x)-dx(k))^2+(YRange(y)-dy(k))^2);
sigxx(x,y)=sigxx(x,y)+(-1*Prefactor*(YRange(y)-dy(k)));
sigy(x,y)=sigy(x,y)+Prefactor*(XRange(x)-dx(k));
y=y+1;
end;
x=x+1;
k=k+1;
end;
%
% Rotates the stress due to tilt at every point above the graded buffer by 90° to be out of plane
% L is the rotation matrix.
L=[0 1 0; -1 0 0; 0 0 1];
4
x=1;
while x<=X
y=1;
while y<=Y
sigt=[sigxxt(x,y) sigxyt(x,y) 0; sigxyt(x,y) sigytt(x,y) 0; 0 0 sigzzt(x,y)];

Appendix E
rsigt=L*sigt*L;
sigxxt(x,y)=rsigt(1,1);
sigyyt(x,y)=rsigt(2,2);
sigzzt(x,y)=rsigt(3,3);
sigxyt(x,y)=rsigt(1,2);
y=y+1;
end
x=x+1;
end

% Adds all the stress components at every point above graded buffer and rotates by 45 degrees.
% This makes the x and z direction the <110> in-plane directions, the actual crystallographic
% directions of the dislocations in the graded buffer.
L=[1/2^0 5 0 1/2^0 5 0 1/2^0 5 0 1/2^0 5];
5
x=1;
while x<=XPoints
  y=1;
  while y<=YPoints
    sigtot=[sigxxt(x,y)+sigxxt(x,y),sigxyt(x,y)+sigxyt(x,y),sigxzt(x,y),sigxzt(x,y),sigyzt(x,y),sigyzt(x,y)];
    rsigtot=L*sigt*L;
    sigxxtot(x,y)=rsigtot(1,1);
    sigyytot(x,y)=rsigtot(2,2);
    sigzztot(x,y)=rsigtot(3,3);
    sigxytot(x,y)=rsigtot(1,2);
    y=y+1;
  end
  x=x+1;
end

% Creates the stiffness matrix taking into account the cubic symmetry and calculates its inverse
C=[C11 C12 C12 0 0 0;C12 C11 C12 0 0 0;C12 C12 C11 0 0 0;C44 C44 0 0 0 0;C44 0 0 0 0 0;C44 0 0 0 0 0];
Cinv=inv(C);

% Loop to calculate the strains from the corresponding stresses
6
x=1;
while x<=XPoints
  y=1;
  while y<=YPoints
    sigtot=[sigxxtot(x,y)+sigxxtot(x,y),sigxytot(x,y)+sigxytot(x,y),sigxztot(x,y),sigxztot(x,y),sigyztot(x,y),sigyztot(x,y)];
    etot=Cinv*sigtot;
    exxtot(x,y)=etot(1,1);
    eytot(x,y)=etot(2,1);
    ezztot(x,y)=etot(3,1);
    exytot(x,y)=etot(4,1)/2;
    ezxtot(x,y)=etot(5,1)/2;
    eyztot(x,y)=etot(6,1)/2;
    y=y+1;
  end
  x=x+1;
end
end

% Plots the noted strains and the positions of the dislocations in the graded buffer
figure (1)
meshc (YRange,XRange,exxtot);
figure (2)
meshc (YRange,XRange,eyytot);
figure (3);
meshc (YRange,XRange,ezztot);
figure (4);
plot(dx,dy,'c+');

% Saves all variables to a file
save onemica3

% PLOTNORM.M
% This program normalizes and plots a given component of a tensor calculated from BUFSIMX.M
% The normalization is necessary to correct for the edge effects in the calculation. The edge effects create a parabolic profile towards the edges and this effect is subtract by this program.
% Model 7-0-6, 8-0-7-3, 4-21, Robot Sonic

% Clears all variables
clear

% Loads data file saved by BUFSIMX.M
load d:\mayank\beaujo\thesis\matlab\onemica3.mat

% X is the center point in the calculation and this is used as the offset in the calculation
X=round (XPoints/2);

% y is a counter
y=1;

% Loop to fit a parabola to the calculated ε_u in this case and subtract out the fit from the data
while y<=YPoints
    [p]=polyfit (XRange,ezztot(:,y)',2);
    fit=p(1)*XRange.^2 + p(2)*XRange + p(3);
    ezznorm(:,y)=[ezztot(:,y)-fit+ezztot(X,y)';
    y=y+1;
end

% Converts units from Å to μm
YRange=YRange/10000;
XRange=XRange/10000;

% Plots normalized value of ε_u
whitebg
mesh (YRange,XRange,ezznorm);
axis ([0 1 20 -1e-3 1e-3])

Appendix E
Appendix F

Matlab Code for Calculation of Strain Field From Graded Buffer

Viewed in Plan-View

% BUFSIMPV.M
% This program computes the strain fields which result above a graded buffer in plan-view. The
% reference frame is the same as that in Appendix C.

% clears all variables
clear

% The values below are for materials properties of the end members of interest.
% Variables ending with 'A' refers to InAs and 'S' refers to GaAs. The units
% for the lattice parameter are Å and the stiffness components are in dynes/cm².
AA = 6.0584;
C11A = 8.329e11;
C12A = 4.526e11;
C44A = 3.959e11;
AS = 5.64191;
C11S = 11.88e11;
C12S = 5.38e11;
C44S = 5.94e11;
AA = 6.0584;
C11A = 8.329e11;
C12A = 4.526e11;
C44A = 3.959e11;

% Final indium conc. of graded buffer and percent relaxation
xIn=0.22;
percrelx=100;
percrelz=100;

% Linear interpolation of materials properties for buffer layer
% Note that the expression only considers the final indium composition for the buffer layer.
C11 = xIn * (C11A) + (1-xIn) * (C11S);
C12 = xIn * (C12A) + (1-xIn) * (C12S);
C44 = xIn * (C44A) + (1-xIn) * (C44S);
G=C44/(2*C44+C12-C11)/2;
Y=C11+C12-2*C12*C11/C11;
nu=C12/(C12+C11);

% Determines lattice constant and magnitude of Burgers vector components
Abuf = xIn*AA + (1-xIn) * AS;
b = 2^0.5/2*Abuf;
beff = b/2;
btilt = b*2^0.5/2;
% Total lattice mismatch
Mismatch = (AS-Abuf)/Abuf;

% Set height above graded buffer for calculation, total thickness of buffer, % and x/z range of interest (all in Å)
yplan = 15000;
tbuffer = 10000;
xtotal = 50000;
ztotal = 50000;

% Determines spacing of dislocations, allowed positions for dislocations, and number of % points (x,z) for calculation
Sx = beff/(-1*Mismatch*percrelx/100);
Sz = beff/(-1*Mismatch*percrelz/100);
XRange = [0:200:xtotal];
ZRange = [0:200:ztotal];
BRange = [0:50:tbuffer];
XPoints = size (XRange,2);
ZPoints = size (ZRange,2);

% Determines number of dislocations in x-range of interest
Numx = round(xtotal/Sx);
Numz = round(ztotal/Sz);

% Loop to generate x and y values of position for each dislocation randomly % The sign of the screw and tilt components is picked randomly % The in-plane edge component is fixed to point in one direction. Note that % the direction of the in-plane edge component is set to make sure that the % extra half plane for each dislocation is in the substrate.

k=1;

while k<=Numx
    dx(k) = round(rand*xtotal/50)*50;
    dy(k) = round(rand*(tbuffer-50)/50)*50;

    q = round(rand);
    if q == 0
        bt(k) = -1*bt[tl];
    else
        bt(k) = bt[tl];
    end

    q = round(rand);
    if q == 0
        bs(k) = -1*beff;
    else
        bs(k) = beff;
    end

    be(k) = beff;
    k=k+1;

Appendix F
end

% Loop to generate z and y values of position for each dislocation randomly
% The sign of the screw and tilt components is picked randomly
% The in-plane edge component is fixed to point in one direction. Note that
% the direction of the in-plane edge component is set to make sure that the
% extra half plane for each dislocation is in the substrate.

k=1;

while k<=Numz
    dz(k)=round(rand*xtotal/50)*50;
    dyz(k)=round(rand*(tbuffer-50)/50)*50;

    q=round(rand);
    if q == 0
        btz(k)=-1*tilt;
    else
        btz(k)=tilt;
    end

    q=round(rand);
    if q == 0
        bsz(k)=-1*beff;
    else
        bsz(k)=beff;
    end

    bez(k)=-beff;

    k=k+1;
end

1

% Creates stress matrices at every point. All values are set to zero initially. Note
% that tilt components have two sets of matrices, one for the x-dislocations and the other for the z.
sigxxe=zeros(XPoints,ZPoints);
sigyye=zeros(XPoints,ZPoints);
sigzze=zeros(XPoints,ZPoints);
sigxye=zeros(XPoints,ZPoints);
sigxxt=zeros(XPoints,ZPoints);
sigyyt=zeros(XPoints,ZPoints);
sigzzt=zeros(XPoints,ZPoints);
sigxyt=zeros(XPoints,ZPoints);
sigxtxz=zeros(XPoints,ZPoints);
sigyytz=zeros(XPoints,ZPoints);
sigzztz=zeros(XPoints,ZPoints);
sigxytz=zeros(XPoints,ZPoints);
sigxztz=zeros(XPoints,ZPoints);
sigyyztz=zeros(XPoints,ZPoints);
% Loop to compute the stress at each point above the graded buffer from each dislocation (edge comp)
k=1;
while k<=Numx
    x=1;
    while x<=XPoints
        Prefactor=G*be(k)/2/3.1428/(1-nu)/((XRange(x)-dx(k))^2+(yplan-dy(k))^2)^2;
        sigxse(x,:)=sigxse(x,:)+(-1*Prefactor*(yplan-dy(k))*(3*(XRange(x)-dx(k))^2+(yplan-dy(k))^2));
        sigyse(x,:)=sigyse(x,:)+(Prefactor*(XRange(x)-dx(k))*(XRange(x)-dx(k))^2-(yplan-dy(k))^2));
        sigysse(x,:)=sigysse(x,:)+(Prefactor*(yplan-dy(k))*(XRange(x)-dx(k))^2-(yplan-dy(k))^2));
        sigzse(x,:)=sigzse(x,:)+(-1*G*be(k)*nu/3.1428/(1-nu)*(yplan-dy(k))/(XRange(x)-dx(k))^2+(yplan-dy(k))^2));
        x=x+1;
    end;
    k=k+1;
end;

% Loop to compute the stress at each point above the graded buffer from each dislocation (tilt comp)
2
k=1;
while k<=Numx
    x=1;
    while x<=XPoints
        Prefactor=G*bt(k)/2/3.1428/(1-nu)/((XRange(x)-dx(k))^2+(yplan-dy(k))^2)^2;
        sigxst(x,:)=sigxst(x,:)+(-1*Prefactor*(yplan-dy(k))*(3*(XRange(x)-dx(k))^2+(yplan-dy(k))^2));
        sigyst(x,:)=sigyst(x,:)+(Prefactor*(XRange(x)-dx(k))*(XRange(x)-dx(k))^2-(yplan-dy(k))^2));
        sigystt(x,:)=sigystt(x,:)+(Prefactor*(yplan-dy(k))*(XRange(x)-dx(k))^2-(yplan-dy(k))^2));
        sigzst(x,:)=sigzst(x,:)+(-1*G*be(k)*nu/3.1428/(1-nu)*(yplan-dy(k))/(XRange(x)-dx(k))^2+(yplan-dy(k))^2));
        x=x+1;
    end;
    k=k+1;
end;

% Loop to compute the stress at each point above the graded buffer from each dislocation (screw comp)
3
k=1;
while k<=Numx
    x=1;
    while x<=XPoints
        Prefactor=G*bs(k)/2/3.1428/((XRange(x)-dx(k))^2+(yplan-dy(k))^2);
        sigxsz(x,:)=sigxsz(x,:)+(-1*Prefactor*(yplan-dy(k)));
        sigysz(x,:)=sigysz(x,:)+Prefactor*(XRange(x)-dx(k));
        x=x+1;
    end;
    k=k+1;
end;

Appendix F
% Rotate the stress due to tilt component at every point above the graded buffer by 90° to be out of plane.
% L is the rotation matrix.
L=[0 1 0;-1 0 0;0 0 1];
4
x=1;
while x<=XPoints
    z=1;
    while z<=ZPoints
        sigt=[sigxxt(x,z) sigxyt(x,z) 0;sigxyt(x,z) sigyyt(x,z) 0;0 0 sigzzt(x,z)];
        rsigt=L'*sigt*L';
        sigxxt(x,z)=rsigt(1,1);
        sigyyt(x,z)=rsigt(2,2);
        sigzzt(x,z)=rsigt(3,3);
        sigxyt(x,z)=rsigt(1,2);
        z=z+1;
    end
    x=x+1;
end

% Loop to compute the stress at each point above the graded buffer from each dislocation (edge comp)
k=1;
while k<=Numz
    z=1;
    while z<=ZPoints
        Prefactor=G*bez(k)/2/3.1428/(1-nu)/((ZRange(z)-dz(k))^2+(yplan - dyz(k))^2)^2;
        sigxxe(:,z)=sigxxe(:,z)+(-1*Prefactor*(yplan - dyz(k))*(3*(ZRange(z)-dz(k))^2+(yplan -
                         dyz(k))^2));
        sigxye(:,z)=sigxye(:,z)+((Prefactor*(ZRange(z)-dz(k)))*(ZRange(z)-dz(k))^2-(yplan-
                         dyz(k))^2));
        sigyye(:,z)=sigyye(:,z)+((Prefactor*(yplan-dyz(k)))*(ZRange(z)-dz(k))^2-(yplan-
                         dyz(k))^2));
        sigzz(e(:,z)=sigzz(e(:,z)+((-1*G*bez(k)*nu/3.1428/(1-nu)*(yplan-dyz(k))/(ZRange(z)-
                         dz(k))^2+(yplan-dyz(k))^2));
        z=z+1;
    end;
k=k+1;
end;

% Loop to compute the stress at each point above the graded buffer from each dislocation (tilt comp)
2
k=1;
while k<=Numz
    z=1;
    while z<=ZPoints
        Prefactor=G*btz(k)/2/3.1428/(1-nu)/(ZRange(z)-dz(k))^2+(yplan - dyz(k))^2)^2;
        sigxxtz(:,z)=sigxxtz(:,z)+(-1*Prefactor*(yplan - dyz(k))*(3*(ZRange(z)-dz(k))^2+(yplan-
                         dyz(k))^2));
        sigxytz(:,z)=sigxytz(:,z)+((Prefactor*(ZRange(z)-dz(k)))*(ZRange(z)-dz(k))^2-(yplan-
                         dyz(k))^2));
        sigyytz(:,z)=sigyytz(:,z)+((Prefactor*(yplan-dyz(k)))*(ZRange(z)-dz(k))^2-(yplan-
                         dyz(k))^2));
        sigzztz(:,z)=sigzztz(:,z)+((-1*G*bez(k)*nu/3.1428/(1-nu)*(yplan-dyz(k))/(ZRange(z)-
                         dz(k))^2+(yplan-dyz(k))^2));
z=z+1;
end;
k=k+1;
end;

% Loop to compute the stress at each point above the graded buffer from each dislocation (screw comp)
3
k=1;
while k<Numz
    z=1;
    while z<=ZPoints
        Prefactor=G*bsz(k)/2/3.1428/((ZRange(z)-dz(k))^2+(yplan-dyz(k))^2);
sigxztz(:,:,z)=sigxztz(:,:,z)+(-1*Prefactor*(yplan-dyz(k)));
sigyz(:,:,z)=sigyz(:,:,z)+Prefactor*(ZRange(z)-dz(k));
z=z+1;
    end
    k=k+1;
end

% Rotate the stress due to tilt component at every point above the graded buffer by 90° to be out of plane
% L is the rotation matrix.
L=[1 0 0;0 0 -1;0 1 0];
4
x=1;
while x<=XPoints
    z=1;
    while z<=ZPoints
        sigt=[sigxxtz(x,z) sigxytz(x,z) 0;sigxytz(x,z) sigyytz(x,z) 0;0 0 sigzztz(x,z)];
        rsigt=L*sigt*L';
        sigxxtz(x,z)=rsigt(1,1);
        sigyytz(x,z)=rsigt(2,2);
        sigzztz(x,z)=rsigt(3,3);
        sigxytz(x,z)=rsigt(1,2);
        z=z+1;
    end
    x=x+1;
end

% Sums all tilt component from both x and z components
sigxxt=sigxxt+sigxxtz;
sigyyt=sigyyt+sigyztz;
sigzzt=sigzzt+sigzztz;
sigxyt=sigxyt+sigxztz;

% Adds all the stress components at every point above graded buffer and rotates by 45 degrees
% This makes the x and z direction the <110> in-plane directions, the actual crystallographic
% directions of the dislocations in the graded buffer.
5
L=[1/2^.5 0 -1/2^.5;0 1 0;1/2^.5 0 1/2^.5];
x=1;
while x<=XPoints
    z=1;
    while z<=ZPoints
        sigxxt=sigxxt+z*sigxxtz;
sigyyt=sigyyt+z*sigyztz;
sigzzt=sigzzt+z*sigzztz;
sigxyt=sigxyt+z*sigxztz;
        end
    end

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\[
\text{sigtot} = [\text{sigxx}(x,z) + \text{sigxx}(x,z), \text{sigxy}(x,z) + \text{sigyx}(x,z), \text{sigzx}(x,z) + \text{sigxz}(x,z), \text{sigzy}(x,z) + \text{sigyz}(x,z), \text{sigzy}(x,z) + \text{sigyz}(x,z), \text{sigzz}(x,z) + \text{sigzz}(x,z)]; \\
\text{rsigtot} = \text{L} \times \text{sigtot} \times \text{L}'; \\
\text{sigxxtot} = \text{rsigtot}(1,1); \\
\text{sigyytot} = \text{rsigtot}(2,2); \\
\text{sigzztot} = \text{rsigtot}(3,3); \\
\text{sigxytot} = \text{rsigtot}(1,2); \\
z = z + 1;
\]

end
x = x + 1;
end

\% Creates the stiffness matrix taking into account the cubic symmetry and calculates its inverse
\text{C} = \begin{bmatrix} \text{C11} & \text{C12} & 0 & 0 & 0; \\
\text{C12} & \text{C11} & \text{C12} & 0 & 0; \\
0 & \text{C12} & \text{C11} & 0 & 0; \\
0 & 0 & \text{C44} & 0 & 0; \\
0 & 0 & 0 & \text{C44} & 0; \\
0 & 0 & 0 & 0 & \text{C44} \end{bmatrix}; \\
\text{Cinv} = \text{inv(C)};

\% Loop to calculate the strains from the corresponding stresses
6 \\
x = 1; \\
\text{while} \ x <= \text{XPoints} \\
    \text{z} = 1; \\
    \text{while} \ z <= \text{ZPoints} \\
        \text{rsigtot} = [\text{rsigxxtot}(x,z); \text{rsigyytot}(x,z); \text{rsigzztot}(x,z); \text{rsigxytot}(x,z); \text{rsigzx}(x,z); \text{rsigzy}(x,z)]; \\
        \text{etot} = \text{Cinv} \times \text{rsigtot}; \\
        \text{exxtot}(x,z) = \text{etot}(1,1); \\
        \text{eyytot}(x,z) = \text{etot}(2,1); \\
        \text{ezztot}(x,z) = \text{etot}(3,1); \\
        \text{exytot}(x,z) = \text{etot}(4,1)/2; \\
        \text{exztot}(x,z) = \text{etot}(5,1)/2; \\
        \text{eyztot}(x,z) = \text{etot}(6,1)/2; \\
z = z + 1;
    \text{end}
\text{x} = \text{x} + 1;
\text{end}

\% Saves all variables to a file
\text{save plan1}
%BUFThERM.M
% This program loads the stress-strain data calculated with BUFSIMPV.M, normalizes the curves, and
% calculates the strain energy/volume. The free energy of mixing of In,Ga,As is also calculated
% for comparison to the strain energy. This program was used to calculate the phase separation criterion
% due to dislocation strain fields discussed in Chapter V.

% Loads stress-strain data stored by BUFSIMPV.M
load planI1n

% Avogadro's number, ideal gas constant, and atomic weights of In, Ga, and As
R=8.314
Avog=6.022E23
AwGa=69.72;
AwIn=114.82;
AwAs=74.92;

% Mass of one unit cell of InAs and GaAs
MassInAs=4/Avog*AwIn+4/Avog*AwAs;
MassGaAs=4/Avog*AwIn+4/Avog*AwAs;

% The values below are for materials properties of the end members of interest.
% Variables ending with 'A' refers to InAs and 'S' refers to GaAs. The units
% for the lattice parameter are A and the stiffness components are in Pa.
AA = 6.0584;
C11A = 8.329e10;
C12A = 4.526e10;
C44A = 3.959e10;
AS = 5.6419;
C11S = 11.88e10;
C12S = 5.38e10;
C44S = 5.94e10;

% Expressions from Stringfellow's DLP model
K = 1.26E7*4.19
deltA=AA-AS;

% Linear interpolation of materials properties for buffer layer. Note that
% the expression only considers the final indium composition for the buffer layer
C11= xIn * C11A + (1-xIn) * C11S;
C12= xIn * C12A + (1-xIn) * C12S;
C44 = xIn * (C44A) + (1-xIn) * (C44S);
Y=C11+C12-2*C12^2/C11
nu=C12/(C11+C12);

% Number of points in x and z range
XPoints = size (XRange,2);
ZPoints = size (ZRange,2);
Abuf = xIn*AA + (1-xIn) * AS;

% Density and molar volume of In,Ga,As solution.
% Note N, was calculated and a tabeled value was used. Typically the value changed the model results by
% 15-20 percent
Dens = (xIn*MassInAs+(1-xIn)*MassGaAs)/(Abuf*1E-10)^3;

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\[ N_v = \frac{1}{(x \ln(a + b) + (1-x) \ln(b + c)) \cdot \text{Dens}} \]

\[ N_v = 3.6 \times 10^{-4} \]

\% Temperatures to calculate free energy of mixing for InGaAs
\[ T_1 = 550 + 273; \]
\[ T_2 = 625 + 273; \]
\[ T_3 = 700 + 273; \]

\% Entropy of mixing and enthalpy of mixing based on DLP model
\[ S_{mix} = (-8.314) \cdot (x \ln(x) + (1-x) \ln(1-x)) \cdot T \cdot S_{mix} \]
\[ S_{mix, T} = (-1) \cdot T \cdot S_{mix} \]
\[ S_{mix, T^2} = (-1) \cdot T^2 \cdot S_{mix} \]
\[ S_{mix, T^3} = (-1) \cdot T^3 \cdot S_{mix} \]
\[ H_{mix} = K \cdot ((1-x) \ln AS^2 + x \ln AA^2 - (A_b f)^2) \]

\[ G_{mix} = H_{mix} - T \cdot S_{mix} \]
\[ G_{mix, T} = H_{mix} - T \cdot S_{mix} \]
\[ G_{mix, T^2} = H_{mix} - T^2 \cdot S_{mix} \]

\% Loop to normalize (i.e., subtract out parabolic edge effects) from all stress and strain components
\% in z direction

\% z is a counter
\[ z = 1; \]

\[ X = \text{round} \left( X_{\text{Points}} / 2 \right); \]
\[ \text{while } z <= Z_{\text{Points}} \]

\[ [p] = \text{polyfit} \left( X_{\text{Range}}, \text{ezztot}(; z), 2 \right); \]
\[ \text{fit} = p(1) \cdot X_{\text{Range}}^2 + p(2) \cdot X_{\text{Range}} + p(3); \]
\[ \text{ezznorm}(; z) = \left( \text{ezztot}(; z) \cdot \text{fit} + \text{ezztot}(X, z) \right)^2; \]

\[ [p] = \text{polyfit} \left( X_{\text{Range}}, \text{exztot}(; z), 2 \right); \]
\[ \text{fit} = p(1) \cdot X_{\text{Range}}^2 + p(2) \cdot X_{\text{Range}} + p(3); \]
\[ \text{exznorm}(; z) = \left( \text{exztot}(; z) \cdot \text{fit} + \text{exztot}(X, z) \right)^2; \]

\[ [p] = \text{polyfit} \left( X_{\text{Range}}, \text{sigztot}(; z), 2 \right); \]
\[ \text{fit} = p(1) \cdot X_{\text{Range}}^2 + p(2) \cdot X_{\text{Range}} + p(3); \]
\[ \text{szznorm}(; z) = \left( \text{sigztot}(; z) \cdot \text{fit} + \text{sigztot}(X, z) \right)^2; \]

\[ [p] = \text{polyfit} \left( X_{\text{Range}}, \text{sigxztot}(; z), 2 \right); \]
\[ \text{fit} = p(1) \cdot X_{\text{Range}}^2 + p(2) \cdot X_{\text{Range}} + p(3); \]
\[ \text{sxznorm}(; z) = \left( \text{sigxztot}(; z) \cdot \text{fit} + \text{sigxztot}(X, z) \right)^2; \]

\[ [p] = \text{polyfit} \left( X_{\text{Range}}, \text{sigxz}(; z), 2 \right); \]
\[ \text{fit} = p(1) \cdot X_{\text{Range}}^2 + p(2) \cdot X_{\text{Range}} + p(3); \]
\[ \text{sxznorm}(; z) = \left( \text{sigxz}(; z) \cdot \text{fit} + \text{sigxz}(X, z) \right)^2; \]

\[ z = z + 1; \]

Appendix F
end

% Loop to normalize (i.e., subtract out parabolic edge effects) from all stress and strain components
% in z direction

% x is a counter
x=1;
Z=round (ZPoints/2);
while x<=XPoints

[p]=polyfit (ZRange, ezznorm(x,:),2);
fit=p(1)*ZRange.^2 + p(2)*ZRange + p(3);
ezznorm(x,:)=(ezznorm(x,:)-fit+ezznorm(x,Z));

[p]=polyfit (ZRange, exxnorm(x,:),2);
fit=p(1)*ZRange.^2 + p(2)*ZRange + p(3);
exxnorm(x,:)=(exxnorm(x,:)-fit+exxnorm(x,Z));

[p]=polyfit (ZRange, exznorm(x,:),2);
fit=p(1)*ZRange.^2 + p(2)*ZRange + p(3);
exznorm(x,:)=(exznorm(x,:)-fit+exznorm(x,Z));

[p]=polyfit (ZRange, szznorm(x,:),2);
fit=p(1)*ZRange.^2 + p(2)*ZRange + p(3);
szznorm(x,:)=(szznorm(x,:)-fit+szznorm(x,Z));

[p]=polyfit (ZRange, sxznorm(x,:),2);
fit=p(1)*ZRange.^2 + p(2)*ZRange + p(3);
sxznorm(x,:)=(sxznorm(x,:)-fit+sxznorm(x,Z));

x=x+1;
end

% Loop to calculate strain energy due to dislocation strain fields
x=1;
while x<= XPoints
    z=1;
    while z<=Zpoints
        bufstrain(x,z)=(1/2*(sxznorm(x,z)*exxnorm(x,z)+szznorm(x,z)*ezznorm(x,z)+2*sxznorm(x,z)*ezznorm(x,z))/Nv;
        Gstrain(x,z)=bufstrain(x,z);
        z=z+1;
    end
    x=x+1;
end

Appendix F
% Total free energy at different temperatures
Gtotal1=Gstrain+Gmix1;
Gtotal2=Gstrain+Gmix2;
Gtotal3=Gstrain+Gmix3;

% Plot free energies over given ranges
whitebg
figure (1)
surfc (ZRange, XRange, Gtotal1);
%figure (2)
%surfc (ZRange, XRange, Gtotal2);
%figure (3)
%surfc (ZRange, XRange, Gtotal3);
save planIn2;
Appendix G

Miscellaneous Matlab Code

% GAPVSXIN.M
% This program plots the bandgap of In\textsubscript{1-x}Ga\textsubscript{x}As over the entire alloy range
% Clears all variables
clear;

% Range of indium alloy compositions
Xin=linspace(0,1,100)

% y is a counter. Loop to determine $E_g$ as a function of alloy content. The loop calls
% on the function alloy.m defined in Appendix B
y=0;
while y<100
    y=y+1;
    Eg(y)=alloy(Xin(y));
end

% Plots bandgap as a function of indium content
plot(Xin,Eg)

% Ao.M
% function for calculating lattice constant of an InGaAs film
% given the atomic fraction of Indium

function Lattice = Ao(Xin)

% Vegard's law which linearly interpolates the lattice
% constant of a film based on the end members. The
% end members are GaAs and InAs
Lattice = 5.64191 + (6.0584-5.64191)*Xin

% RSM.M
% This program, developed by Filippo Romanato and modified by Mayank Bulsara and Chris Leitz, plots
% an x-ray reciprocal space map in angular coordinates.

clear('all');

% Defines angles
theta=0.73291
phi=0.61548
omega=theta+phi
% Number of columns is equal to the number of scans
col=51;

% Loop to strip the header from the data files and load the \theta position (thv) vs. intensity data (cont)
for j=2:col
    ten=fix(j/10);
    unit=j-ten*10;
    s=['C:\chris\xray\06119702\2nd_try\224gersm.x',int2str(ten),int2str(unit)];
    fid=fopen(s,'r');
    ['loading file=','s]
    for i=1:31
        line=fgetl(fid);
    end
    [a,count]=fscanf(fid,'%f %f', [2 inf]);
    a=a';
    cont(:,j)=a(:,2);
    thv=a(:,1)/180*pi/3600;
    fclose(fid);
end

% Defines orange which was scanned
wv=-400:30:1100;
wv=wv/180*pi/3600;

[w,th]=meshgrid(wv,thv);
% Plots reciprocal space map
whitebg
contour (wv, thv, cont, 15)
title ('061197mb_02 224rsm, angular coordinates')
figure (1)
meshc (wv, thv, cont)
Bibliography


Bibliography


