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*Quantum Well Intermixing of InGaAs(P)/InP
Heterostructures*

by
Joan E. Haysom

**A thesis submitted in partial fulfillment
of the requirements for the degree of**

Doctor of Philosophy

**Department of Physics
University of Ottawa**

submitted April 30, 2001

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to my Mom, Dad and brother Keith

(who will be forgiven if they do not read much beyond this page)

Abstract

This thesis studies several aspects of the interdiffusion of InGaAs(P)/InP quantum well (QW) heterostructures, from the fundamental defect mechanisms, through optimization of processing parameters, to novel device applications. Conclusions from each of these areas have been drawn which further the scientific understanding and the manufacturability of the technique.

The thermal stability of a series of different wafers is studied to highlight how poor quality of growth can cause increased interdiffusion, and to review the requirements for achieving repeatable annealing. Purposeful and controlled interdiffusion is accomplished through the introduction of excess defects into layers above the QWs, which during a subsequent anneal, diffuse through the QWs and enhance interdiffusion of atoms of the QWs with atoms of the barriers. These excess defects are introduced using two different techniques, via growth at low temperatures (LT) using chemical beam epitaxy (CBE), and via implantation of phosphorus ions.

The CBE LT growth technique is new, and reported for the first time in this thesis. Characterization of the as-grown layers leads us to believe that they have an excess of phosphorus. The diffusion rate of the mobile defects which cause the intermixing is also measured, and the interdiffusion is shown to occur predominantly on the group-V sublattice. Due to many similarities between this and the results of the implantation technique, it is proposed that these mobile defects are the same for both intermixing approaches, and that the behaviour can be explained by a phosphorus interstitial mechanism. Annealing recipes for the implantation-induced technique are optimized, and the sample-to-sample reproducibility of the blueshift for this method was found to be quite good (standard deviations of ~ 6 meV on blueshifts of ~70 meV). The lateral selectivity and refractive index changes are characterized, and used in combination to create novel buried waveguide devices.

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Publications

Contained within this thesis:

Paper 1: J. E. Haysom, G. C. Aers, S. Raymond, and P. J. Poole; A Study of Quantum Well Intermixing Caused by Grown-in Defects; J. Appl. Phys. 88, 3090, 2000.

Paper 2: J. E. Haysom, P. J. Poole, G. C. Aers, S.J. Rolfe, S. Raymond, I. V. Mitchell, and S. Charbonneau; Quantum well intermixing caused by non-stoichiometric InP; oral presentation and paper at the 12th International Conference on Indium Phosphide and Related Materials, Williamsburg, Virginia, May 14-18, 2000.

Paper 3: J. E. Haysom, P. J. Poole, S. Raymond, and G. C. Aers; Diffusion Rates of Grown-in Defects Studied Using Quantum Well Intermixing; Solid State Commun. 116, 187, 2000.

Paper 4: J. E. Haysom, P. J. Poole, Y. Feng, Emil S. Koteles, J. J. He, S. Charbonneau, R. D. Goldberg, I. V. Mitchell; Spatial Resolution of Ion-induced Quantum Well Intermixing; J. Vac. Sci. Technol. A, 16, 817, 1998.

Paper 5: J. E. Haysom, A. Delage, J.-J. He, Emil S. Koteles, P.J. Poole, Y. Feng, R.D. Goldberg, I.V. Mitchell and S. Charbonneau; Experimental Analysis and Modeling of Buried Waveguides Fabricated by Quantum Well Intermixing; J. Quantum Electron. 35, 1354. 1999.

Related to this thesis:

S. Charbonneau, E.S. Koteles, P.J. Poole, J.J. He, G.C. Aers, J. Haysom et. al; Photonics Integrated Circuits Fabricated Using Ion Implantation (invited paper); IEEE J. Select. Topics Quantum Electron., 4, 772, 1998.

J.E. Haysom, P.G. Piva, P.J. Poole, G.C. Aers, S. Charbonneau, and I.V. Mitchell; Furthering the Understanding of Quantum Well Intermixing in InP (invited), 11th Semiconductor and Insulating Material Conf., Canberra, Australia, July 3-7, 2000.

S. Awirothananon, J.E. Haysom, G.C. Aers, P.J. Poole and S. Raymond; Intermixing Properties for $\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{P}_y/\text{InP}$ Quantum Well Structures with Varying Initial Composition and Strain Profiles; Int. Conf. on Applied Photonics Technology, Quebec, Canada, June 12-14, 2000.

J.E. Haysom, P.J. Poole, G.C. Aers, and S. Charbonneau; Dependence of Thermal Stability and Quantum Well Intermixing on Epitaxial Growth; Canadian Semiconductor Technology Conf. Ottawa, Canada, Aug. 7-10, 1999.

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F. Yang, J.E. Haysom, P.J. Poole, G.C. Aers, R.D. Goldberg, I.V. Mitchell, S. Charbonneau; Strain Effects and Ion Implantation Assisted Quantum Well Intermixing; Canadian Semiconductor Technology Conf., Ottawa, Canada, Aug. 12-15, 1997.

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Chapter I – Introduction

Quantum well intermixing (QWI) is a technique which was first discovered in 1980-81 by Laidig and Holonyak using Zn diffusion into an AlAs/GaAs heterostructures¹. Due to its significant promise for advanced engineering of opto-electronic devices, many people have studied it at one time or another, although few have mastered it to the point of commercial application. It is a complicated technique, and many interesting elements of physics and material science can also be learnt from careful study. The purpose of this thesis is to study two particular intermixing approaches on InGaAs(P)/InP heterostructures, determine what important factors must be controlled for successful application, as well as explore some of the underlying physics, and in particular, consider the nature of lattice defects which control the effects.

In this introductory chapter, the motivating reasons for the development of a technique such as QWI for opto-electronics is covered in section A, while section B gives a brief introduction to QWI and review of the various processing approaches that have been used to achieve it. Section C of this chapter gives an overview of the underlying physics, and serves as an introduction to the subjects which are covered in more detail in Chapter II.

A – Opto-Electronic Devices and Monolithic Integration

The optical communication industry is growing at a phenomenal pace at present, fueled by demands for high bandwidth for data and voice transfer. Information is transmitted thousands of kilometers by sending optical signals (modulated infrared light) along silica fibers. Increasing the rate at which information is transmitted can be done in two manners: (a) increasing the data rate on a given channel by increasing the number of pulses per second; or (b) increasing the number of channels. The channels consist of different wavelengths of light (usually near 1.5 μm), which travel along the silica fiber independently; the simultaneous use of multiple wavelengths is commonly referred to as wavelength division multiplexing

(WDM). Current systems can send light pulses at a rate of 2.5 to 10 Gb/s, but significant margins of improvement beyond these values via option (a) will not come easily. WDM is the more recent solution for increasing the bandwidth, and the number of channels in use are increasing at a rapid pace. Systems with up to 160 channels are available on the market today, although most systems currently operate with ~ 4 to 32 channels.

Increasing the number of channels also increases the number of system components. Key components of the fiber optic systems are the compound semiconductor opto-electronic devices which produce, modulate, amplify and detect the optical signals. Currently, these devices are discrete, each packaged separately and then coupled together to form larger functional WDM systems. The spot size of the optical modes at the entrance/exit facets of these devices are the order of a few microns, requiring very precise alignment between different devices in order to minimize losses. Thus packaging comprises a major portion of the expense of the systems. There is a drive to reduce the number of separately packaged components by moving to integrated devices.

Many of the compound semiconductor devices rely on the advantageous properties of quantum wells in order to obtain excellent optical efficiencies and to operate at precise wavelengths. The quantum wells and other necessary hetero-compositional layers of the devices are fabricated by very precise epitaxial growth techniques, such as molecular beam epitaxy (MBE), chemical beam epitaxy (CBE), and metal-organic chemical vapour deposition (MOCVD). These techniques are able to grow, on a crystalline substrate, layers of semiconductor alloys of precise thickness and composition. The epitaxial layers are also crystalline, as long as their composition is such that their lattice constant is similar enough to the starting substrate. An example of the layer structure of a laser emitting at 1.5 μm is shown in figure I-1. In this case, the layers consist of stoichiometric $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ alloys of various x,y compositions. Although the choice of each layer of the structure must be carefully thought out by a device designer, the QW can be considered the most important

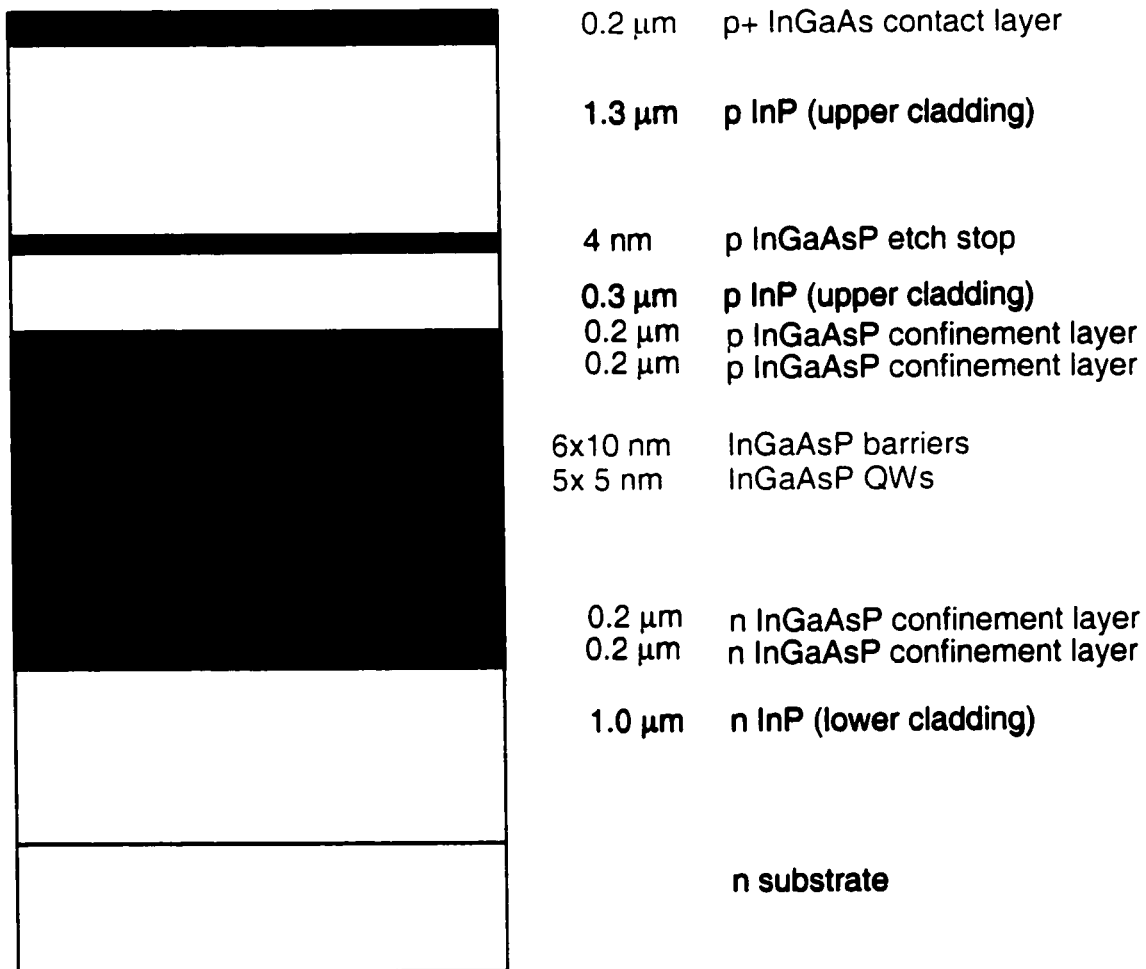


Figure I-1: The material layer structure of a typical laser (layer thicknesses are not to scale). The compositions (the x and y values) of each of the (differently coloured) $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ layers would be different, such that the QW material has the smallest bandgap, followed by the barriers and confinement layers, such that the carriers tend to be confined in the QWs.

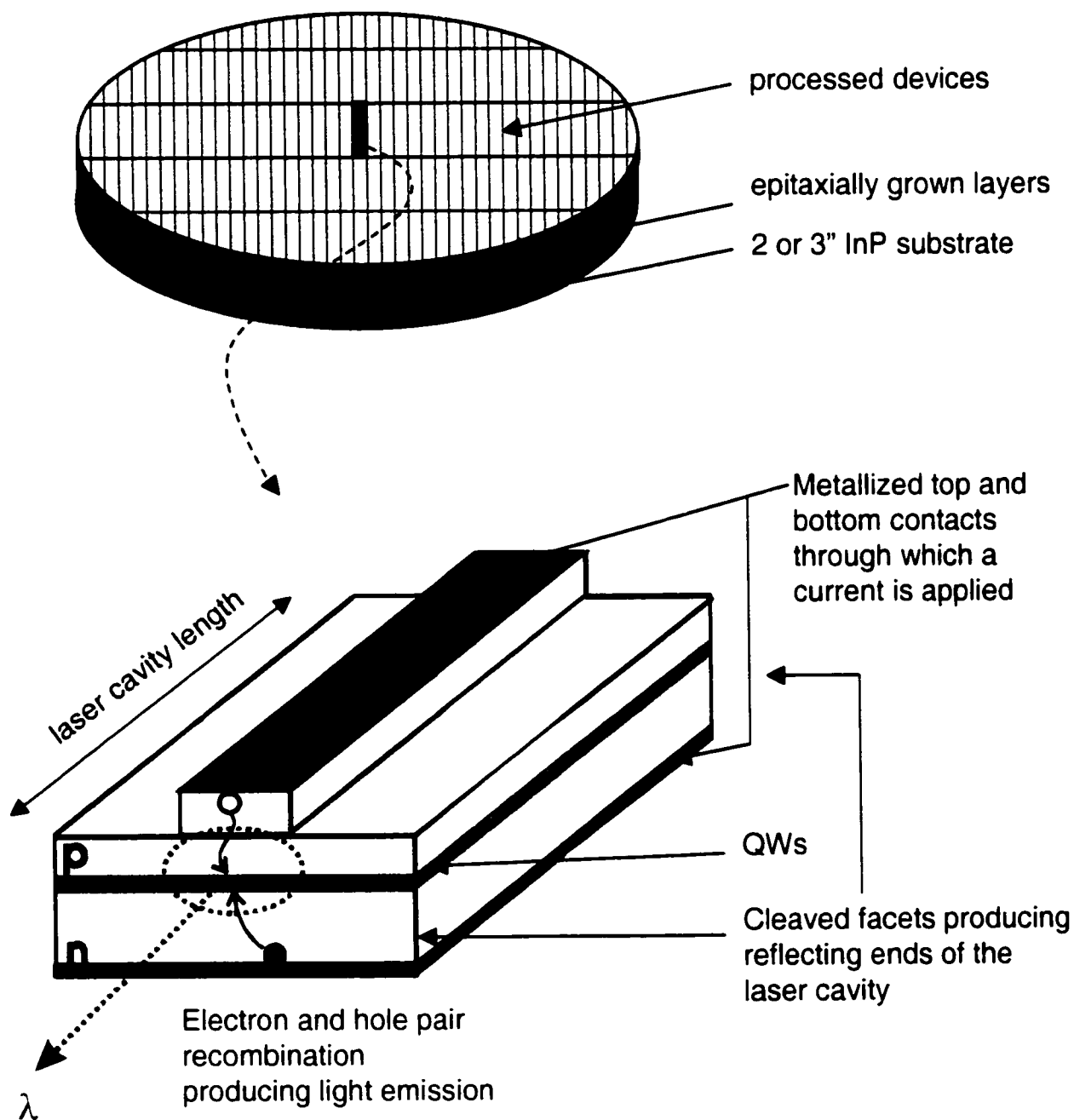


Figure I-2: (a) Illustration of a wafer following epitaxial growth and processing. At this point, the substrate side of the wafer is thinned, and wafer is cleaved into individual devices, which are illustrated in (b).

part - control of its composition and thickness allows for accurate determination of the structure's bandgap energy, thereby determining the wavelength at which the device will operate. One limitation of epitaxial growth techniques is that the very same layer structure is produced across the entire substrate wafer. Thus all devices fabricated on a given wafer will have the same bandgap energy. Wafers are cleaved into individual devices, as illustrated in figure I-2(a), and each device is packaged separately. An example of an InP-based laser structure is shown in figure I-2(b).

Monolithic integration of different devices will require a method of tuning the QW's characteristics in various regions of the wafer, as illustrated in figure I-3. The monolithic integrated circuit depicted in the figure is composed of a laser, a modulator and waveguide/splitter. The bandgap energy of the modulator is slightly higher than the laser, and thus will not absorb the laser signal. But with the application of an electric field (in reverse bias), the modulator's bandgap can be shifted to lower energy (through the quantum confined stark effect), resulting in absorption of the light produced by the laser. Thus control of an applied bias to the modulator results in production of the 1's and 0's required to transmit information. The bandgap of the waveguide/splitter device is significantly above that of the other devices such that absorption losses in these regions are minimized.

A few different options are available for selective control of the bandgap in an epitaxial structure, including:

- (a) Etch and re-growth, where the initially grown layer structure is removed in selected regions of the wafer, and a new epitaxial structure with the desired characteristics is grown in the etched-out regions.
- (b) Growth on patterned substrates, where, using lithographic techniques, the starting substrate is topologically patterned in a way which influences the epitaxial growth. For example, growth at the top of a ridge can result in a different composition and thickness than at the bottom of the neighbouring troughs.

- (c) Quantum well intermixing, where the bandgap of the QWs is altered in selected regions using post-growth processing steps which causes interdiffusion of the QWs.

All three methods are being actively researched, and it is likely that all three will be used for various monolithically integrated devices, depending on the requirements of the application and on the available corporate capabilities. The first method offers the advantage of complete freedom in the layer structure for subsequent growths, thus devices with very different layer structures can be integrated, but achieving high quality re-growth and good interfaces between the different regions is challenging, and multiple growth steps are expensive. The second method requires a significant research effort to understand this new growth regime. The third method, quantum well intermixing, is the subject of this thesis. Its advantage is that it relies on the application of simple processing steps to standard epitaxial growth. Its main disadvantage is the layer compositions and doping will still be very similar across the entire wafer (only the QW will be “tweaked”), which may force a trade-off in the optimal layer structure for different device types which are to be integrated.

B – An Introduction to Quantum Well Intermixing

Intermixing involves the diffusion of atoms, such that the interfaces between the QW and barrier materials are “blurred”. This alters the confinement profile of the QW, and subsequently its transition energies and bandgap. This is illustrated schematically in figure I-4. A more in-depth discussion of these effects are contained in the next section. Generally speaking, the bandgap energy increases after intermixing, which is commonly referred to as an energy blueshift. The amount of interdiffusion required for a significant blueshift is small - typical interdiffusion lengths are of the order of 0.1 to 2.0 nm and the bandgap blueshift are of the order of 20 to 100 meV (depending, of course, on the starting structure). Thus, for a 5.0 nm thick QW, the interface between the QW and the barrier is “blurred” but the QW

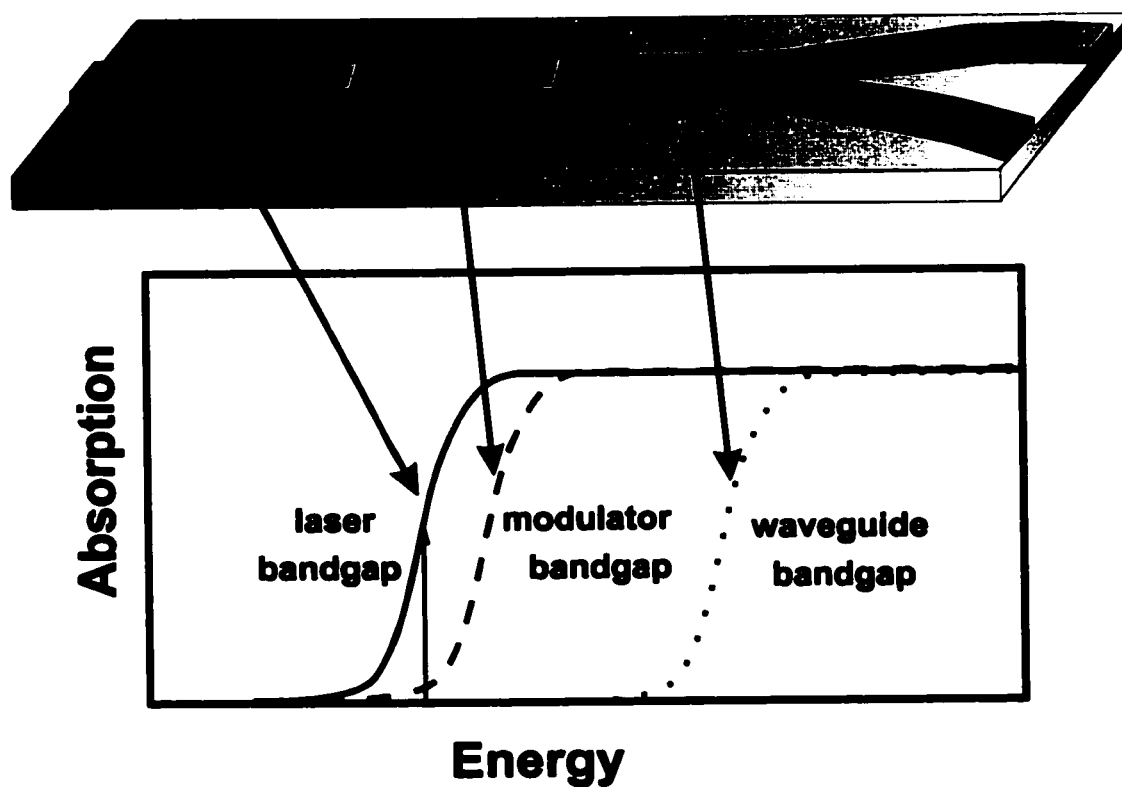


Figure I-3: Illustration of how multiple opto-electronic devices would be integrated monolithically; and the required bandgaps for each of the devices.

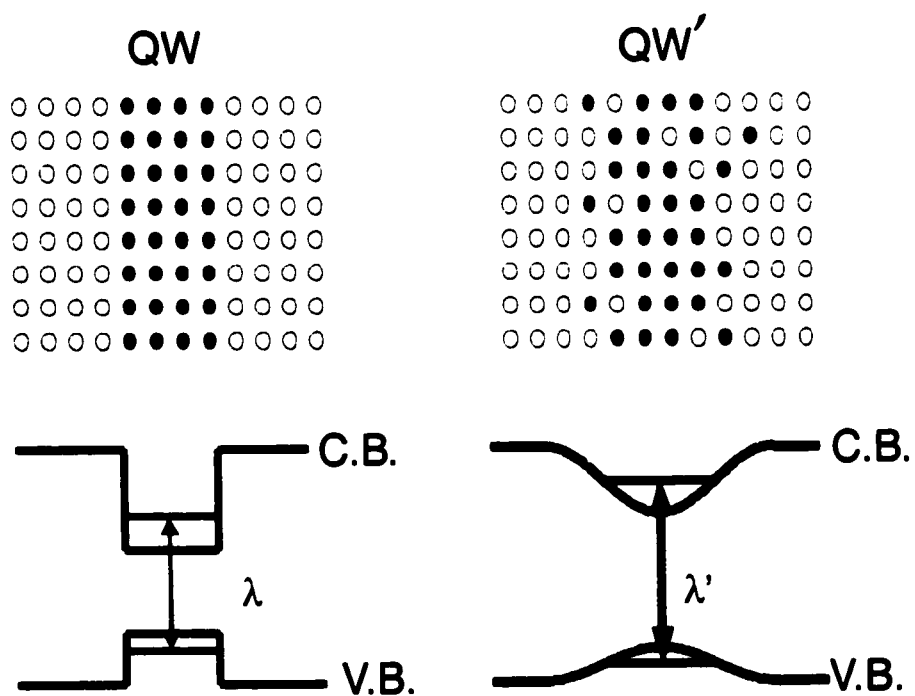


Figure I-4: Schematic of interdiffusion between atoms of the QW and atoms of the barrier material, resulting in a rounding of the conduction band (C.B.) and valence band (V.B.) potential wells, resulting in a change in the emitted wavelength.

still remains. These interdiffusion lengths will be insignificant to the other thicker layers of the structure.

Intermixing is also often referred to as interdiffusion and disordering. In this thesis, I will use QWI or “intermixing” to mean the technique in general, while the term “interdiffusion” will mean the specific phenomenon of exchange of atoms between two layers of different compositions.

There are several different choices of processing steps which cause interdiffusion to occur. All of the possibilities, except choice (f) in the following list, rely on the introduction of lattice defects into selected regions of the wafer to enhance the interdiffusion of atoms at the QWs. The key mechanisms of each technique, as well as its main disadvantage are included in what follows².

(a) Annealing with a Dielectric Cap The presence or absence of a dielectric on the surface of the structure during a high temperature anneal, can create an excess of lattice defects. One theory for GaAs based structures is that Ga preferentially diffuses into SiO₂, thereby leaving behind Ga vacancies which diffuse to the QWs. Other explanations are required for InP and/or other dielectrics. The creation of defects during the deposition³ of the dielectric and/or stress gradients during the annealing⁴ (resultant from different thermal expansion coefficients of the dielectric and the semiconductor) may also influence the interdiffusion, depending on the process^{5,6,7}. Reproducibility seems to be a major challenge here⁸, and different groups do not achieve the same results with the “same” dielectrics. This method is sometimes also called impurity-free vacancy disordering.

(b) Introduction of Impurities A high concentration of dopant atoms, introduced using implantation (followed by high temperature anneal) or in-diffusion, can increase the concentrations of certain lattice defects, and thereby enhance interdiffusion of the QWs^{9,10,11}. This methods has substantial limitations, since the

dopant atoms alter the electric field in the device, and increase absorption losses, both of which will degrade device performance.

(c) Implantation/Cascade Mixing Implantation of non-dopant atoms into or through the QW creates lattice defects directly in the QW, which enhance interdiffusion during a subsequent high temperature anneal^{12,13,14,15}. Implantation into the QWs leaves damage in them, which significantly reduces optical efficiency, Implantation through the QW improve this issue¹⁶, but it requires a high energy implanter to place the ions deep within the layer structure. Implant is selective through use of a mask, but creating and patterning a mask to block such high energy ions is difficult.

(d) Shallow Ion Implantation When non-dopant atoms are implanted into layers above the QW, lattice defects are created. During a subsequent high-temperature anneal, these defects diffuse to and through the QWs, where their presence enhances interdiffusion. By keeping the majority of the implant damage away from the QWs, the problems of (c) are avoided. This method seems to work very well for InP-based structures¹⁷, producing prototype devices with excellent characteristics¹⁸.

(e) Grown-in Defects Intentionally poor epitaxial growth of a layer results in the introduction of a large number of lattice defects, which can subsequently enhance intermixing during a high temperature anneal. Patterning of the defective layer before the anneal allows for selective shifting. Only a handful of papers exist on this subject^{19,20,21}, all pertaining to very low temperature growth in GaAs.

(f) Laser heating: a laser beam is used to directly heat selected regions of the wafer. Wherever the temperature is raised sufficiently, interdiffusion will occur^{22,23}. This requires direct writing of the laser across the wafer, which will be slow for production, and the lateral selectivity will be limited by thermal gradients.

Techniques (d) and (e) from this list are studied in this thesis. Research on shallow ion-implantation began at NRC in the early 1990's, and significant number of papers

and three patents have been produced by the group - a review of much of work can be found by Charbonneau et al.²⁴ When applied to the InP-based QW structures required for optical telecommunications, the disadvantages of this technique appear to be minimal. To the best of our knowledge we are the only group studying the shallow ion-implantation induced QWI. A much more detailed discussion of the technique will be provided in Chapter V. At this point, we will restrict ourselves to stating that, although the implantation technique has been shown to be useful and prototype devices have been fabricated, several effects needed to be further studied. In particular, a significant variability in blueshift was observed between similar wafers, and the basis for this variability needed to be addressed. Additionally, research on the thermal stability of as-grown material resulted in a whole series of fruitful experiments devoted to grown-in defects (method (e)). Throughout the research, additional effort have been applied, wherever possible, to further the understanding of the physical mechanisms at play. The next section briefly discusses how these processes can be partitioned into smaller topics.

C – Physical Processes in Quantum Well Intermixing

The physical processing which occur in all QWI techniques can be broken down into three main topics, as is illustrated in figure I-5, and discussed in the following:

(1) Defects

The QWI technique relies on the presence of excess lattice defects, here created either during growth or by ion-implantation. For implantation, one desires starting material which is relatively free of excess grown-in defects, since they will cause unwanted intermixing in non-implanted regions. In the applications throughout this thesis, the defects will be located in layers above the QWs. The subject of defects has perhaps the most unanswered questions, especially in the case of InP-based structure. Questions which can be asked are: What are the identities of all the defects present?, What is the identity of the intermixing-causing defects (to be referred to as QWI-defects)? What effects enhance or diminish their concentration,

their diffusion mechanism and rate, and the mechanism by which they cause the interdiffusion?

(2) Compositional Changes – Interdiffusion

The key to understanding a given QWI experiment is, of course, to know what changes have occurred to the QW. There are two key questions: What is the shape of the atomic concentration profile after the diffusion? Do the group-III and group-V sublattices of the III-V semiconductor diffuse similarly? Various models for how the interdiffusion proceeds exist in the literature, but none have been proven right or wrong yet. Then when comparing results from different layer structures, an additional set of questions must also be addressed: How do different compositions and lattice strains in the QW and barrier affect the interdiffusion? What about doping in the QW, barrier and in the surrounding layers?

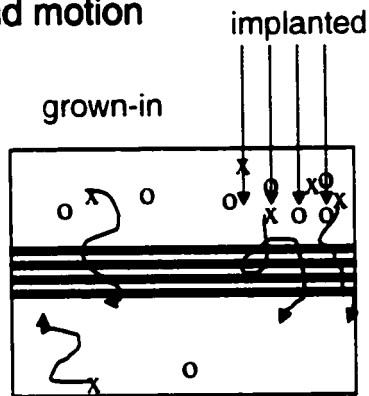
(3) Optical Transitions of interdiffused QWs

Unfortunately, the length scales involved in the QWI process are very small (in the order of 0.5 to 1 nm) making direct physical characterization of the compositional changes very challenging. But the changes to the optical transitions are easily measurable, thus a theoretical connection between optically measurable effects and the actual structure is required. For a given compositional change (either measured or assumed), the determination of the transition energies is mostly a matter of computation using material parameters found in the literature. It is important to have a computational “tool” for QWI studies, since a well designed experiment can then use the blueshifts in a series of samples to test the different models of interdiffusion. Such a tool, as was developed by a colleague, was used extensively in the work of this thesis.

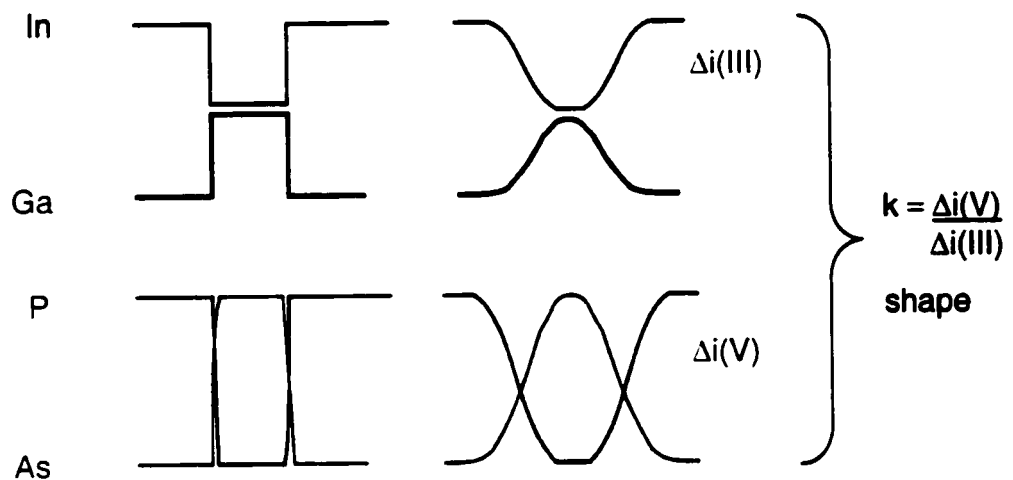
D – Summary

The above physical processes must be understood in order to make QWI a flexible predictable tool for use by industry. However, it can be a challenging endeavor to answer any one of the questions raised above. The important point to take away

1. Defect creation and motion



2. Compositional changes



3. Changes to confinement and optical transitions

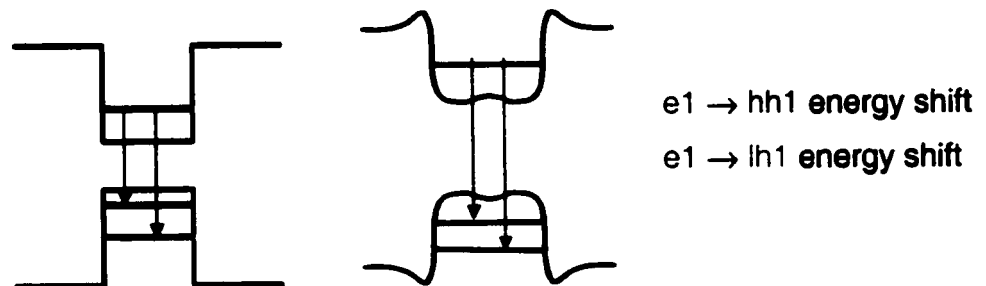


Figure I-5: Illustration of the three main topics surrounding quantum well intermixing.

from this introduction is that these three topics are strongly interrelated, and one must have a good understanding of all three topics in order to be able to study any one topic. Chapter II will review theoretical background information required for the study of these three topics. Chapter III provides information on the characterization techniques, while the experimental results are discussed in Chapters IV and V. Chapter IV includes work on the optimization of the annealing procedure, analysis of the thermal stability of a number of wafers, and studies of grown-in defects. Chapter V includes all the results relating to implantation, including a further optimization of annealing of implanted material, an examination of the defect kinetics, the reproducibility, the lateral selectivity, the refractive index changes and a look at implantation-created waveguide devices.

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Chapter II – Diffusion Theory and QWI Modeling

A – Introduction

The three main topics relating to QWI, as introduced in the previous chapter, are: (1) defects, (2) compositional changes, and (3) optical transitions. This chapter will discuss in more detail each of these topics, which will be covered in sections B, C, and D, respectively. Section B gives a review of lattice defects and the microscopic nature of diffusion, necessary for addressing the first topic and connecting it to the second topic. Section C addresses the macroscopic/phenomenological diffusion equations used to study the compositional changes to the QW (topic 2) after interdiffusion. An overview of how the optical transition energies are calculated (topic 3) is given in section D. Finally, section E will provide a summary of the important points made in the chapter. The appendix contains details of equations and material parameters used in the calculations described in D.

A textbook by Tuck¹ is a useful source for additional details relating to defects and diffusion (sections B and C), while quantum and/or semiconductor physics textbooks such as Bastard² contain more details relating to section D.

B – The Role of Defects in Diffusion

Defects and Activation Energies

Under equilibrium conditions, atoms vibrate about their lattice position, with amplitude given by their thermal energy (their temperature). If an atom's thermal energy is large enough, it can overcome an energy barrier and hop off its lattice site. In the process, it becomes an interstitial while leaving behind a vacant lattice site (a vacancy). This interstitial + vacancy combination is known as a Frenkel pair. There is a certain instability associated with this configuration, and two things could occur: (a) the interstitial atom may move back to its original site, thereby annihilating the Frenkel pair; or (b) the interstitial and vacancy could move away from this initial

location, possibly in different directions, and possibly causing other atoms to also hop on and off their sites. The creation of these defects will increase as the temperature of the material increases. The presence of either a vacancy or an interstitial can enhance the probability of further atomic hopping, as described below and illustrated in figure II-1.

Vacancies: When a vacancy on site n moves to site $n+1$ this automatically means that an atom has moved from site $n+1$ to site n .

Interstitials: Motion of an interstitial in the spaces between lattice sites (the interstitial sites) does not necessarily cause atomic exchange, however, an interstitial has a probability of exchanging with an atom on a lattice site, thereby causing the former occupant to become a new interstitial. This is commonly referred to as a kick-out mechanism. Alternatively, if the interstitial recombines with a vacancy (at a position different from its starting location), this is referred to as the interstitialcy mechanism.

Assuming no external influences, the movement of these defects will be a random walk process. There will be a certain energy barrier that must be overcome for any of the above processes to occur, which will relate to energies required for an atomic hop. In general, the frequency of atomic hopping, ν , will be dependent on the temperature, T , and the energy barrier or activation energy, E_a , for the given mechanism, which can be expressed by an Arrhenius type equation:

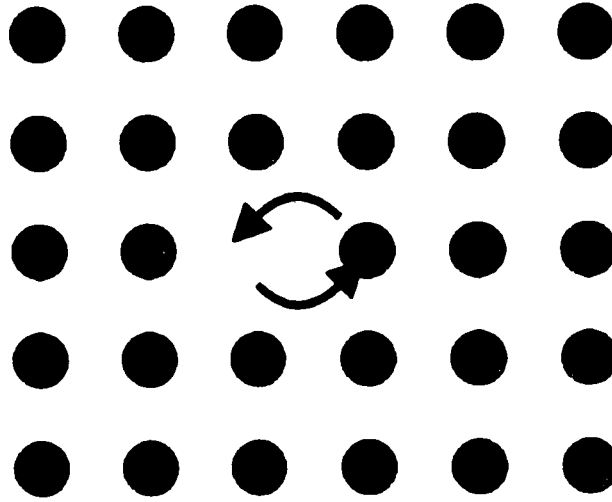
$$\nu \propto \exp(-E_a / kT) \quad [1]$$

where k is the Boltzmann constant. Then, the diffusion coefficient for the motion of a defect or atom is related to this hopping rate by:

$$D \propto \lambda^2 \nu \quad [2]$$

where λ is the hop distance (usually one lattice spacing). A larger D implies that the defect can move (diffuse) more easily and therefore more rapidly. The two

(a) vacancy diffusion



(b) interstitial diffusion and a kick-out mechanism

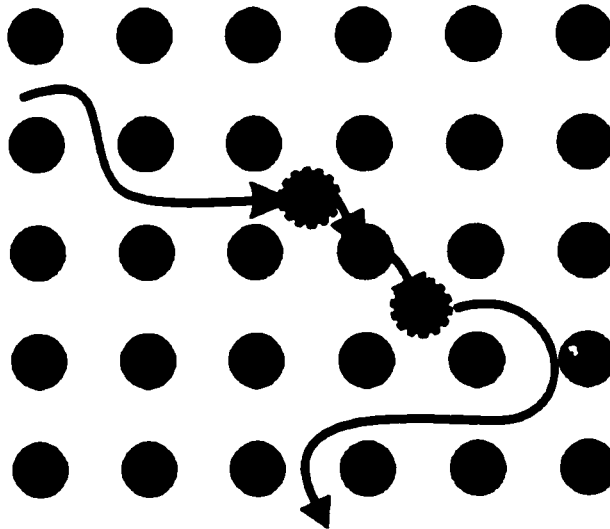


Figure II-1: Two standard mechanisms by which interdiffusion occurs (a) vacancy hopping (b) interstitial diffusion with a kick-out mechanism.

above equations can be combined into the commonly used form:

$$D = D_0 \exp(-E_a / kT) \quad [3]$$

Both D_0 and E_a are dependent on lattice structure and the type of hopping mechanism.

The random walk motion of the defect through a thin layer will create the opportunity for atoms of a thin layer to exchange with the neighbouring material, resulting in compositional changes. Thus, changes to compositional profiles, or interdiffusion, result from atomic hopping in the presence of defects. The creation of a Frenkel pair, as described above, is an example of thermal equilibrium generation of defects. Under equilibrium conditions, an interdiffusion process which is mediated by one of these defects will have an activation energy which consists of energy of *formation* of the defect³ plus the energy of *motion* for the defect. However, when defects are already present, the interdiffusion will occur more readily and at lower temperatures, with a smaller activation energy due only to the *motion* of the defects. The latter scenario is the general picture assumed for QWI caused by implantation or by grown-in defects⁴.

Although it is likely that more than one type of defect is present in a material, in a given experiment the interdiffusion is usually assumed to be primarily controlled by one defect mechanism⁵. Factors which influence which defect is dominant include concentration of the defect, diffusion rate, as well as propensity to cause interdiffusion (interstitials do not necessarily cause interdiffusion). External conditions to the crystal, such as gas overpressure of a constituent can also influence the relative concentrations of different defects. For example, annealing GaAs at high overpressures of group-V constituents may result in the creation of group-V interstitials and/or group-III vacancies. When maintaining the experimental parameters of temperature and overpressure constant, it is usually fair to assume that one mechanism dominates a given series of experiments. Analysis of the temperature dependence of a result, by plotting $\ln(D)$ vs $1/T$, allows one to

determine the E_a of the mechanism. But determining what the actual mechanism is can be much more challenging, since several possibilities should always be considered.

Defects in III-V Semiconductors

The lattice structure of the compound semiconductors of interest here, including GaAs and InP, is zinc blende, which consists of two interpenetrating face-centered-cubic (FCC) sublattices, as shown in figure II-2. The group-III atoms (Ga, In) reside on one sublattice, and the group-V (As, P) on the other, such that each atom is surrounded by four atoms of the other sublattice. In comparison to studying elemental semiconductors like Si and Ge, the two sublattices of the zinc blende structure dramatically complicates many issues. For example, there are two “flavours” to the interstitial and vacancy defects, as well as a new type of defect – antisites, which are atoms sitting on the wrong sub-lattice resulting in six different simple lattice defect (herein given for InP):

- In and P vacancies - V_{In} , V_P
- In and P interstitials – In_i , P_i
- In and P antisites – In_P , P_{In}

The defects can be ionized and thus have an electrical charge, similar to how a substitutional impurity atom of different valence behaves as a dopant when located on a lattice site. Thus the presence of these defects can create new energy states and alter electronic properties⁶. At present, a complete picture of the nature of all the defects in compound semiconductors is far from complete. Dabrowski⁷ provides a good overview of the many issues that must be considered. Below, a brief overview of the theoretical and experimental work on native defects in III-Vs compound semiconductors is given.

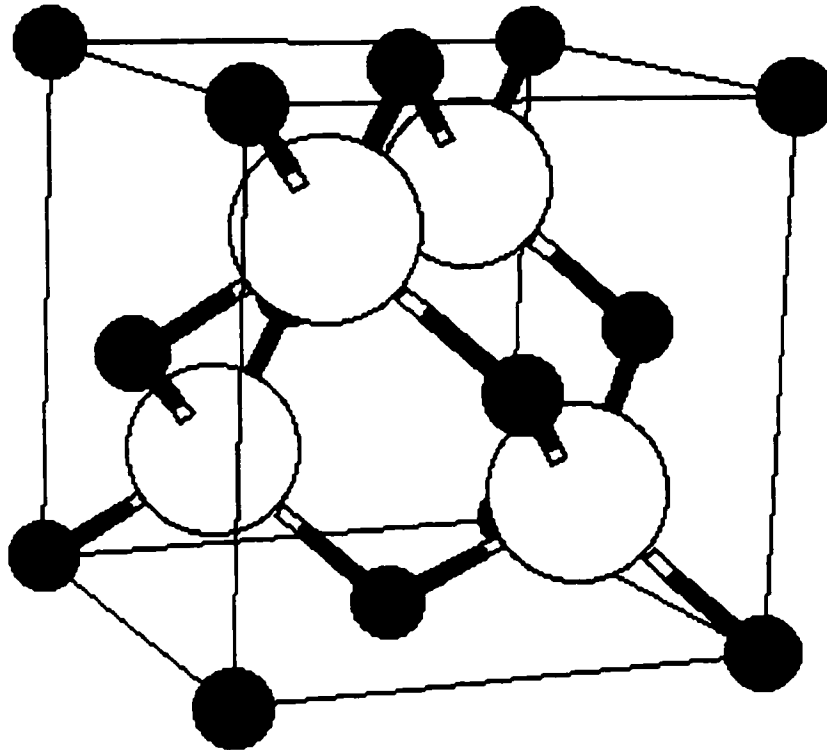


Figure II-2: Zinc-blende structure for InP and other III-V semiconductors. Group-III atoms (In, Ga) are represented by yellow balls, and group-V atoms (As, P) are represented by brown balls.

Theoretical Predictions of Defect States

Theoretical predictions using density functional theory or linear combinations of atomic orbitals have been applied to calculate defect energy levels. With regards to site defects (vacancies, antisites), the energy levels of a defect's states are related to how the bonding electrons of the surrounding lattice re-organize themselves due to this imperfection, or in other words, the relaxation of the lattice around the defect. By accepting or donating electrons to the crystal, a defect may exist in a number of different charge states⁸, and each charge state will occur with a probability dependent on the crystal's Fermi level, stoichiometry, strain, and surface environment⁹. The electronic energy level for each charge state can be calculated - generally they increase in energy (relative to the valence band) as the charge becomes negative¹⁰. Although the trends are similar across many of the III-V compound semiconductors, the extent of the lattice relaxation depends somewhat on the atomic sizes, and the energy level depends somewhat on the ionicity of the bonding (which is greater in InP than GaAs). These effects make the In_P a very low probability defect, while V_{In}, P_{In}, and V_P are expected to exist in appropriate instances¹⁰. In contrast, it is expected that interstitials bond only very weakly with the lattice, and thus only a small difference in energy levels is expected between the group-III and V interstitials⁹. Interstitial defects are located on open tetrahedral sites, either surrounded by four group-III atoms or surrounded by four group-V atoms, and these two positions may have slightly different energy levels.

There will be an equilibrium concentration for each charge state of each of the six types of defects (vacancy, interstitial, antisites on each sub-lattice), for a given set of conditions (temperature, stoichiometry, doping, etc.)³ and defect interactions¹¹ will occur whenever there is a change to these conditions^{12,13}. For example, a V_{In} and a In_i can combine to create a filled lattice site, or V_{In} with P_i can combine to create a P_{In} antisite. It is also expected that the native defects form complexes with themselves (such as di-vacancies, antisite/vacancy pairs, etc) and complexes with impurity atoms.

Experimental Evidence of Defect States

The Ga vacancy is the most studied defect, and charge levels 0, -1, -2, -3 have been confirmed, with the -3 charge being most commonly observed^{14,15}. Some agreement with experimental results are found for other site defects (vacancies and antisites). To date, the charge states of interstitials in InP have not been measured experimentally³, and thus the possibility that they most often are neutral¹⁶ exists, although there are some reports that the Ga_i in GaAs has a charge of +2^{14,17}. The best understood intrinsic defect in InP is P_{In} , because it has a strong hyperfine interaction which makes it resolvable by magnetic resonance techniques³.

Most experimental work on defects, using electrical techniques such as deep level transient spectroscopy⁶, can quantify the energy levels, and thermal properties of the defects, and in some cases the charge state, but cannot actually determine what the defect is. Thus these approaches must resort to assigning labels to the observed state (relating to the type of trap that it is (electron or hole) and the type of growth of the crystal¹⁸) and can only provide assignments of the physical nature of the defect based on the inference from growth and processing conditions. The defect in GaAs labeled EL2¹⁹, which is found in neutral and +1 charges²⁰, is thought to be either an isolated As_{Ga} ²¹ or an $\text{As}_{\text{Ga}}\text{-As}_i$ pair²². Magnetic resonance techniques are very useful for some defects, such as the P_{In} , which have distinct signatures²³. Positron annihilation can be used to observe vacancies and other hole traps^{24,25}, but tends to be insensitive to concentrations lower than 10^{16} cm^{-3} .

Defect identification in III-V semiconductors is by no means straightforward. The theoretical and experimental work briefly outlined above are informative, but by no means does an overall picture of the defects in InP exist. For example, in the two volume series Identification of Defects in Semiconductors (1998)²⁶, InP is discussed on only ten pages, and these are scattered throughout the chapters. Since InP and the InGaAsP alloys are currently such important materials for opto-electronic devices, one would hope that further research will generate a cohesive picture of the defects.

As the nature of the defects present in a sample depends significantly on the processing, more detail on the two means by which defects are introduced into the material in this thesis, namely grown-in defects and defects created by implantation, will be covered within Chapters IV and V, respectively.

C – Compositional Changes - Interdiffusion

A common starting point in QWI studies is to disregard which defect(s) actually caused the interdiffusion, and simply begin analysis of the compositional changes. One might consider this to be the macroscopic picture, while the preceding section dealt with the microscopic picture of diffusion. The basic diffusion theory generally used is well established, having been used for over 40 years on many material systems.

Diffusion of a particular species of atoms occurs as a result of (defect mediated) atomic hopping in combination with a concentration gradient of that species. The flux of atoms will be towards the region with the lower concentration, such that the crystal moves towards homogenization^a. In the simplest picture, this is described by Fick's first law (one-dimensional case, with gradients in the z-direction):

$$J_z = -D \frac{\partial C}{\partial z} \quad [4]$$

where J is the flux and D is the constant of proportionality, usually called the diffusion coefficient (assumed to be time-independent). For example, with an InGaAs layer bordering an InP layer, As will diffuse from regions of high concentration of As to low, i.e. from InGaAs into the InP (the other species will likely diffuse too, as will be discussed later).

^a In fact, the diffusion occurs down a chemical potential gradient, which most often is the concentration gradient, but not always. In this formulation equation [4], it is possible to have negative D.

The rate of change (with time) of a concentration at given location is found by combining the above equation with a standard continuity equation (rate of change is equal to the flow into, minus the flow out-of of a region) to get the following equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) \quad [5]$$

Note that the rate of change will decrease with time as the driving force (the concentration gradient) diminishes, even if the diffusion coefficient remains the same with time. The latter will be true if the defects mediating the compositional change are supplied at a constant rate, i.e. equilibrium defect generation at high temperatures. When a non-equilibrium population of defects is present (such as is the case for implantation and grown-in defect induced intermixing), the diffusion coefficient for the atoms will change with time, dependent on how the defect population changes (usually decreases) with time.

Quite often, the D is assumed to be constant with position, i.e. independent of changes in the composition and thus independent of z , thus equation [5] becomes:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad [6]$$

Equation [6] is usually referred to as Fick's second law (and diffusion that follows this equation is called Fickian). Again using our InGaAs/InP example, applying this equation requires that the As diffusion rate is constant throughout the whole sample, independent of whether we focus on the QWs or the barriers. Equation [6], in combination with appropriate boundary conditions which properly describe the experiment, can be used to determine the concentration as a function of position for a given amount of diffusion. The solutions of importance for this thesis, and their boundary conditions, will be discussed below.

Fickian Solutions

For an infinitely thin layer of diffusant surrounded by infinitely thick layers, the solution to the above equations give a Gaussian distribution after a time t :

$$C(z,t) = \frac{M}{2\sqrt{\pi Dt}} \exp\left(-\frac{z^2}{4Dt}\right) \quad [7]$$

where M is the quantity of diffusant in the starting material. The Gaussian shape is a natural consequence of the random behaviour of the atom motion. Several solutions to this equation are shown in figure II-3(a).

The solution for a thick film where the concentration, C , of the atom of interest is C_0 and surrounded by material where $C=0$, can be found by summing many thin films together. The result is:

$$C(z,t) = \frac{C_0}{2} \left[\operatorname{erf}\left(\frac{h+z}{2\sqrt{Dt}}\right) + \operatorname{erf}\left(\frac{h-z}{2\sqrt{Dt}}\right) \right] \quad [8]$$

where h is half the width of the layer (centered about $x=0$) and erf is the error function, an indefinite integral which obtained by summing the thin film Gaussians, as defined by:

$$\operatorname{erf}(\mu) = \frac{2}{\sqrt{\pi}} \int_0^{\mu} \exp(-\eta^2) d\eta \quad [9]$$

Several solutions for different amounts of diffusion are shown in figure II-3(b), where a common way of expressing the amount of interdiffusion is the interdiffusion length, defined as:

$$\Delta_i = \sqrt{Dt} \quad [10]$$

This is an important definition, used throughout most diffusion analysis, including this thesis. Equation [8] can thus be used to describe the distribution of As after interdiffusion of an InGaAs QW, as long as Fickian behaviour (or error function

solutions) is assumed. Experimentally, if the compositional profile of a diffused structure can be fit by an error function, then it is straightforward to obtain D . However, since in the case of implantation and grown-in defect induced intermixing, the diffusion coefficient is a function of time (resulting from a pulse of defects), this D and Δ_i are effective values, for a particular set of experimental conditions.

Non-Fickian Solutions

It turns out that non-Fickian diffusion behaviour occurs quite frequently and in many different material systems^{27,28}. It can occur because of a composition dependence of the diffusion coefficient, $D(C)$ or because defect reactions are taking place. For example, As and P within an InGaAs QW (i.e. As in high As concentration) might diffuse much more quickly than in the InP (where As concentrations are low). Schematic profiles for three non-Fickian cases are shown in figure II-4(a) to (c).

There are many different possible variants, and in general all solutions will require more parameters than the Fickian case. Thus, additional knowledge, such as a detailed knowledge of $D(C)$ is required, and generally this information is not available, especially in the case of III-V semiconductors. In the case of most quantum well interdiffusion studies, the compositional profile is not directly accessible (due to the challenges of characterizing such a thin layer), and it is *standard to assume* that the interdiffusion is Fickian. A handful of papers on QWI attempt to fit their data of blueshift as a function of RTA temperature and/or time by non-Fickian profiles. Fleming et al. use a formula of $D(C)=D_0\exp(\alpha C)$ where D_0 and α are constants and C is the concentration of Ga in a GaAs/AlAs MQW²⁹. Mukai et al. assume different, but constant, diffusion rates inside and outside the QW, along with a constant ratio of concentration at the interface when modeling both InGaAs/InP and AlGaAs/GaAs systems³⁰. These models achieve reasonable fits to their data, but are not any more convincing than fits that Gillin et al. achieve by assuming Fickian diffusion³¹.

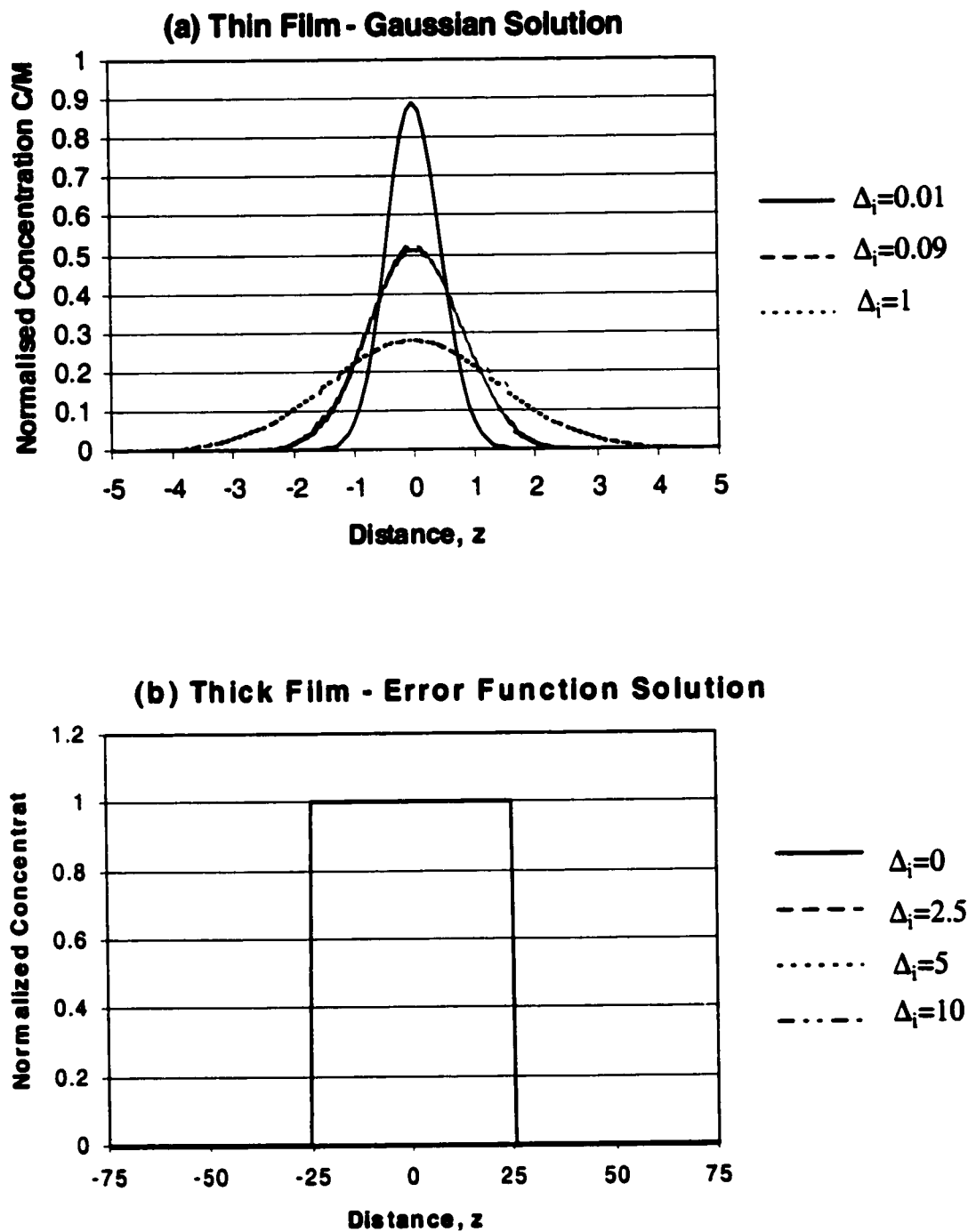


Figure II-3: Solutions to the Fickian diffusion equation for (a) a thin film of one material surrounded by a second material; (b) a thick film of one material surrounded by a second material.

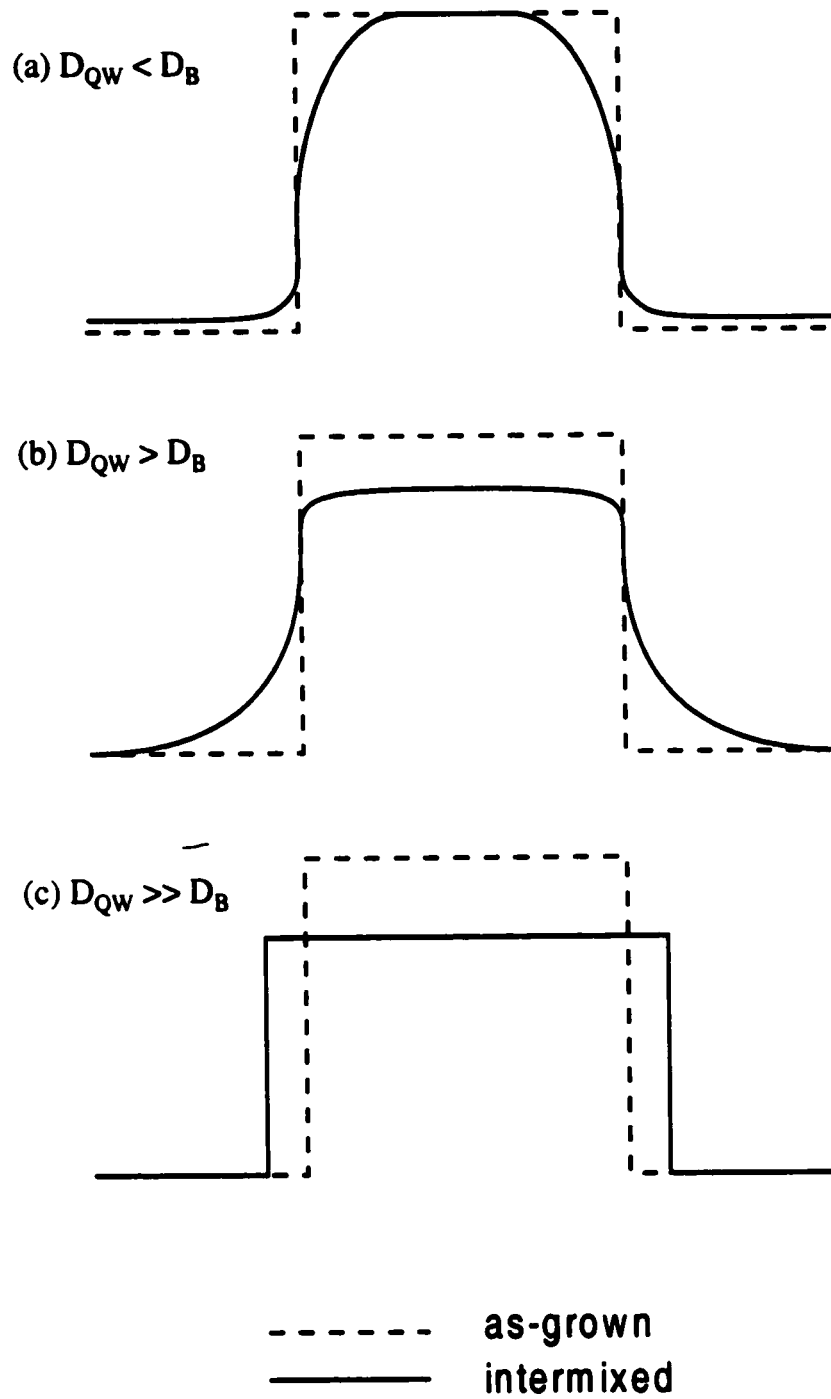


Figure II-4: Schematic of concentration profiles for as-grown and interdiffused QWs under different non-Fickian models where the diffusion coefficient in the quantum well (D_{QW}) is different from the diffusion coefficient in the barrier (D_B). The square well model is illustrated in (c).

One alternate model that has been occasionally used in the literature^{32,33} and that will be considered in this thesis, is the square well model. In this, one assumes that the QW remains square, essentially proposing that diffusion within the QW is extremely rapid in comparison diffusion in the barriers, such that any outward motion of QW constituents immediately widens the QW. The interdiffusion length for the square well model, Δ_L , is defined to be equal to the change in QW width.

In terms of diffusion rates, this model puts an odd requirement on the diffusion rates of the various constituents at different positions, but from a mathematical point of view the model is simple and does not requires any more parameters than the Fickian error function solutions. The compositional profiles are obviously quite different in shape than the error function diffusion; a schematic of the concentration profile under this model is shown in figure II-4(c). For the purposes of this work, the square well model and the Fickian (error function) model provide extreme limits to what may actually be happening in the sample.

Compositional Changes in III-V Semiconductors

It is generally accepted that with regards to diffusion, each sublattice of III-V semiconductor structure operates predominantly independently³⁴. Thus in an InGaAs/InP interface, the As and P will exchange places while remaining on the group-V sublattice, and similarly for the In and Ga atoms. This means that if we know (or assume) the diffusion rate for As atoms, we automatically know it for the P atoms, and similarly for the In/Ga atoms. The presence of an atom on the wrong sublattice, an antisite, is possible, but expected to be quite unstable (at least at the anneal temperatures used for QWI). The diffusion rate for the In/Ga sublattice and the As/P sublattice have the potential to be quite different. It is useful to define the ratio of the interdiffusion of each sublattice by:

$$k = \frac{\Delta_{i(V)}}{\Delta_{i(III)}} \text{ if error function} \quad [11]$$

OR

$$k = \frac{\Delta_{L(V)}}{\Delta_{L(III)}} \text{ if square well}$$

where Δ_{III} and Δ_V are the interdiffusion lengths of each sublattice. This k ratio is an important parameter that will be studied and discussed throughout the thesis.

The data for diffusion in III-V semiconductors is surprisingly scarce - the best researched areas are of course ones with technological interest. To that end, the largest number of studies have been on diffusion of impurities (dopants) into GaAs, with a fair number of studies also on the interdiffusion of AlGaAs/GaAs, InGaAs/GaAs and In(Ga)As/Al(Ga)As QW structures. Because the majority of the dopants sit substitutionally on the group-III sublattice, and the above mentioned interdiffusion studies also probe only this sublattice, it is much more thoroughly studied than the group-V sublattice. It is generally believed that the V_{Ga} controls diffusion on the group-III sublattice of GaAs, although the role of the Ga_i is also argued for p-type materials³⁵. A few recent studies seem to indicate that diffusion on the group-V sublattice of GaAs is governed by group-V interstitials³⁶. These studies included GaAsP/GaAs and GaAsSb/GaAs QW structures and impurity diffusion of S. In the case of InP, no definitive studies illuminating diffusion mechanisms have been performed.

Interdiffusion experiments on the InGaAs(P)/InP system are in general more difficult to analyze than the GaAs-based systems mentioned above for two important reasons: (a) there is the possibility of interdiffusion on both sublattices; and (b) lattice strain is likely to occur. To be more precise, for AlGaAs/GaAs and InGaAs/GaAs structures, there is diffusion on both sublattices, but since As is the only group-V constituent and is constant across the structure, only one interdiffusion coefficient (for Al/Ga) is required to describe the solution. Additionally, all

compositions of AlGaAs are mostly lattice matched to GaAs, thus lattice strain is never an issue in this material system. Most of the technologically interesting InP-based structures have differences in both the group-III and the group-V constituents at the QW/barrier interface, thus interdiffusion on both sublattices is likely to occur. Since there is only a small range of InGaAsP compositions which is lattice matched to InP, even if a structure starts off lattice matched (e.g. $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ QW on InP), the quaternary alloys that develop during the interdiffusion may be strained. The net strain in the structure will not be altered, but a local variation in strain will develop³³. This depends on the k ratio, since k determines how the net compositions change, herein described for an as-grown lattice matched structure. If the interdiffusion is the same on both sublattices ($k=1$), then the structure remains lattice matched. For $k>1$, compressive spikes will develop at the QW/barrier interfaces, with tensile strain developing in the well center. The opposite strain profile will occur if $k<1$. Even a QW intermixed using square well approximation will have strain development if $k\neq 1$. This is because the square profile of the group-III sublattice will have a different width than the square profile of the group-V sublattice, resulting in interface layers of a mixed composition. Examples of these strain profiles will be illustrated in next section of this chapter.

At present there is no concrete experimental evidence of the role that lattice strain may have on enhancing or reducing interdiffusion, although most papers tend to indicate that small strains should have minimal effect^{28,37,38}. Since strain development has been found to occur during intermixing (as will be further examined in later chapters of this thesis), it seems unlikely that it would be major driving force for causing intermixing.

D – Modeling Interdiffusion

A program written by Dr. Geof Aers of the NRC has become a standard tool for our group when studying QWI. It allows us to determine the compositional profiles of the interdiffused QW based on the different interdiffusion models described in the previous section, and to then calculate the transition energies for the as-grown and

interdiffused QW. This program is a very important tool in QWI studies, since it provides the link between physical changes to the QW and the resultant optical changes. The physical basis for the computations are reviewed in this section.

The program requires the input of only a few parameters. The user must simply enter the following parameters for the structure and the diffusion model (a perfectly square starting QW is usually assumed):

- the composition of QW and barrier in terms of values of x and y for quaternary alloys of $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$
- the quantum well width (L_z)
- the diffusion model required (error function or square well)
- the interdiffusion length step sizes for the group-III and group-V sublattices $\{\Delta_{i(\text{III})}, \Delta_{i(\text{V})}\}$ for error function, or $\{\Delta_{L(\text{III})}, \Delta_{L(\text{V})}\}$ for square well
- the number of interdiffusion steps required

The combined selection of the group-III and V diffusion lengths determine the k ratio. The user can also choose to have the optical transition energy results calculated for temperatures at 4K or at 300K. Outputs from the program include the compositional and strain profiles, optical transition energies and shifts, as well as other characteristics such as wave function distribution, as will be described in more detail and illustrated below.

Compositional Profiles

The compositional profiles for the group-III sublattice and group-V sublattice are calculated independently. For Fickian diffusion or the error function model, equation [12] (a re-written version of equation [8] to be specific to InGaAsP QW/Barrier systems) is used. The group-III solution is expressed in terms of concentration of Ga as a function of z position, and is calculated for each required $\Delta_{i(\text{III})}$ step.

Similarly, the group-V solution is expressed in terms of concentration of As as a function of z position, and is calculated for each required $\Delta_{i(V)}$ step:

$$C_{(III/V)}(z) = C_{B(III/V)} + \frac{C_{QW(III/V)} - C_{B(III/V)}}{2} \left[\operatorname{erf} \left(\frac{\frac{L_z}{2} + z}{2\Delta_{i(III/V)}} \right) + \operatorname{erf} \left(\frac{\frac{L_z}{2} - z}{2\Delta_{i(III/V)}} \right) \right] \quad [12]$$

where $C_{III/V}$ indicates the Ga or As concentration at a given position z, while $C_{QW(III/V)}$ and $C_{B(III/V)}$ indicate the starting concentrations of Ga and As in the well and barrier, respectively, and $\Delta_{i(III/V)}$ indicates the group-III or group V interdiffusion length.

For the square well model, the approach is rather different but also straightforward. Again, the equation is calculated independently for the group-III and group-V sublattices. For a given change in the group-III and group-V well widths, given by $\{\Delta_{L(III)}, \Delta_{L(V)}\}$ the concentration within the QW is simply determined by maintaining a constant amount of diffusing material (i.e. the product of concentration times well width is kept constant), as given by:

$$C_{(III/V)} = C_{B(III/V)} + \frac{(C_{QW(III/V)} - C_{B(III/V)}) \cdot L_z}{L_z + \Delta_{L(III/V)}} \quad [13]$$

where $C_{III/V}$ now indicates the final Ga or As concentration in the well, $\Delta_{L(III/V)}$ indicates the change in width of the group-III or group-V square profile, and $C_{QW(III/V)}$ and $C_{B(III/V)}$ are as before.

The program generally assumes a single QW surrounded by infinitely wide barriers, and for all structures studied in this thesis, this is a reasonable assumption. If the barriers are narrow and/or significant amounts of diffusion occur, such that “communication” between neighbouring QWs in a QW stack is expected, the equivalent calculations using a superlattice structure are also available in the program. Examples of the output of compositional profiles are shown in figure II-5, with error function solutions down the left hand side and square well solutions down the right hand side. The starting structure is a lattice matched 5.0 nm InGaAs QW surrounded by InP barriers. All profiles are for a blueshift of 75 meV and assume

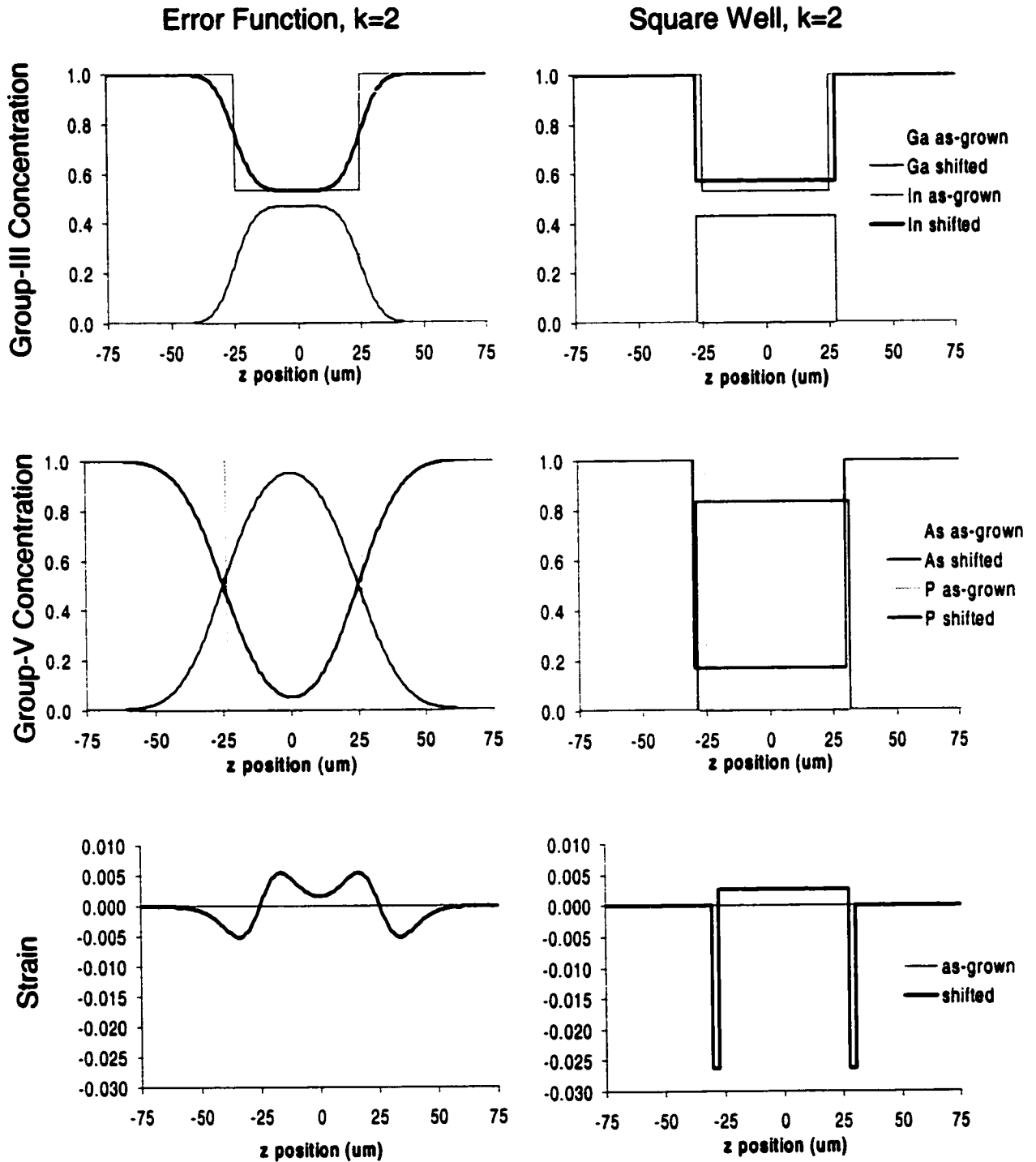


Figure II-5: Profiles of the group-III concentrations, the group-V concentrations, and the strain for an InGaAs/InP structure. As-grown profiles are shown in faint lines, while calculated profiles a blueshift of 75 meV are shown in dark lines for the error function (left column) and square well (right column) models. A value of $k=2$ was used throughout.

that $k=2$. This gives interdiffusion lengths of $[\Delta_{i(III)}, \Delta_{i(V)}]=[0.45, 0.90]$ nm for the error function modeling, and well width changes of $[\Delta_{L(III)}, \Delta_{L(V)}]=[0.5, 1.0]$ nm for the square well modeling. Profiles illustrating the local development of strain under each model are also included.

Quantum States for a Lattice-Matched Square QW

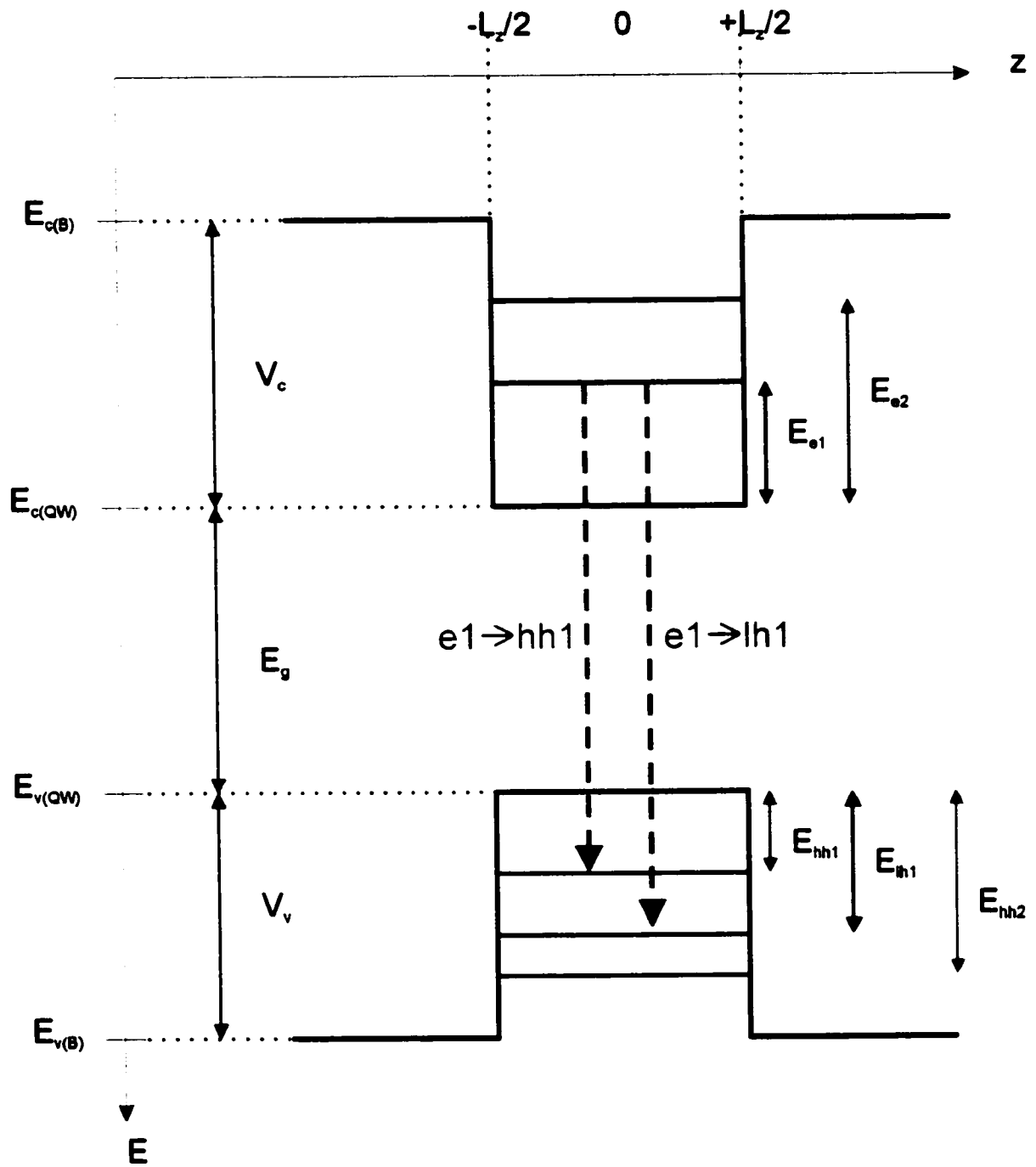
Once the composition as a function of z position has been calculated, one can make use of band structure parameters of the various compositions in order to determine the transition energies of the interdiffused QW. In this subsection we will start with a review of the problem of a simple unstrained square QW, before adding the complexities of strain and arbitrarily shaped QWs of the interdiffused QW. Figure II-6 gives a schematic representation of the problem for a square well. An important simplification that is used throughout these calculations is that only the Γ point of the Brillouin zone is considered (wavevector $k=0$), where there is no mixing between the valence bands. This assumption will be further discussed towards the end of the section.

For the calculations, ten band structure parameters of the materials must be known:

- bandgap of the unstrained bulk material for both the QW and barrier, $E_{g(QW)}$ and $E_{g(B)}$
- effective mass for each carrier in the QW and barrier, $m_{j(QW)}^*$ and $m_{j(B)}^*$, where j represent e (electron), hh (heavy hole) or lh (light hole)
- the absolute valence band energies of the QW and barrier materials, $E_{V(QW)}$ and $E_{V(B)}$ (in order to know the band offset between the two materials)

In the program, these ten parameters are determined for a quaternary In_1-

$xGa_xAs_yP_{1-y}$ of any $0 \leq x, y \leq 1$ by interpolation between empirical values for the four binaries $InAs$, InP , $GaAs$, and GaP . Details of the values and the interpolation scheme are described in the appendix to this chapter. The confinement potential in

Figure II-6: Potential energy diagram for a square quantum well of width L_z .

the z direction for the conduction, V_C , and valence bands, V_V , are determined from the differences in band energies of the well and barrier materials, as follows:

$$V_C = \begin{cases} E_{\alpha B} - E_{\alpha QW} = (E_{v(B)} + E_{g(B)}) - (E_{v(QW)} + E_{g(QW)}) & \text{for } |z| \geq L_z / 2 \\ 0 & \text{for } |z| < L_z / 2 \end{cases} \quad [14]$$

$$V_V = \begin{cases} E_{v(QW)} - E_{v(B)} & \text{for } |z| \geq L_z / 2 \\ 0 & \text{for } |z| < L_z / 2 \end{cases}$$

We now have the basic setup for particles confined to square potential wells in the z direction³⁹. In general, the wavefunction of the particle, $\Phi_{j,n}$, must satisfy the Schrödinger's equation:

$$\left(-\frac{\hbar^2}{2} \frac{\partial}{\partial z} \frac{1}{m_j^*(z)} \frac{\partial}{\partial z} + V_j(z) \right) \Phi_{j,n} = E_{j,n} \Phi_{j,n} \quad [15]$$

For the simple square well $V_j(z)$ has two constant values for each carrier (one for the QW and one for the barrier material). Within the QW, the solution for equation [15] is a sum of forward and backward traveling plane waves, while in the barriers, in the case of $E_{j,n} < V_j$, the general solution is a sum of exponentials (with appropriate coefficients set to zero in order to have physically correct solutions on each side of the QW):

$$\Phi_{j,n(B)} = \alpha_1 \cdot e^{+k_B z} + \alpha_2 \cdot e^{-k_B z} \quad [16]$$

$$\Phi_{j,n(QW)} = \beta_1 \cdot e^{+ik_{QW} z} + \beta_2 \cdot e^{-ik_{QW} z}$$

$$\text{where } k_B = \sqrt{\frac{2m_{j(B)}^*}{\hbar^2} (V_j - E_{j,n})} \quad \text{and} \quad k_{QW} = \sqrt{\frac{2m_{j(QW)}^*}{\hbar^2} E_{j,n}}$$

The quantization, or eigen energies $E_{j,n}$ for this particle in a box problem will be obtained by applying appropriate boundary conditions to equation [16], that is, the

wavefunctions and the flux^b (wavefunction derivative divided by effective mass) are continuous at the well/barrier interface. This yields three transcendental equations (one for each carrier) of the form $f(E_{j,n}, m_j^*, L_z, V_j)=0$ which can be solved graphically or numerically (analytic solution is only possible in the case of $V_j=\infty$). Note that $V_j=V_c$ for the electron problem, and $V_j=V_v$ for both heavy and light hole problems (in the lattice matched case), but due to the two different masses of the holes, the final quantum energies of heavy and light holes states will be different (for a given n , the heavy hole quantization energies are smaller).

The effect of quantum confinement is to increase the bandgap energy. In the X and Y directions the particles are free (ignoring excitonic binding, to be discussed below), and thus the total energy of each particle will be:

$$E = E_{xy} + E_z \quad [17]$$

$$= \frac{\hbar^2 (k_x^2 + k_y^2)}{2m_j^*} + E_{j,n}$$

where k_x and k_y are the wavevectors in the x and y plane of the QW.

Effects of Strain on the Bandgap Energies

Lattice strain may be grown into a heterostructure, or may develop during interdiffusion (as discussed in section C). It occurs whenever the bulk lattice constant of the InGaAsP alloy layer is different from that of InP's lattice constant. If the quaternary layer is thin, it will conform to the InP substrate in the x and y directions, but undergo a tetragonal deformation in the z direction. These changes to the lattice structure result in changes to the energy of the electronic bonds and thus to the band energies of the thin layer in comparison to the bulk values for the same alloy. The changes are significant, and must be taken into account. An additional six material parameters are required for the calculation of the strained band energies, E_j' , from the unstrained band energy, E_j :

^b known as the Bastard boundary condition.

- the bulk lattice constant of the quaternary, a
- the elastic coefficients, C_{11} and C_{12} of the quaternary
- the hydrostatic and shear deformation potentials, A_C , A_V , and B of the quaternary

These six parameters are also calculated for a quaternary $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ of any $0 \leq x, y \leq 1$ using an interpolation scheme (included in the appendix of this chapter).

The stress in the layer is biaxial in the xy plane, which can also be considered to be a hydrostatic stress minus a uniaxial stress in the z direction. A tensile hydrostatic stress raises the conduction band and lowers both valence bands by an amounts P_C and P_V respectively. The uniaxial stress shifts the two valence (hole) bands in opposite directions and by different amounts, thereby lifting the degeneracy of the heavy hole and light hole in a bulk layer (It does not affect the conduction band at the Γ point). The result will be different confinement potentials V_i for each of the three carriers in the z direction, again found using equation [14] but using the following equations for the strained bands E_i' instead of the unstrained bands E_i (these equations are only valid for the Γ point and for growth on [001] substrates) :

$$\begin{aligned} E_C' &= E_C - P_C \\ E_{hh}' &= E_V + P_V - Q \\ E_{lh}' &= E_V + P_V + \frac{1}{2} \left(Q - \Delta_o + \sqrt{\Delta_o^2 + 2\Delta_o Q + 9Q^2} \right) \end{aligned} \quad [18]$$

where Δ_o is the spin orbit splitting energy. The dependence of the E_{lh}' on Δ_o occurs because of the coupling between these two bands in biaxially strained material. The hydrostatic deformation potentials, P_V and P_C , and the shear deformation potential, Q , are determined from:

$$\begin{aligned} P_C &= A_c (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \\ P_V &= -A_v (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \\ Q &= -\frac{B}{2} (\epsilon_{xx} + \epsilon_{yy} - 2\epsilon_{zz}) \end{aligned} \quad [19]$$

where the strains in each of the three directions are defined by:

$$\varepsilon_{xx} = \varepsilon_{yy} = \frac{a_0 - a}{a}, \quad \varepsilon_{zz} = -2 \frac{C_{12}}{C_{11}} \varepsilon_{xx} \quad [20]$$

where a_0 is the substrate lattice constant and a is the lattice constant of the quaternary layer if it were unstrained. These calculations treat the strain as a small perturbation, thus they are only valid for small strains (up to ~2%). A good reference for the effect of strain on semiconductor bands is by Chao and Chuang⁴⁰.

Quantum States for an Arbitrarily Shaped QW

In an interdiffused QW, the E_j^* vary continuously as a function of z-direction in the interdiffused QW for the error function model, and are multi-valued in the case of the square well model. In the program, the final quantization energies are determined using a transfer matrix approach (in fact, the as-grown square well is also solved using the same algorithm, although it could be solved using the particle in a box solution). The potential profile is divided up into p thin regions where the V_j and m_j^* is assumed to be constant within each region, as shown in figure II-7. In the p^{th} region the wavefunction solution to the Schrödinger equation can be written as a sum of two opposite traveling plane waves:

$$\Phi_{j,n}^p = \beta_+^p \cdot e^{+ik^p z} + \beta_-^p \cdot e^{-ik^p z} \quad [21]$$

$$\text{where } k^p = \sqrt{\frac{2m_j^{*p}}{\hbar^2} (E_{j,n} - V_j^p)}$$

The use of complex arithmetic allows the general treatment of the case where $E_{j,n} > V_j^p$ (plane wave) and $E_{j,n} < V_j^p$ (decaying function). By applying the two boundary conditions (constant Φ and flux) at the two interfaces, the coefficients β_+^p, β_-^p in each region can be related to those in an adjacent region by a 2x2 matrix. These matrices are multiplied together to relate the wavefunction at each end of the system ($p=0$ and $p=P$) by:

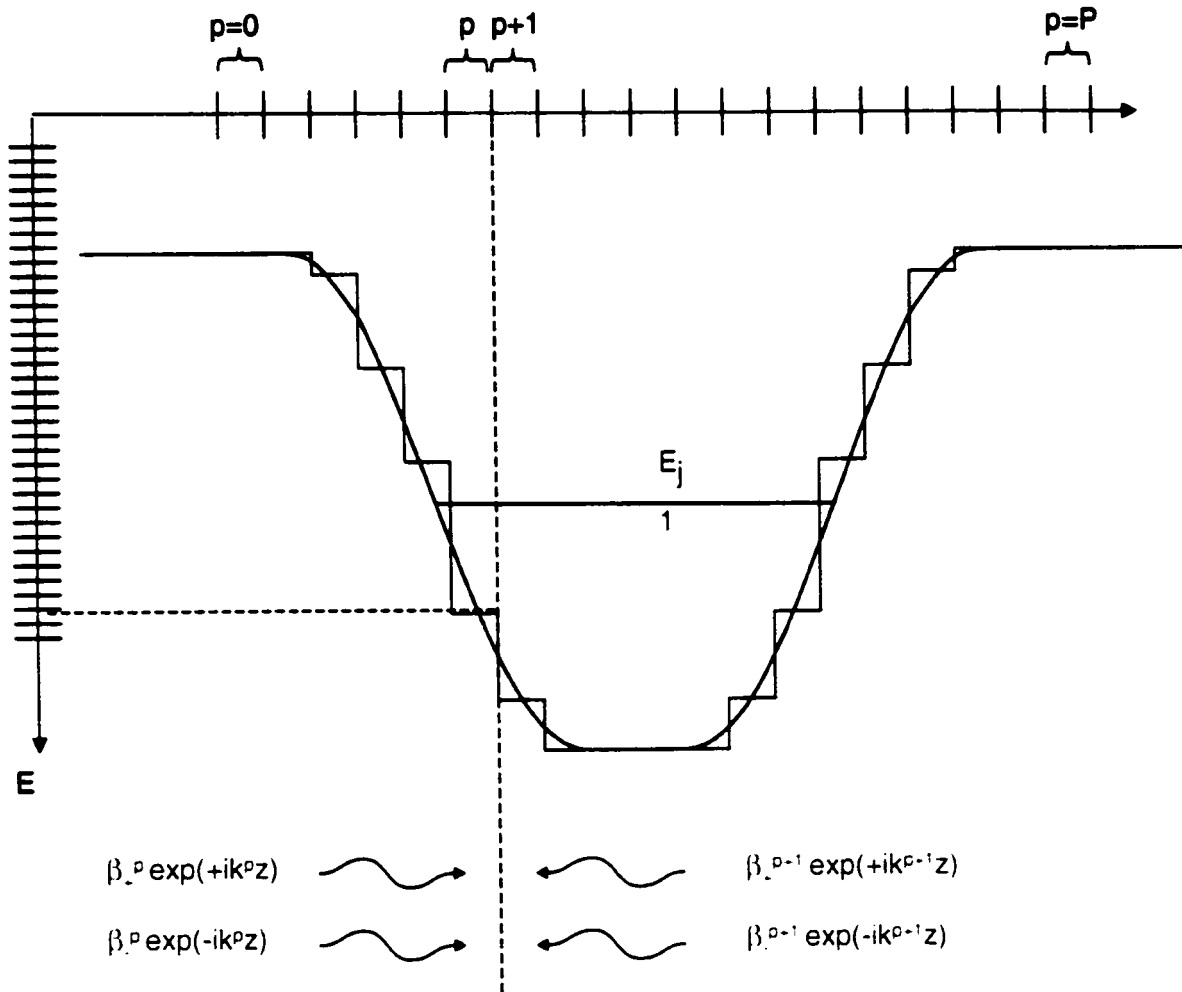


Figure II-7: Schematic illustrating the definition of potentials and wavefunctions under the transfer matrix approach for an arbitrarily shaped QW.

$$\begin{bmatrix} \beta_+^0 & \beta_-^0 \end{bmatrix} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} \beta_+^P \\ \beta_-^P \end{bmatrix} \quad [22]$$

where the matrix elements depend on the k^p 's (and thus on $E_{j,n}$). One of the two equations that comes from multiplying out the matrices of equation [22] is

$$\beta_+^0 = M_{11}\beta_+^P + M_{12}\beta_-^P \quad [23]$$

Since the wavefunctions at each end (at $p=0$ and $p=P$) must decay for a physical solution, we can set $\beta_-^P = \beta_+^0 = 0$. Then, since β_+^0 must have a finite value, equation [23] will only be valid if $M_{11}=0$. The shooting method is applied to find valid choices of $E_{j,n}$ that will satisfy $M_{11}=0$. This is accomplished by using a linear grid of trial values for $E_{j,n}$, (chosen as many equally spaced values between the range of 0 and V_j). Each trial value of $E_{j,n}$ is used to calculate M_{11} . Wherever a change in the sign of M_{11} occurs following a stepwise increase in $E_{j,n}$, a valid choice of $E_{j,n}$ exists. Further trial values of $E_{j,n}$'s falling within that step are evaluated using a bisection method, repeated until a satisfactory accuracy is accomplished.

Examples of the confinement potential, along with wave function shapes and quantized energies are shown in figure II-8, for both error function and square well modeling of the same structure whose compositional profiles were given in figure II-5.

Optical Transition Energies

The optical emission energies can now be determined by adding the appropriate quantization energies, $E_{j,n}$, to the calculated bandgap. For example, the energies of the first electron to heavy hole transition, and first electron to light hole transition are:

$$e1 \rightarrow hh1 = E'_{g(QW)} + E_{e1} + E_{hh1} - E_x \quad [24]$$

$$e1 \rightarrow lh1 = E'_{g(QW)} + E_{e1} + E_{lh1} - E_x$$

where E_x is the binding energy of the exciton in the QW, typically a few meV and $E'_{g(QW)}$ is the bandgap at the center of the interdiffused QW. E_x has been fixed to $E_x=7$ meV for 4K calculations and $E_x=0$ for 300K calculations in this thesis.

Variations of E_x due to its dependence on well width and composition are expected to be small (the order of a few meV) for the magnitude of changes to width or compositions occurring during intermixing.

Use of the Results for QWI Studies

The entire calculation of the eigen energies is repeated several times for the compositional profiles corresponding to a series of interdiffusion lengths. One can then derive information such blueshift, ΔE_{hh} , of the lowest transition (e.g. $e1 \rightarrow hh1$) as a function of interdiffusion length for a given interdiffusion model and k ratio. Plots of ΔE versus $\Delta i_{(V)}$ are shown in figure II-9 for the same InGaAs/InP structure as modeled above. From an experimentally measured ΔE_{hh} , such plots can be used to quantify the amount of interdiffusion. However, in doing so, one must assume a given k ratio and diffused QW shape (error function, square well, or other). Alternately, if one can experimentally measure a second parameter, either Δi or ΔE_{lh} , one can determine k . The former is rarely accessible experimentally, but the latter - ΔE_{lh} , in combination with ΔE_{hh} , will be used in Chapter IV to determine k ratios.

Limitations of the Modeling

The solutions of the compositional profiles for both error function and square well are analytic, and thus are as accurate as the assumptions which underlie the application of the equations. As was discussed previously, the assumption of Fickian behaviour is unproven and is somewhat doubtful, and this is why two different interdiffusion models are considered here.

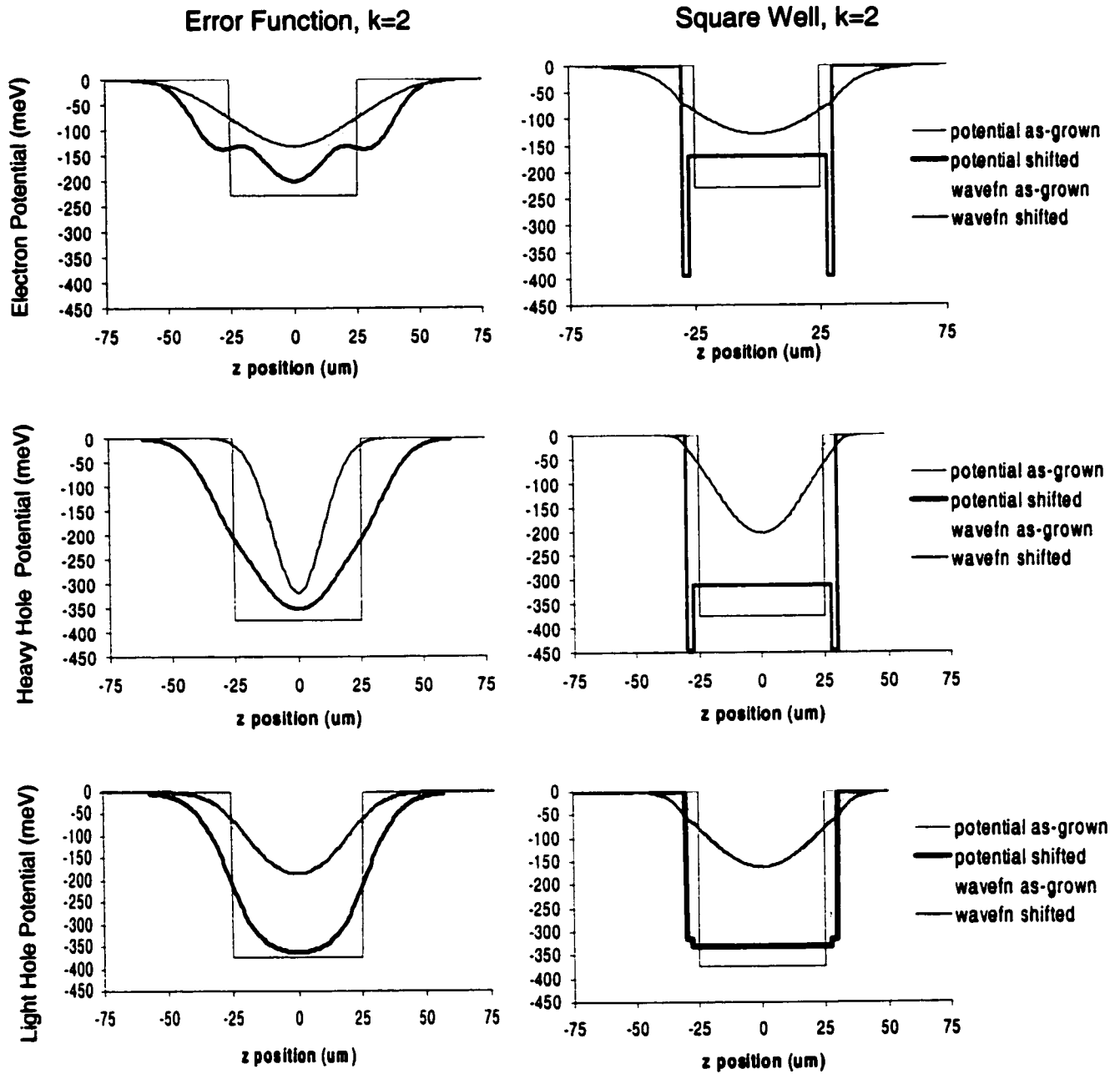


Figure II-8: Profiles of the electron, heavy hole and light hole potentials and wavefunction distributions for an InGaAs/InP structure. The as-grown profiles are shown in faint lines, while calculated profiles for a blueshift of 75 meV structure are shown in dark lines using error function (left column) and square well (right column) models. A value of $k=2$ was used throughout. Wavefunction distributions are in arbitrary units, with equivalent units used in all graphs.

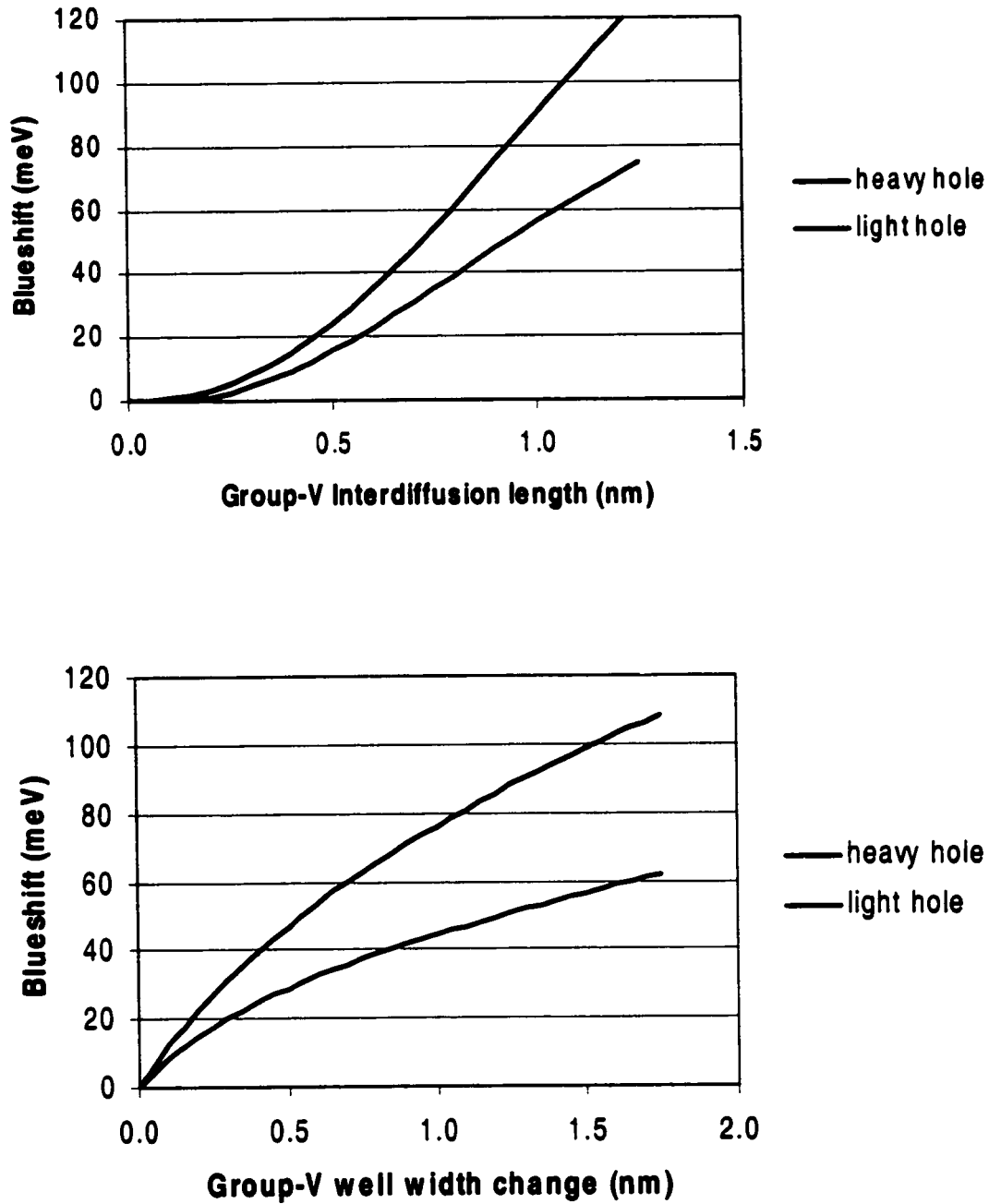


Figure II-9: Blueshift as a function of amount of intermixing (of the group-V sublattice) for an InGaAs/InP structure with 5.0 nm QW. Calculations are done for (a) error function model and (b) square well model. A value of $k=2$ was used for both calculations.

Calculations of the material parameters E_g , Δ_0 , m_j^* , α , C_{11} , C_{12} , A_v , A_c , B , all rely on empirical polynomial fits, as described in the appendix. The expected error in E_g is only a few meV, or $\pm 0.2\%$, and in the lattice constant a it is $\pm 0.0005 \text{ \AA}$ or 0.01% , while the error on the other parameters (which are more difficult to measure) could be as high as $\pm 10\%$. The absolute valence band energy (relative to an average crystal potential) and thus the band offsets between different materials is a more difficult parameter to measure³⁹ and thus one could expect an error in the range of $\pm 20\%$ ⁴¹. However, the calculated quantization energies are not very sensitive to differences in the offsets, especially in the case when the offset in the bands is ~ 0.4 to 0.6 times ΔE_g , as is the case for the materials under study here⁴¹. As a whole, we expect that these calculations provide transition energies which are accurate to within about 5 meV, for a given interdiffusion assumption. Experimentally, we observe variations across samples of the order of 5 meV. Thus, the accuracy of the calculations are sufficient for our studies, as long as we consider blueshifts of the order of 10 meV or greater (blueshifts as large as 189 meV will be shown herein).

A major simplification of these calculations is that we assume the optical transition is direct, and only the zone-center ($\kappa_{xy}=0$) transitions are calculated. For a sufficient tensile strain, an off-zone-center maximum in the “light hole” band can become the highest energy point. Light hole is put in quotations here because it would actually be a mixed hole band when not at the zone-center. The actual transition energy in such tensile strained materials could have an indirect character⁴² and a lower transition energy than that calculated by the program. However, the discrepancy in terms of energies will likely be small, since this off-zone-center maximum is calculated to be only ~ 10 meV different than the zone-center maximum for the materials studied here. But optical properties which depend on carrier overlap, such as carrier lifetimes, could be dramatically altered. This additional complication must be realized when significant tensile strains (of the order 1-2%) in the QW center occur, in particular when examining large blueshifts and $k \gg 1$. This scenario

may occur in a few of the samples in this thesis (InGaAs/InP structures where ΔE is the order of 150 meV or larger).

Comments on As-Grown QWs

Epitaxial growth is a fairly well controlled process, giving accuracy in the QW width of ± 0.5 nm, and compositions within $\pm 1\%$. Predicted transition energies from the nominal structure can be compared with PL measurements. Discrepancies between the calculation and experiment are used to refine the values for the QW width and composition. Additional characterization is also beneficial to further confirm the exact structure. High resolution transmission electron microscopy (TEM) can be used to assess QW thickness with an accuracy on the order of ± 0.5 nm, while high resolution X-ray diffraction (XRD) can also be helpful to assess structure periodicity and mean strains (both characterization techniques will be further discussed in the next chapter). Results are also fed back to the growers in order to maintain predictable growths. As-grown QWs are not perfectly square, as there are usually one to two monolayers (0.29-0.58 nm) of mixed alloy material at the interfaces between the QW and barrier. Their presence will account for minor discrepancies between the results of TEM, PL and XRD and calculations based on a perfect square well. In fact, XRD is an excellent technique for determining the exact nature of the interfaces⁴³. However, for the purposes of analysis in this thesis, the presence of interface layers can be mostly ignored when considering interdiffusion. This is because they are 10 to 20 times narrower than the QW, and thus even when short interdiffusion lengths are considered, they have negligible effects, as was confirmed by intermixing modeling.

E - Summary

The topic of defect formation and defect motion (topic 1) is a complex subject, with many issues yet to be resolved. On a microscopic scale, the interdiffusion of QWs and barriers is mediated by defects of some sort. Background theory and current knowledge of defects identities and diffusion mechanisms has been discussed in this chapter, and will be further discussed in relation to experiments in chapters IV

and V of this thesis. The second topic of QWI - describing the interdiffusion of the QW and barrier – provides some challenges. The basic concepts that must be understood have been covered here, including the use of Fickian and non-Fickian solutions, and the potential for different interdiffusion rates on each sub-lattice. Under the third topic, the optical transitions can be measured experimentally and calculated theoretically. The physical basis behind such calculations has been given in section D. This thesis aims to further the understanding of topics (1) and (2) using a significant number of experimental results, together with analysis using the existing computational tool created to address topic (3).

Appendix

Bilinear Interpolation

For a material parameter, M , this method assumes a linear variation of M for a ternary alloy between its two binary alloys values, and then a bilinear variation of M for a quaternary $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ alloy between the four constituent binaries InP, InAs, GaP and GaAs. This approach, which is essentially an expansion of Vegard's Law, is commonly used in the literature, and is reasonably accurate for a large number of different material properties. The equation is as follows:

$$M_{\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}} = (1-x)yM_{\text{InAs}} + (1-x)(1-y)M_{\text{InP}} + x(1-y)M_{\text{GaP}} + xyM_{\text{GaAs}} \quad [25]$$

The following material parameters for a quaternary alloys are calculated using the bilinear interpolation method:

- lattice constant a
- effective masses m_j^* of all three carriers
- conduction band hydrostatic deformation potential a_c
- valence band hydrostatic deformation potential a_v
- uniaxial deformation potential B
- elastic constants C_{11} and C_{12}

- spin orbit splitting Δ_0

Interpolation for the Unstrained Bandgap (E_g)

A linear interpolation scheme is not accurate enough for the bandgap of ternary and quaternary alloys. However, with the inclusion of one additional term, called the bowing parameters, B , the method again produces results which agree reasonably accurately with experimental results. For each ternary alloy, there is one bowing parameter. A quaternary then depends on the interpolation of the ternary values, with an additional quaternary bowing term. The four ternary equations and one quaternary equation are as follows:

$$\begin{aligned}
 E_{g, In_{1-x}Ga_xAs} &= xE_{g, GaAs} + (1-x)E_{g, InAs} + x(x-1)B_{In_{1-x}Ga_xAs} \\
 E_{g, In_{1-x}Ga_xP} &= xE_{g, GaP} + (1-x)E_{g, InP} + x(x-1)B_{In_{1-x}Ga_xP} \\
 E_{g, GaAs, P_{1-y}} &= yE_{g, GaAs} + (1-y)E_{g, GaP} + y(y-1)B_{GaAs, P_{1-y}} \\
 E_{g, InAs, P_{1-y}} &= yE_{g, InAs} + (1-y)E_{g, InP} + y(y-1)B_{InAs, P_{1-y}} \\
 E_{g, In_{1-x}Ga_xAs, P_{1-y}} &= \\
 &= \frac{x(1-x) \left[yE_{g, In_{1-x}Ga_xAs} + (1-y)E_{g, In_{1-x}Ga_xP} \right] + y(1-y) \left[xE_{g, GaAs, P_{1-y}} + (1-x)E_{g, InAs, P_{1-y}} \right]}{x(1-x) + y(1-y)} \\
 &\quad - x(1-x)y(1-y)B_{In_{1-x}Ga_xAs, P_{1-y}}
 \end{aligned} \tag{26}$$

The bowing parameters have been empirically determined; values are included in table II-1.

Interpolation for Unstrained Valence Band Energy (E_v)

We use the method of Krijn⁴⁴ to interpolate the absolute valence band energy of quaternaries from the binary values. It is similar to the above interpolation scheme for the E_g , but with bowing parameters which are approximately calculated instead of empirically determined. The ternary bowing terms are dependent on the deformation potential and bulk lattice constants of the two binaries, as shown below for the ternary InGaAs:

$$B_{\text{In}_{1-x}\text{Ga}_x\text{As}} = 3 \cdot (A_{\text{V GaAs}} - A_{\text{V InAs}}) \frac{(\alpha_{\text{GaAs}} - \alpha_{\text{InAs}})}{\alpha_0} \quad [27]$$

where α_0 is the lattice constant of the substrate. The bowing parameters for the other ternaries can be determined similarly using the appropriate binary values. Any additional bowing for the quaternary material has not been determined as of yet, so the parameter is set to zero, i.e. $B_{\text{InGaAsP}}=0$. The values of E_v can thus be determined by using these ternary and quaternary bowing parameters in an equation of the form of equation [26]. This interpolation method seems to produce values for relative offsets between materials that agree reasonably well with those that have been measured experimentally (binaries and a few ternaries).

Parameter Values

Table II-1: Binary parameter values.

Parameter	GaAs	InAs	InP	GaP
α (nm)	0.56533	0.60583	0.58687	0.54510
C_{11} ($\times 10^{11}$ dynes/cm ²)	11.88	8.329	10.22	14.12
C_{12} ($\times 10^{11}$ dynes/cm ²)	5.380	4.526	5.760	6.253
m^* electron	0.067	0.023	0.079	0.17
m^* heavy hole	0.377	0.342	0.520	0.500
m^* light hole	0.068	0.025	0.120	0.140
Δ_0 (eV)	0.34	0.371	0.114	0.080
A_v (eV)	1.16	1.00	1.27	1.70
A_c (eV)	-8.00	-4.88	-4.91	-7.75
B (eV)	-1.7	-1.8	-1.5	-1.5
Unstrained E_g at 4K (eV)	1.5192	0.4105	1.4140	2.853
Unstrained E_g at 300K (eV)	1.424	0.360	1.350	2.740
E_v (eV)	-6.726	-6.556	-7.002	-7.033

Table II-2: Ternary and quaternary bowing terms for E_g .

Parameter	InGaAs	InAsP	InGaP	GaAsP
300K unstrained gap bowing (eV)	0.45	0.28	0.79	0.21
4K unstrained gap bowing (eV)	0.475	0.36	0.786	0.166
Quaternary gap bowing (eV)	1			

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Chapter III – Characterization Techniques

A - Introduction

Spectral analysis of QW luminescence (optical emission from the sample) is the most common means of studying QWI because it can be easily implemented, it is non-destructive, and because the luminescence is sensitive to small changes in the structure of the QW (i.e. small amounts of QWI produce easily measurable changes to the QW's optical properties). As well, simple photoluminescence (PL) set-ups are relatively inexpensive, making it an accessible tool for many researchers. And, the non-destructive nature of the techniques has allowed for multiple process-then-characterize steps in some studies. However, this thesis attempts to go beyond the simple uses of the PL set-up, in order to provide additional understanding of the material and the QWI. In particular during the thesis, several different PL set-ups are used, where sample temperatures range from 4K to 300K, as well as two types of transmission measurements over the same temperature range. An overview and discussion of the two main techniques used, photoluminescence and optical transmission, will be discussed in Sections B and C of this chapter. Use of these optical results for analysis of QWI effects rely on modeling of the diffusion (topic 2), and the optical properties (topic 3) as were discussed in Chapter II.

Characterization by X-ray diffraction (XRD) has also been applied to some samples in order to further assess the compositional and strain profiles of the intermixed QWs. The experimental set-up used to obtain XRD spectra will be discussed in section D. Analysis of these spectra relies on modeling of interdiffusion (topic 2), and then also on modeling of the XRD spectra, as will be described therein.

Finally, characterization by transmission electron microscopy and secondary ion mass spectrometry (performed by others), has also been used in a supportive manner in this thesis, and will be briefly described in section E and F.

The details regarding set-ups for any of the processing of the samples will be covered separately in Chapters IV and V.

B – Photoluminescence (PL)

Overview of the Physics of Photoluminescence

The “photo” portion of the term photoluminescence refers to the use of light to excite the sample, while the luminescence refers to light emitted from the sample. PL can be broken down into absorption, relaxation, and emission processes, as illustrated in figure III-1. In the absorption step, light is focused on the sample, and the absorbed photons create excited carriers (electrons and holes) in the sample. For a semiconductor, the traditional way of exciting the structure is by the use of a laser with photon energies larger than the bandgap energy. In the relaxation step, the photo-excited electrons and holes quickly release some of their energy by emitting phonons (lattice vibrations), until they reach the lowest excited state. In the case of a semiconductor, this is often the bottom of the conduction band and top of the valence band for electron and holes, respectively, although in material with a significant number of defects, the carriers may relax to defect states within the bandgap. When the electron and hole recombine, the emitted luminescence can be analyzed using a spectrometer, and thus important information as to the materials band structure and the defect states can be determined. But note that it is usually only transitions from the lowest excited state that will be observed. More detailed descriptions of the technique can be found in the literature^{1,2,3}.

During the relaxation stage, spatial diffusion of the carriers also occurs, and in heterostructures, the carriers will tend to end up in the material with the lowest bandgap, i.e. the QWs. Also during this stage, coulomb forces can attract the electron and hole to each other, creating an electron-hole pair, called a (Wannier) exciton⁴, which can move as a single particle through the lattice. The binding energy of the exciton reduces the energy emitted when the two carriers recombine. The binding energy is usually larger in QWs (~9 meV in GaAs) than in bulk material⁵ (~4 meV in GaAs) because the carriers are confined and forced closer together^{6,7,8}.

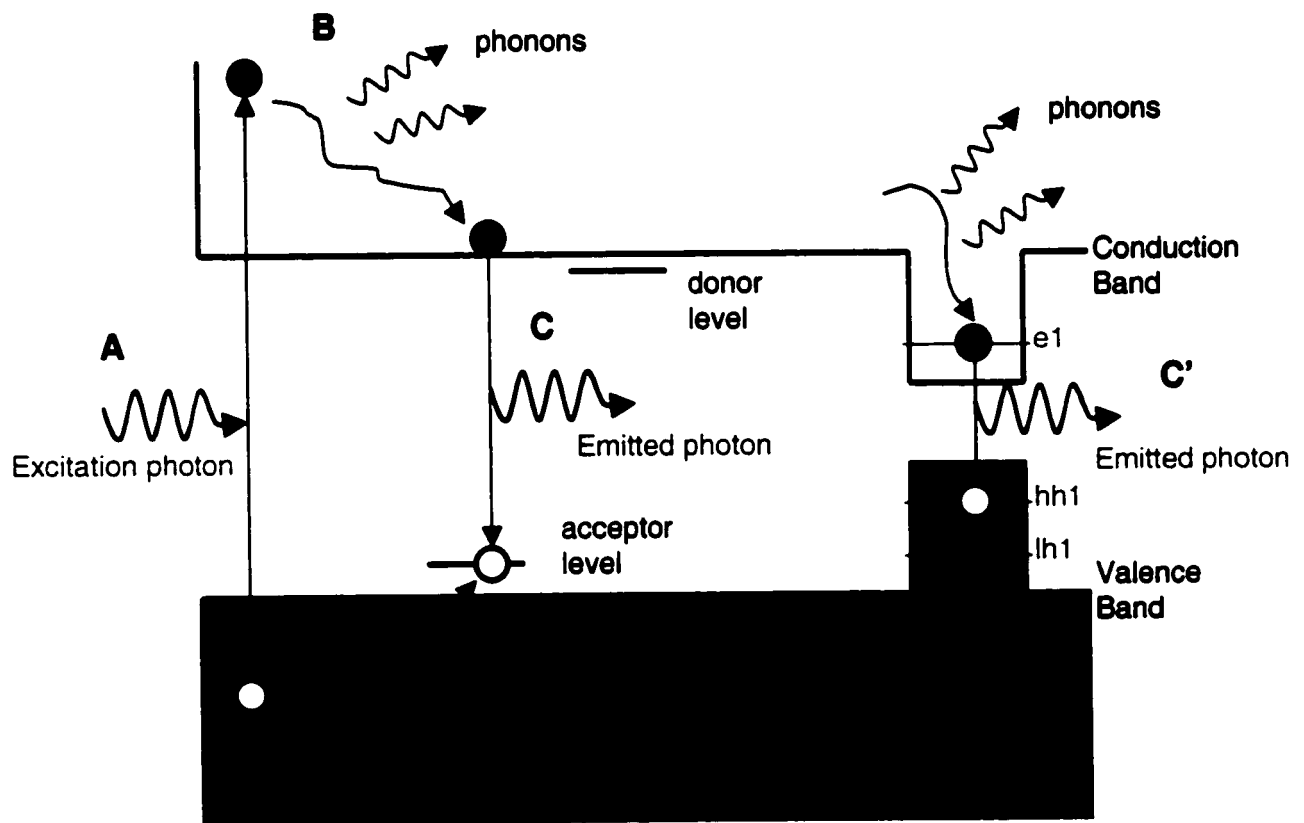


Figure III-1: Schematic of the physical processes for photoluminescence, including A - absorption of a photon, B - thermalization by which excited carriers release energy in the form of phonons, and C - electron-hole recombination with the release of a photon in a bulk structure and C' - emission in a QW structure.

The increased binding energy also means that they are stable at room temperature, and thus QW exciton luminescence is observable at room temperature. In this thesis, the uniformity of the room temperature QW luminescence, both before and after processing, will be assessed using a mapping setup.

Cooling the samples to near liquid helium temperatures (4K) reduces lattice vibrations and carrier thermal distributions, thereby improving the emission intensity and line width of a given signal and allowing analysis of weak and/or closely spaced transitions. At these low temperatures, where thermal energy is insufficient to overcome the various binding energies, several new transitions will also be observable in the bulk material⁹, relating to free excitons, as well as carriers and excitons bound to impurities¹⁰. Single carriers are attracted to ionized impurities of opposite charge, and recombination will result in a band-to-defect transition with energy of E_g minus the impurity's ionization energy. The donors have the lowest ionization energy (~7 meV in GaAs) and thus the hole-to-donor transition appears at higher photon energies than the electron-to-acceptor transitions (acceptor ionization energies are ~30 meV in GaAs)¹¹. Furthermore, an electron bound to an acceptor can recombine with a hole bound to a donor, resulting in donor-acceptor pair recombination. Excitons are also attracted to shallow donors or acceptors in the material¹², resulting in a slight reduction of the excitonic transition energy by the localization energies (~1 meV). The highest energy peak is from the free exciton (already ~4 meV below E_g due to the exciton binding energy), followed by peaks relating to excitons bound to donors, followed by excitons bound to acceptors. The excitonic transitions have very narrow line widths (~100 μ eV)¹³.

The relative intensities of the above transitions depend of course, on the impurity concentration levels, and thus PL can be used as a means of assessing relative impurity levels and, if carefully done, absolute impurity levels as low as 10^{13} cm^{-3} ^{14,15}. Only impurities with energy states quite close to the conduction or valence band (shallow impurities) are observable by PL – defects with larger ionization

energies (states near the middle of the bandgap) will instead induce recombination through non-radiative mechanisms. Most native defects fall into the latter category¹⁶, although radiative transitions due to native defects can sometimes be observed, in particular when at high concentrations following processing^{17,18}. It is also possible to see bound exciton transitions in QW structures, but because the exciton lifetime is shorter in a QW compared to the bulk, and because the probability that the defect is in the QW is not high (due to simple relative volume considerations), the probability of the transition is much lower¹⁹.

Excitation Lasers

During the PL experiments, different excitation lasers were chosen from the following list, depending on whether the bulk InP or the QW excitons were being probed (experimental details will be described in what follows):

- Ar⁺ gas laser, main emission at 514 nm, able to provide high powers (up to 500 mW used)
- HeNe gas laser, emission at 632.8 nm, power of 3 mW
- Ti-Sapphire tunable laser, pumped by the Ar⁺ laser, and tuned between 880 and 920 nm, providing powers in the range of 1 to 100 mW
- semiconductor diode laser, emission at 980 nm, power of 1 to 20 mW (acquired more recently to provide IR laser source which was easier to use than the Ti-sapphire)

The Ar and HeNe lasers provide light in the visible region of the spectrum, which is absorbed within the first few 100 nm of the surface by the InP buffer layers.

Excitation of this wavelength was used to study the emission of these bulk layers, although some of the photo-excited carriers may diffuse far enough to reach the deeper QWs, and thus emission from the QWs is often also detectable, although weaker. The Ar⁺ laser is the highest power source, and was used to study excitation power dependence of both QWs and bulk InP. InP is transparent to wavelengths longer than ~ 900 nm (photon energies less than 1.35 eV), since this

photon energy is less than the InP bandgap, but the InGaAs and InGaAsP compositions used for QWs and barriers have much small bandgap energies (1.1 μm to 1.65 μm), and will absorb the IR laser light, thus creating photo-excited carriers only within the QW/barrier layers only. Therefore, the laser diode and Ti-Sapphire lasers were used exclusively for studying the QW emission.

Laser power was measured just before the focussing lens but after any neutral density filters, which were used to adjust the power of the incoming beam (e.g. ND10 filter reduces the power by a factor of 10). All lasers operated continuous wave (i.e. no pulsed sources).

Low Temperature PL Set-up

The low temperature PL set-up is shown in figure III-2 (a). The sample was mounted on a copper block using two strips of teflon tape in a manner that does not strain the samples. The cryostat is a continuous flow type, in which some $\text{He}_{(l)}$ is allowed into the sample chamber, and theoretically maintains the sample temperature very near 4.2 K - a temperature sensor attached to the copper block typically gives a value of 4.4 to 5.0 K. The focusing lens generally provided a spot size of 50 to 100 μm on the sample.

A majority of the PL emitted from the sample was collected using a lens with large numerical aperture, and the collimated beam was sent to a spectrometer. Neutral density filters again were sometimes used in this optical path to reduce the signal intensity at the spectrometer port, while a long-wave pass filter was used to block any stray or reflected laser light from entering the port, while still allowing the luminescence of interest to pass.

For most of the studies, a Bomem MB160 Fourier Transform infrared (FTIR) spectrometer with InGaAs diode detector was used to analyze the PL. It offers the advantage of very fast collection – one spectrum can be collected in 1-10 seconds (depending on resolution), and multiple spectra can be automatically co-added to

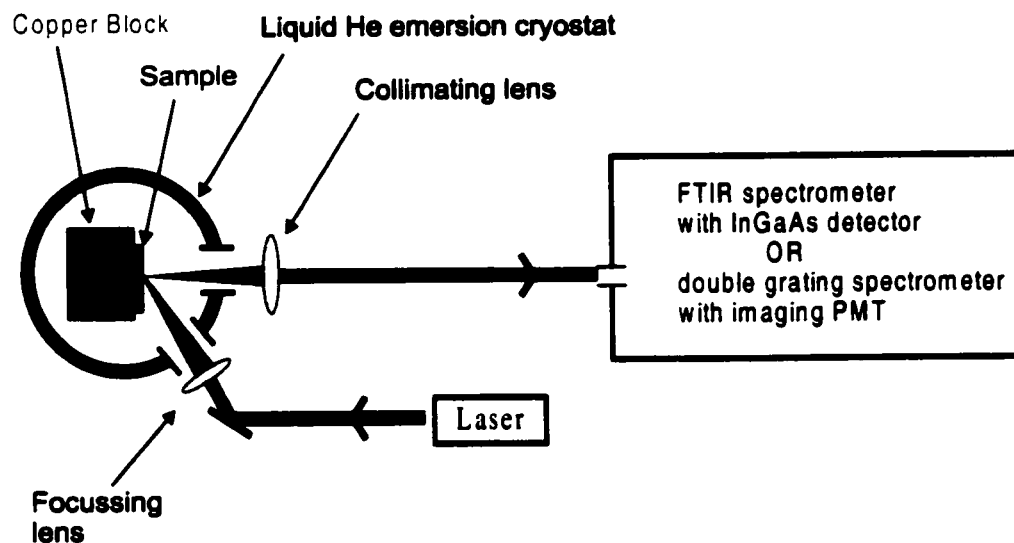
provide good signal-to-noise ratios. The system can be used to analyze light in the 0.65 to 1.70 μm range. The resolution of the FTIR (down to 0.25 meV) was adequate for analysis of QW emission, (which in most samples had a linewidth of the order of 15 meV). Low temperature (4K) PL using the FTIR was mostly used to assess the quality of growth of the QWs. A large linewidth at 4K is indicative of composition variations²⁰ within a QW or across multiple QWs, while a multi-peak spectra is indicative of monolayer fluctuations in the QW width²¹.

High-resolution experiments of bulk InP samples were performed to analyze the details of the excitonic transitions and defect states, and for these measurements, a 0.75 m double grating spectrometer with 1200 grooves/mm gratings was employed to obtain the required high spectral resolution. The detector at the output of the spectrometer was a Quantar Technology imaging photomultiplier tube with three micro-channel plates, which can resolve the position of a photon hitting its surface with an accuracy of 60 μm in both the x and y directions²². The optically active surface of the detector is 25 mm. The multi-alkyl photocathode provides response over 400-900 nm range, as well as very high optical sensitivity. It was cooled to -25°C and operated with a gain of $\sim 10^7$. Following dispersion by the spectrometer (with the final slits left open), the set-up allowed for simultaneous collection of a spectrum with a optical width of 12.2 nm. The spectral resolution is then given by $(12.2 \text{ nm} \times 60 \mu\text{m} / 25 \text{ mm}) = 0.03 \text{ nm}$, which translates into an energy resolution of about 50 μeV at a wavelength of 900 nm (1.4 eV).

PL Mapping Set-up

Using the above set-up, the PL of only one position on the sample is analyzed at a time. Even when several points are measured by manually moving the sample, it is difficult to assess the uniformity of the sample. To investigate this important characteristic of the samples, an automated PL mapping system was built (in part by the author), where the sample is placed on an x-y stage, as illustrated in figure III-2(b). It is logistically difficult to use a cryostat in this set-up, so samples were at room temperature, which is sufficient for analysis of QW excitonic transitions. The

(a)



(b)

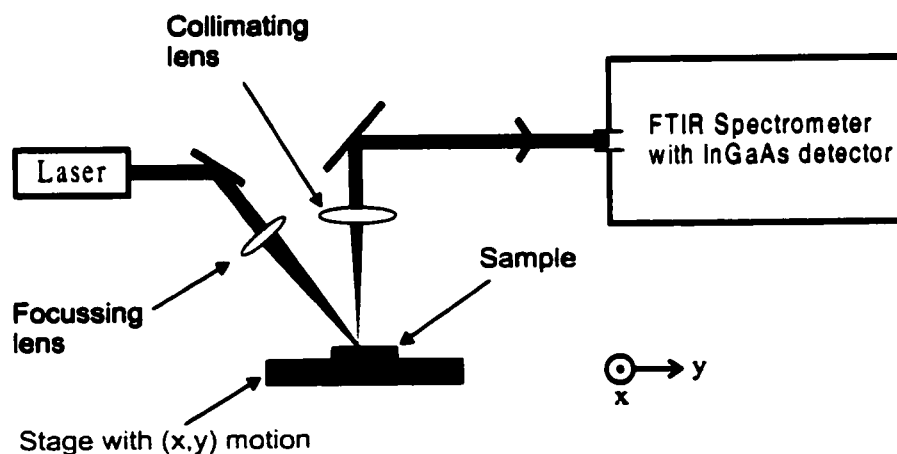
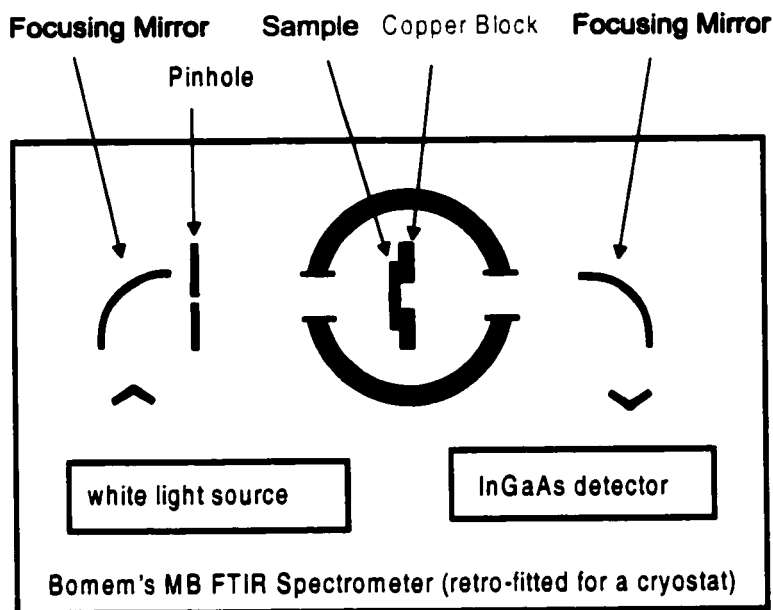


Figure III-2: (a) Top view of the low temperature PL set-up; (b) front view of the room temperature PL mapping set-up.

(a)



(b)

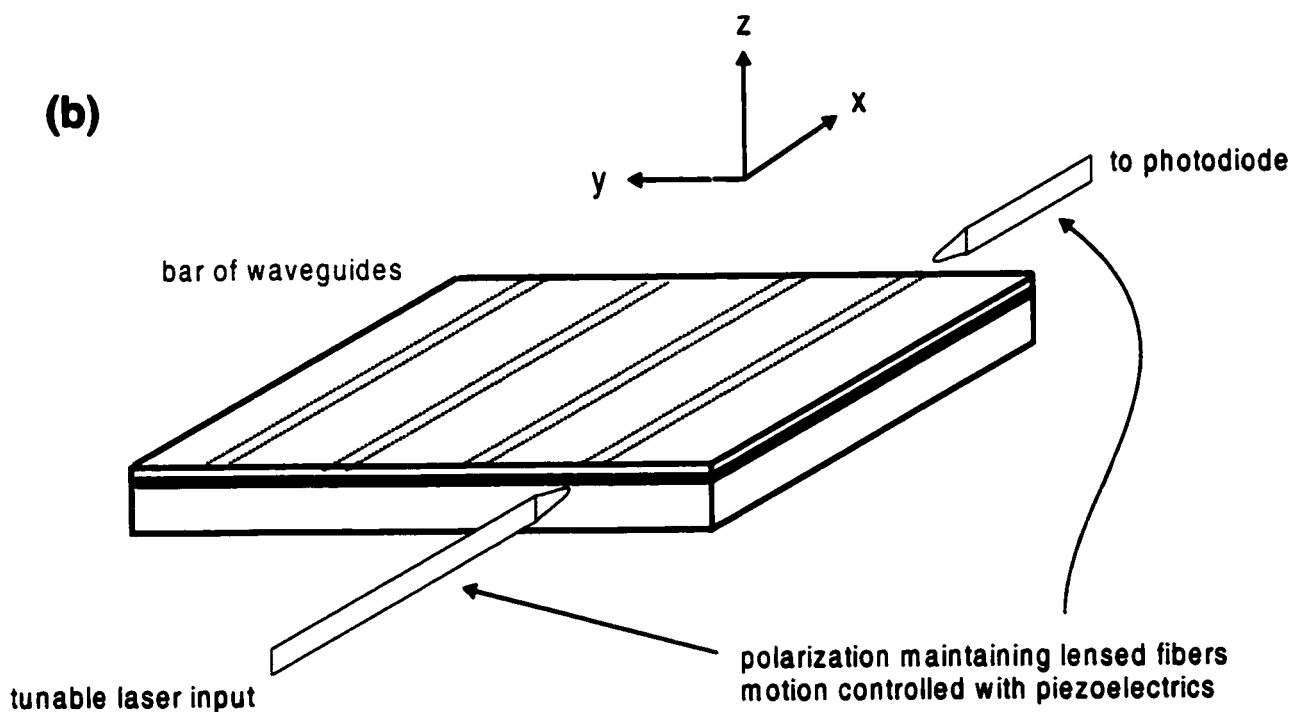


Figure III-3: (a) top view of the low temperature normal incidence transmission set-up; (b) the room temperature waveguide transmission set-up.

sample sat face-up on an x-y stage, with a focused laser beam directed at an angle onto the sample. The luminescence was collected using a large numerical aperture lens vertically above the sample and directed towards an FTIR spectrometer using a mirror. The use of an FTIR spectrometer offers the ability to collect complete (broad energy) spectra for every x-y point, a distinct advantage over grating spectrometers used in conventional in PL mapping systems. The system is computer controlled using custom written software which controls the x-y stage and interfaces with the FTIR spectrometer to receive the spectral data. Depending on the strength of the luminescence, several spectra were averaged together to improve signal-to-noise, resulting in one spectrum per x-y point. The software then analyzed the spectra and provided 2-dimensional maps of various spectra qualities, such as peak position and peak intensity as a function of x-y position on the sample. The spot size of the laser was of the order of 250 μm , and the step size was 500 μm . A small sample could be mapped in about one hour, while a full 2" wafer would be mapped in about seven hours. For all the PL maps in this thesis, the 980 nm diode laser was used to excite with a power of 20 mW.

C – Optical Transmission

Introduction

By analyzing the intensity of light transmitted through a sample as a function of wavelength, one gets characteristic absorption edges relating to the optical transitions. The lowest bandedge will be at approximately the same energy as the peak seen in PL, but additional resonances relating to higher energy transitions will also be visible. Thus we use this technique to gain information on the energy position of both the heavy hole (hh) and light hole (lh) $n=1$ transitions, which can be used to gain knowledge of the intermixing details. Specifically, the splitting between these two states can be used to determine a k ratio (Δ_V/Δ_{III}), as will be shown in Chapter IV.

Normal Incidence Transmission Set-up

Bomem's MB FTIR spectrometer has a broad band white light source and the necessary optics in place for room temperature transmission. Transmission at 4K was performed using an FTIR spectrometer that was modified (in part by the author) to accommodate a small cryostat, as illustrated in figure III-3 (a). Samples were again mounted on a copper block using teflon tape, but over a hole in the copper block such that the mount would not block the light that passed through the sample. Because this cryostat was a cold-finger type, small amounts of thermal compound were used to improve the thermal conductivity between the sample and the copper. Again, a temperature sensor on the copper block gave readings of 5-6 K, although due to the dependence on thermal conduction via the copper block, the expected actual temperature of the samples is warmer than this, perhaps ~20 K (the temperature of the samples is not key to the experimental results presented here, since the transition energies are not compared with results from other systems, and because the bandgap is expected to be relatively temperature insensitive below 70 K). The advantage of cooling the samples is that the strength of the excitonic QW transitions increased and their line widths decreased.

Two measurements were required in order to produce the required absorption spectra. First the transmission through an InP substrate is taken and used as the reference spectra, and then the transmission through the sample with QWs was taken. By subtracting the reference from the QW sample, we obtained a spectra consisting of optical resonances relating to the QWs. The spectra yielded information on the transition energies of the first few QW states, namely the $n=1$ electron to heavy hole and electron to light hole transitions, as well as the $n=2$ electron to heavy hole transition.

The intensity of the white light source and the percentage of light that was transmitted through our samples was too strong for the detector, thus a means of reducing the white light source intensity was sought. One option was to use several neutral density filters, but these created interference fringes in the measured

spectra (from multiple bounces at the various surfaces of the filters). Instead, it was found that physically blocking a portion of the light using a 200 μm pinhole prior to the final focusing mirror produced better results. In addition, interference fringes due to multiple reflections within the upper 1.5 μm thick InP buffer layer of the sample were also observed. This layer was removed by selective wet chemical etching (thus the uppermost QW was exposed at the surface). Unfortunately, this made the technique destructive in nature.

Waveguide Geometry Transmission Set-up

Variations in refractive index in a semiconductor structure will guide light. For example, the QW and barrier layers have a higher refractive index than the InP material, and thus guide light along their [001] plane, creating a slab waveguide. Additionally, lateral variations in the refractive index can be accomplished by several means in order to confine light along a particular direction of this plane. In Chapter 5, it is shown that QWI can be used to create such a lateral variation, resulting in what we term a buried waveguide device. Samples were prepared by first processing large pieces, followed by mechanical polishing (to thin the substrate) and cleaving into bars of 1 mm in length, and ~10 mm in width, enough to contain many waveguides. Analysis of the optical properties of (a) the unprocessed and uniformly processed slab waveguides and the (b) stripe buried waveguides is accomplished by studying the transmission of light along the waveguides, as illustrated in figure III-3 (b). Light is coupled into and out of the edges of the sample using special fibers which have lensed tips, providing a spot size of ~3 μm . Input from a tunable (1.45 to 1.59 nm) diode laser is coupled in the waveguide, which then propagates along the sample and is collected at the far edge by the second lensed fiber. The signal intensity is measured using an optical power meter. Proper alignment of the fibers is important for adequate signal intensity, and is accomplished using computer control of piezoelectric motion actuators, both to optimize alignment and provide spatial scan measurements. Measurements were performed at room temperature.

The wavelength of the laser source is scanned and output intensity monitored to give a transmission spectrum, from which the QW resonances can be observed. The input laser signal is linearly polarized, and the fibers are polarization maintaining, thus by rotation the input fiber by $\pm 90^\circ$, the transverse electric (TE) and the transverse magnetic (TM) spectra can be measured separately. Due to the standard selection rules, differences in the bandedge for each polarization allow us to determine both the heavy and light hole transition energies²³. The system also allows for spatial scans (at a fixed wavelength) by scanning the x, y or z position of either of the fibers. For example, scanning the y or z position of the collection fiber, with all other variables fixed, gives a spatial profile of the optical mode. This has been used to assess the modal behaviour of the device and thus the profile of the optical confinement produced by the processing.

D - High-Resolution X-ray Diffraction (XRD)

Introduction

High-resolution x-ray diffraction (XRD) analysis is performed to study small variations in strain of the epitaxial layers for both as-grown wafers and intermixed samples. This was performed using a standard 5-crystal HR-XRD set-up using a Philips' Material's Research Diffractometer (MRD) and computer controlled using Philips' PC-MRD software. A brief overview of the physics of x-ray diffraction and a description of the equipment is discussed below. The techniques used here are very standard to the field of heteroepitaxy²⁴. In particular, all of the samples were on (001) substrates, and ω -2 θ scans about the [004] diffraction condition for InP were performed. Additional explanation can be found in the Philips User Guide²⁵ and in a textbook by Bauer and Richter²⁶.

Diffraction Basics

Diffraction of an optical beam will occur due to reflection by a periodic planar structure where the wavelength of the beam is similar to the spacing between planes. Thus a semiconductor crystal whose lattice spacing is $d \approx 0.5\text{nm}$ will diffract

x-rays with a wavelength $\lambda \approx 0.1 \text{ nm}$. A maximum in the diffraction occurs when the path difference ($2d \sin \theta$) between rays diffracted from adjacent planes is equal to an integral number of wavelengths ($n\lambda$), as given by Bragg's law:

$$n\lambda = 2d \sin \theta \quad [1]$$

where θ is the angle of incidence. For the structures studied in this thesis, the perfect crystal structure of the InP substrate gives very strong and sharp diffraction peaks at known angles, the angle of each peak determined by the miller indices of the diffracting planes. Here, the fourth diffraction maximum (from the [004] planes) was studied. The epitaxial layers which are not lattice-matched to the substrate will have slightly different lattice spacing in the z-direction, and thus yield diffraction peaks at slightly different angle of incidence, θ' . However, the intensity of this diffraction will be significantly weaker due to the reduced number of diffracting planes (less material), requiring long data accumulations to achieve acceptable signal-to-noise ratios.

The Diffractometer

The diffractometer can be considered to be composed of four main elements: the incident beam optics, the goniometer, the sample stage, and the diffracted beam optics. Front and top views of the set-up are shown in figure III-4 (a) and (b), and each of the main elements is briefly explained below.

Incident beam optics: K_α and K_β x-rays are produced in an x-ray tube with Cu anode, and then passed through a Ge [220] four crystal monochromator (also known as a Bartels monochromator²⁷). Here, the beam is diffracted four times (once by each crystal), and the crystal orientation is such that only the $K\alpha_1$ line ($\lambda = 0.154051 \text{ nm}$) is properly diffracted by all four crystals. This results in a beam with wavelength divergence of $\Delta\lambda/\lambda \approx 2 \times 10^{-5}$. In addition, only completely horizontal beams are properly diffracted through all four crystals, resulting in a horizontal angular divergence of $\Delta\theta = 12 \text{ arcsec}$ (0.0033°)²⁴. The low values of these two divergences are required for studying very small differences in lattice constant

found in perfect or near perfect crystals, such as the samples of this thesis, while the vertical angular divergence was much less critical. The resultant spot on the sample has a size of 0.5 mm x 10 mm in the horizontal and vertical directions, respectively. The detection limit of this system, can be found by differentiation of Snell's law:

$$\frac{\Delta a}{a} = \frac{\Delta \lambda}{\lambda} - \frac{\Delta \theta}{\tan \theta} \quad [2]$$

This yields a $\Delta a/a$ value as low as 0.0001% using the above mentioned values.

Goniometer: The incident beam optics are rigidly fixed to the base plate of the goniometer such that the beam passes through the diffraction axis of the sample stage. The sample stage is attached to an angular drive unit of the goniometer that allows it to be rotated by an angle ω about the diffraction axis. The diffracted beam optics are attached to a second angular drive of the goniometer, which allows it to be rotated by an angle 2θ about the same diffraction axis. The accuracy of the two drives are 0.9 arcsec and 1.8 arcsec for the ω and the 2θ drives, respectively.

During a ω - 2θ scan the angle of incidence (ω) and angle of diffraction (θ) are kept equal by rotating the diffracted beam optics drive unit at twice the rate and in the same direction as the incident beam optics (this type of scan is also called a θ - 2θ scan, or a rocking curve). The scans are performed for $\omega \sim 31.67^\circ \pm 2.5^\circ$, where 31.67° is the Bragg condition for [004] InP, and the 5° scan width allows for detection of several strained layer peaks (to be further described below).

Sample Stage: The stage is designed to hold samples vertically. The z position of the stage allows the stage to be moved so that the diffraction axis passes along the front of the sample's surface. The stage also allows the sample to be rotated (rocked) by an angle ϕ to set the reflecting planes perfectly vertical.

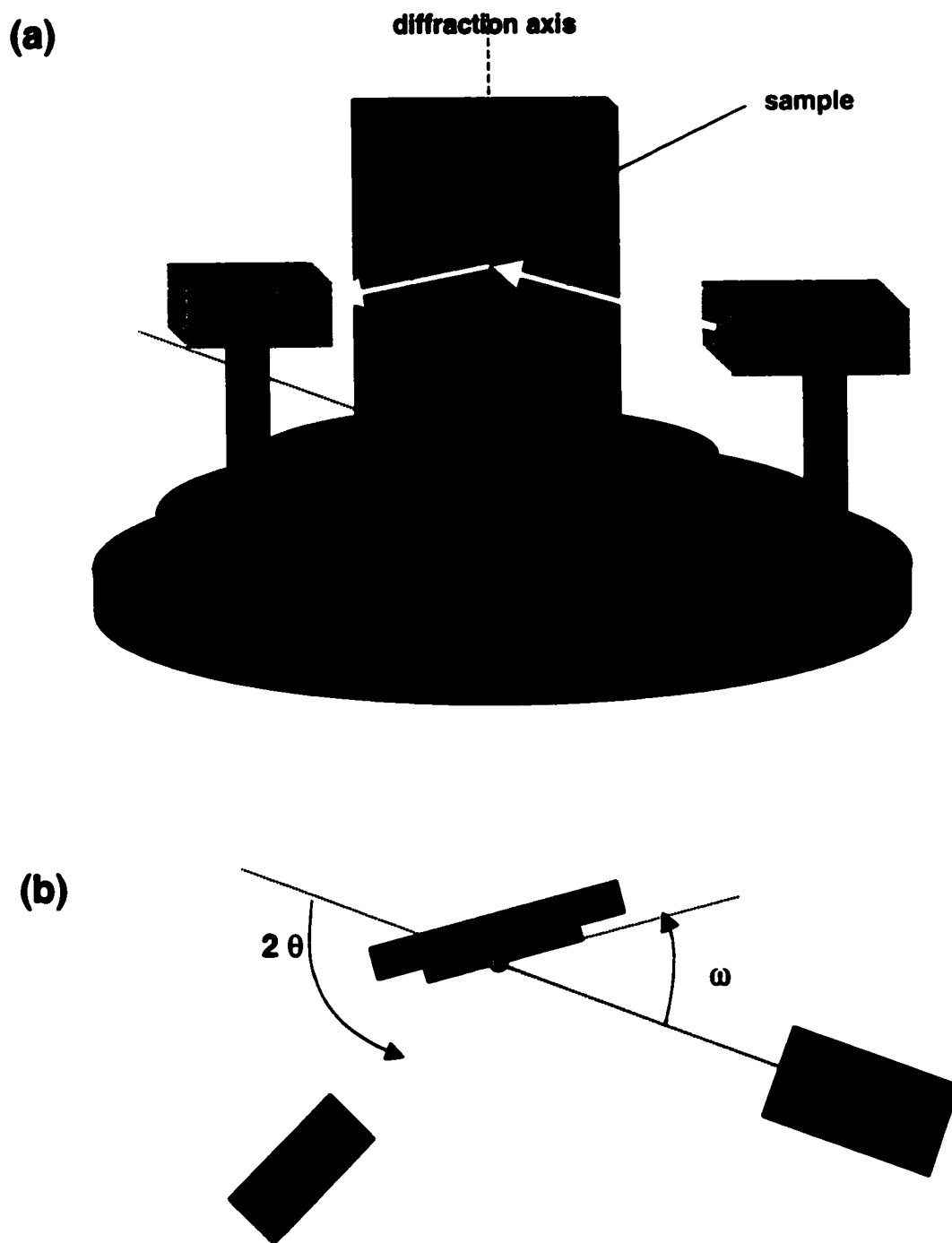


Figure III-4: X-ray diffractometer as seen from (a) front view and (b) top view.

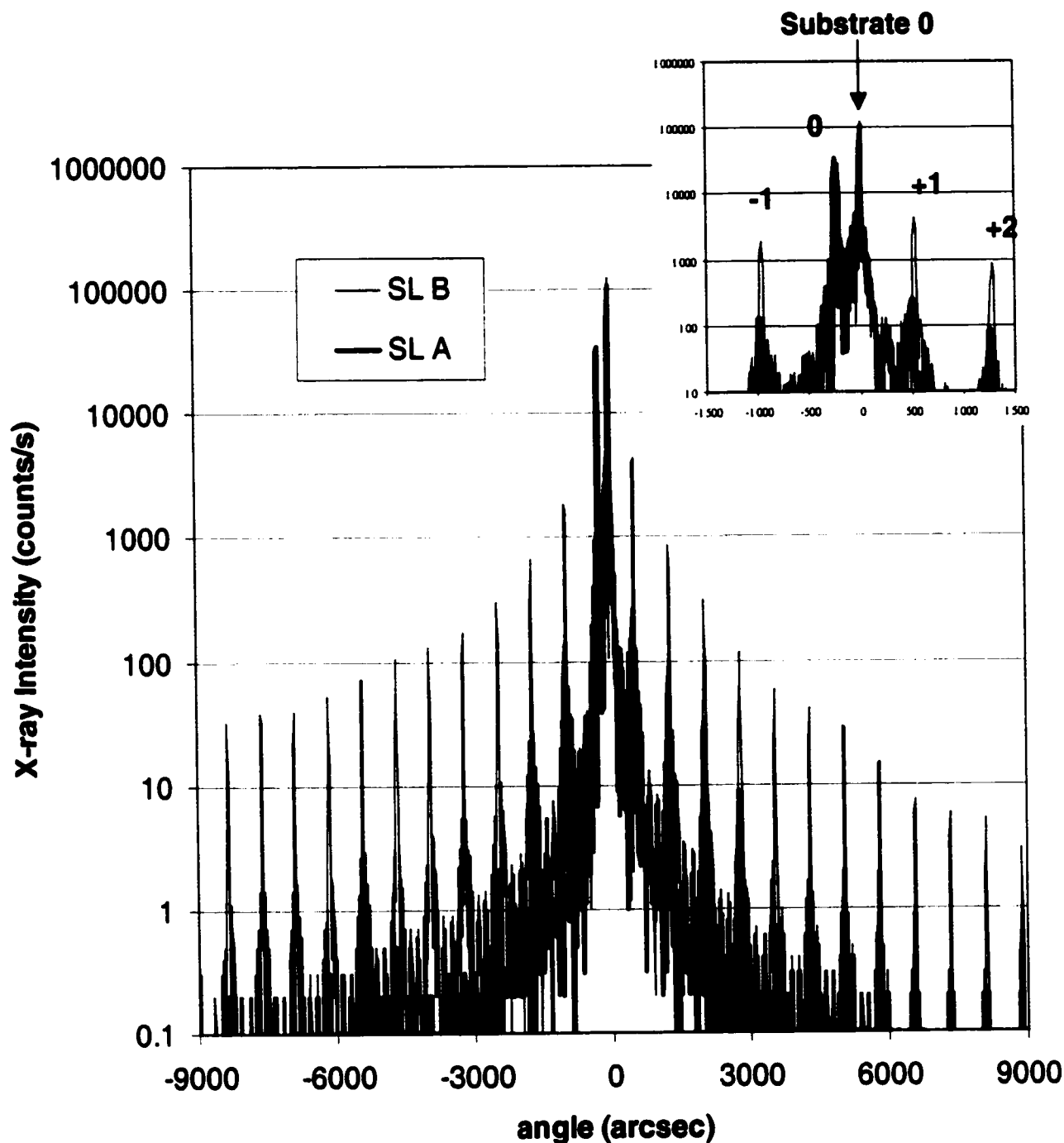


Figure III-5: Simulated XRD spectra for two InGaAs/InP superlattices (SL) with identical net strain (0.2% compressive) and 20 periods (25.0 nm). SL-A (blue) has a tensile QW with compressive barriers while SL-B (pink) has lattice matched QWs and barriers, but one tensile and one compressive interface. The inset shows a magnified view of the central peaks, with SL peak order indicated numerically.

Diffacted beam optics: Detection of the x-rays was accomplished with a $\text{Xe}_{(g)}$ proportional counter with a window made of Be. Each x-ray creates several photoelectrons, which are accelerated towards the anode. The accelerated electrons created additional photoelectrons, resulting in a amplification by a factor of 10^3 to 10^5 , and the creation of an electrical pulse. Each pulse, and thus x-ray, can be individually counted, as long as the count rate is kept $< 10^6/\text{s}$. A discriminator is employed to count only pulses with a height corresponding to K_α x-rays. Furthermore, a slit was placed in front of the window to reduce the background counts. This had a width of 0.45 mm, which corresponded to an acceptance angle of 0.2° .

Diffraction by superlattices

Here, superlattice (SL) is defined in a broad sense, being a heteroepitaxial structure with a periodic variation in composition (period D) along the growth direction, thus, this definition encompasses the multi-QW structures studied in this thesis. The x-ray spectrum from a periodic modulation in composition is characterized by satellite peaks around each zero order Bragg peak of the SL. The position of the zero order peak relative to the substrate peak give the net strain in the SL. The more strain and the more SL periods (the more material) there is, the more intense the satellite peaks will be. The satellite peaks are essentially equivalent to the optical diffraction pattern of a multi-slit experiment. The spacing between adjacent satellite peaks is determined by the SL period²⁸:

$$D = \frac{\lambda}{2(\sin \theta_m - \sin \theta_{m \pm 1})} \quad [3]$$

where θ_m is the angle of diffraction of the m^{th} order satellite peak.

The intensities of the satellite peaks relate to the magnitude of the strain and/or compositional variations within one period of the SL (and can be derived from the Fourier components of the composition modulation^{26,29}). Diffraction due to chemical

modulation from different lattice-matched compositions, which occurs because of differing strengths of interaction between the x-rays and atom type, will not be detectable in the conditions described above for the InGaAsP alloys. Thus the diffraction observed here is dominated by modulation in the strain. Thus, as local strain across a QW increases during intermixing when $k \neq 1$, the intensity of the satellite peaks will increase³⁰. Additionally, the relative intensities of the satellite peaks will depend on the distribution of the strain, and thus a significant amount of information is contained in them. However, to access that information, simulations must be performed and compared with the experimental results. Choosing the most appropriate values for layer strain and layer width is challenging since there are many variables that can be adjusted during simulations, and the uniqueness of the fit is not guaranteed. Thus some parameters must be assumed and/or known from other characterization methods. Working with samples that provide many satellite peaks (large and/or many SL periods) in combination with long scans to observe weak peaks can aid significantly. A good discussion of appropriate strategies for rocking curve simulations can be found in Bower and Tanner³¹.

In this thesis, the XRD spectra required 14 hours to acquire. The simulations are performed using Philips PC-HRS software version 1.3 (copyright 1993), which uses dynamic diffraction theory^{32,33}. Dynamic theory takes into account losses in the x-ray beam's intensity as it passes through the material; it is generally required in order to obtain satisfying fits to semiconductor heterostructures.

To illustrate briefly how the satellite peaks can vary, simulated spectra for two different theoretical InGaAs/InP superlattices are compared in figure III-5, both with mean strain of +0.2% in-plane compressive and the same period (25.0 nm). SL-A has tensile QWs and compressive barriers, while SL-B has lattice-matched QW and barriers, but one tensile interface and one compressive interface layer, as detailed in table III-1. These SLs represent rather extreme limits on what may happen during a poor growth of a nominally lattice matched structure. Note that the zero order peaks of both superlattices are the same distance away from the substrate

peak (same mean SL strain), and that the spacing of the satellite peaks are the same (same periods). The most obvious differences in the resultant spectra is that the intensity of the satellite peaks for SL-B are much stronger, due to the much larger magnitude of the strain variation across this structure. Note as well, that the right-hand-side peaks of SL-A are generally more intense than those of the left-hand-side, which is related to the tensile nature of the QW³⁴. Vandenberg also illustrates how smaller differences between interface layers can be determined by fitting the satellite peaks³⁵.

Table III-1: layer structures used in XRD simulations.

	layer	thickness	composition	strain ^a
SL-A:	QW	5	In _{0.5309} Ga _{0.4691} As	+0.01%
	barrier	20	InAs _{0.035} P _{0.965}	-0.24%
SL-B:	upper interface	1	InAs _{0.7377} P _{0.2623}	-5.0%
	QW	5	In _{0.5316} Ga _{0.4684} As	0
	lower interface	0.5	In _{0.7347} Ga _{0.2653} As _{0.5} P _{0.5}	+0.5%
	barrier	18.5	InP	0

The approach taken in this thesis is to compare simulated spectra, created under a series of different interdiffusion assumptions, with the spectra of the intermixed sample. The method is not intended to be rigorous, but it does provide some indications as to the k ratio and the shape of the interdiffused QW, as well as indicate how the technique could be used in a more refined manner.

E – Transmission Electron Microscopy (TEM)

Electron microscopes rely on electrons to image a sample, thus allowing for very high imaging resolutions, since the wavelength of electrons is of the order of 5×10^{-3}

^a negative strain is in-plane (planes parallel to the surface) compressive.

nm, although in practice the imaging resolution is at best 0.1 nm, and is limited by equipment and sample issues. In transmission electron microscopes (TEM), a beam of parallel, essentially monochromatic electrons is sent through a thin sample. The electrons are diffracted by the atoms of a crystalline sample, and will form a diffraction pattern on a fluorescent plate or camera, the pattern being representative of the crystal structure. Electron diffraction has many analogies with x-ray diffraction, but the electrons can be focused with electromagnetic lenses, and thus more manipulation of the diffracted beams can be done. For example, a series of lenses after the sample allow one to adjust the magnification of the diffraction pattern on the screen or camera. Samples must be thin enough (~100 nm thick or less) that the probability of multiple scattering is low³⁶, which would distort the diffraction pattern and reduce intensity. Good introductory references for TEM can be found in works by Williams and Carter³⁷, and Romig³⁸.

In a second mode of operation, an intermediate electromagnetic lens (located after the sample) can be used to refocus the electron beam into a spatial image. An aperture, placed just after the sample can be used to select only one diffracted beam for the production of this image. When the transmitted (undiffracted electrons) are used to create the image, it is known as bright field imaging, and here the contrast is mainly determined by mass/thickness variations in the sample. In dark field imaging, a single diffracted beam is selected, and then the image contrast contains specific information on strain and compositional variations along the crystal orientation of that diffracted beam. Samples for this thesis were prepared from <110> bars (cleaved cross-sections through the QWs) and analysis was performed using (200) dark field³⁶. The atomic structure factors provide the contrast in these images, thus layers of different compositions were observable, and layer thicknesses could be measured.

The imaging resolution is limited by the quality of the incident electron beam, aberrations in the lenses, sample preparation and sample type, but was slightly better than 0.5 nm for the III-V heterostructures in this thesis. Thus individual

atomic planes could not be resolved, but the widths of the as-grown QWs (from a cross-section sample) could be measured with this acceptable accuracy.

F - Secondary Ion Mass Spectrometry (SIMS)

The technique of SIMS uses a beam of primary ions to bombard a sample surface, causing the emission (sputtering) of secondary ions from the sample's surface, which are then analyzed using a mass spectrometer. By sputtering at constant rate and continuously analysing the sputtered secondary ions, data of concentration as a function of depth (depth profiles) can be obtained. Species most commonly used for the primary beam are Cs^+ and O_2^+ . The impact energy of the primary ions will cause mixing in the first 5 to 10 nm of the sample (depending on ion energy and angle), thus limiting the depth resolution (and preventing the use of all but the most modern of SIMS instruments as a tool for quantitative analysis on interdiffusion). The particles sputtered from the surface will include neutrals, positives, and negative monotomic and polytomic molecules. Typically, only one of the charged sputtered species will be analyzed. The yield of a particular ion depends on the ionization potential of the element, the species of the primary beam, and the sample's composition (or matrix). SIMS offers a wide dynamic range and high sensitivity, which make it an excellent tool for assessing impurity concentrations in a wide range of different material systems. It is a standard tool used to measure doping concentrations in semiconductors. A good tutorial and other references can be found on the Charles Evans& Associates web page³⁹, by Clegg⁴⁰, or by Sykes⁴¹.

During the measurements, the depth profiles initially take the form of counts versus sputter time. The sputter time is converted to depth by measuring the depth of the sputtered crater, while the ion counts are converted to concentration by multiplying by the relative sensitivity factor (RSF, for a particular ion in a specific matrix material) and dividing by the counts for an ion of the matrix (taken simultaneously). It is necessary to have matrix matched standards in order to determine the RSF factors accurately. In this thesis, depth profiles of the p-dopants Be and Zn were taken using the primary ion beams of O_2^+ and Cs^+ , respectively. Data has been left

in the form of counts versus depth because the heterostructures samples have thin layers of different compositions within which the RSF factors are expected to vary (the depth resolution and the accuracy of the various RSF factors required for these particular measurements were not sufficient to do a reliable conversion to concentration for the region of interest around the QWs and barriers), but this data format is sufficient for the relative comparison between different samples.

G – Summary

Probing of the optical transition energies is a simple way to gain information on the properties of a sample, and to monitor the small changes to the QW induced by QWI. PL gives access to only the lowest energy transition, and the QW luminescence was always strong enough to be detectable at room temperature. Therefore room temperature PL-mapping was the primary tool for monitoring of blueshifts of the e1-hh1 transitions, as well as simultaneously assessing the uniformity across a sample. PL-mapping has been applied to most samples throughout the thesis, including samples intermixed by thermal-only processing (Chapter IV) and implantation (Chapter V). PL is non-destructive in nature, allowing for multiple process-characterize cycles, and this has been done to both of the above mentioned types of intermixed samples. Thus, information on the time evolution of the interdiffusion has been gained, from which we can infer information relating to the location and nature of the defects causing the intermixing. The low-temperature PL set-up with FTIR spectrometer was primarily used for confirming the quality of as-grown structures, while the high-resolution spectrometer at low temperatures was useful for analysis of defect-related transitions in bulk material, and was used for defect identification of grown-in defects in bulk material (Chapter IV).

Unlike PL, transmission (or absorption) measurements can provide information on more than the lowest optical transition. Both types of transmission described herein have been used to assess the hh and lh splitting. First, the low temperature normal incidence transmission spectra provides fairly accurate determination of transition

energies, which allows for determination of intermixing k ratio in Chapter IV.

Second, the room temperature waveguide transmission set-up is also used to study the lateral optical confinement profiles of buried waveguide devices fabricated using QWI, as will be covered in Chapter V.

XRD provides a means of direct characterization of the mean strain in a QW structure, and the strain modulation across the QWs, which was used to assess compositions in as-grown structures and strain development during intermixing.

The TEM and SIMS measurements provide direct physical information on the QW structures. While the spatial resolutions of the instruments available for this work were sufficient to assess certain details of the as-grown structures, they were insufficient to be applied directly to the quantification of intermixing. However, with the continual development and improvement of these instruments, it seems feasible that the newest generation of instruments (just becoming available at the time of writing this thesis) will have the capabilities to provide quantifiable information on compositional profiles of the interdiffused QWs⁴².

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Chapter IV – Thermal Stability and Grown-in Defects

A - Introduction

For most practical applications in opto-electronics, intermixing should be selective, that is, it should occur only in the selected regions of a wafer where defects are introduced (by implantation or other processing). It is the motion of these defects through the QWs that enhances the interdiffusion of the QW/barrier material. The temperature of the RTA must be hot enough to allow these defects to diffuse from the damaged region through the QWs. But if it is too hot, a large equilibrium generation of lattice defects occurs in non-implanted regions, resulting in unwanted intermixing across the entire wafer. To obtain selectivity, the anneal temperature should be kept just low enough to prevent the latter from occurring. Thus, it is important to understand the thermal behaviour of as-grown material in order to properly select the RTA conditions. By annealing a series of unimplanted samples at different temperatures but for the same time, one can determine the blueshift as a function of anneal temperature, which we refer to as the “knee curve”. The knee point is the temperature at which the optical bandgap begins to shift, and is the desired temperature for annealing of implanted material.

We have observed a significant variability in the knee point of various QW heterostructures, and have endeavored to learn more about what controls it. Figure IV-1 shows some knee curves that have been obtained for various structures with different doping and strains in the QWs and buffer layers, all for 90 s anneals. The details of the layer structures will be discussed later in this chapter. The magnitude of blueshift is expected to vary with layer structure, even if diffusion is assumed to be independent of composition. First, for a given interdiffusion length, narrow QWs (small L_z) will be more affected than wide ones (unless $L_z < 3.5$ nm). Second, for a given interdiffusion length, there will be a larger change to the confinement potential when the structure has a larger difference between the bandgap of the QW and that of the barrier. However, to first order, one might expect that the knee point of

different structures will still be the same, since this should be connected to the activation energy for the equilibrium generation of defects. However, it is quite obvious from the knee curves shown in figure IV-1, that the knee point of these structures varies considerably. There are a few possible reasons as to why this occurs:

- a) intermixing is dependent on composition and/or doping
- b) following growth, some of the wafers were not in an equilibrium state
- c) there was a problem with the RTA procedure such that the temperature and/or processing conditions varied from one set of data to the next

This chapter will primarily review the work that has gone into studying possibilities b) and c). It is necessary to rule out both of these possibilities (i.e have good control over both the material and the processing) before one can study any dependence on layer structure. Annealing is a key processing step applied to every sample studied in this thesis, and section B is dedicated to reviewing the annealing procedure and discuss its reproducibility. Section C examines variations in the knee curves of several nominally identical wafers. From this study we find that the thermal stability of QW structures varies, in part due to the quality of the growth. A detailed look at intermixing caused by grown-in defects is given in section C. Our understanding of the defect diffusion and the QW interdiffusion is furthered by this study, and valuable insights with regards to defect identity, defect motion, interdiffusion mechanisms, and a k ratio are all determined. Portions of the work have been published, and these papers are included within the chapter. In section D, we return to the knee curves of figure IV-1, and be able to make some preliminary comments with regards to the composition and doping dependence of the thermal stability.

B – Annealing Procedure

Most publications only briefly mention annealing procedure, but there are important parameters that must be properly accounted for in order to achieve reproducibility

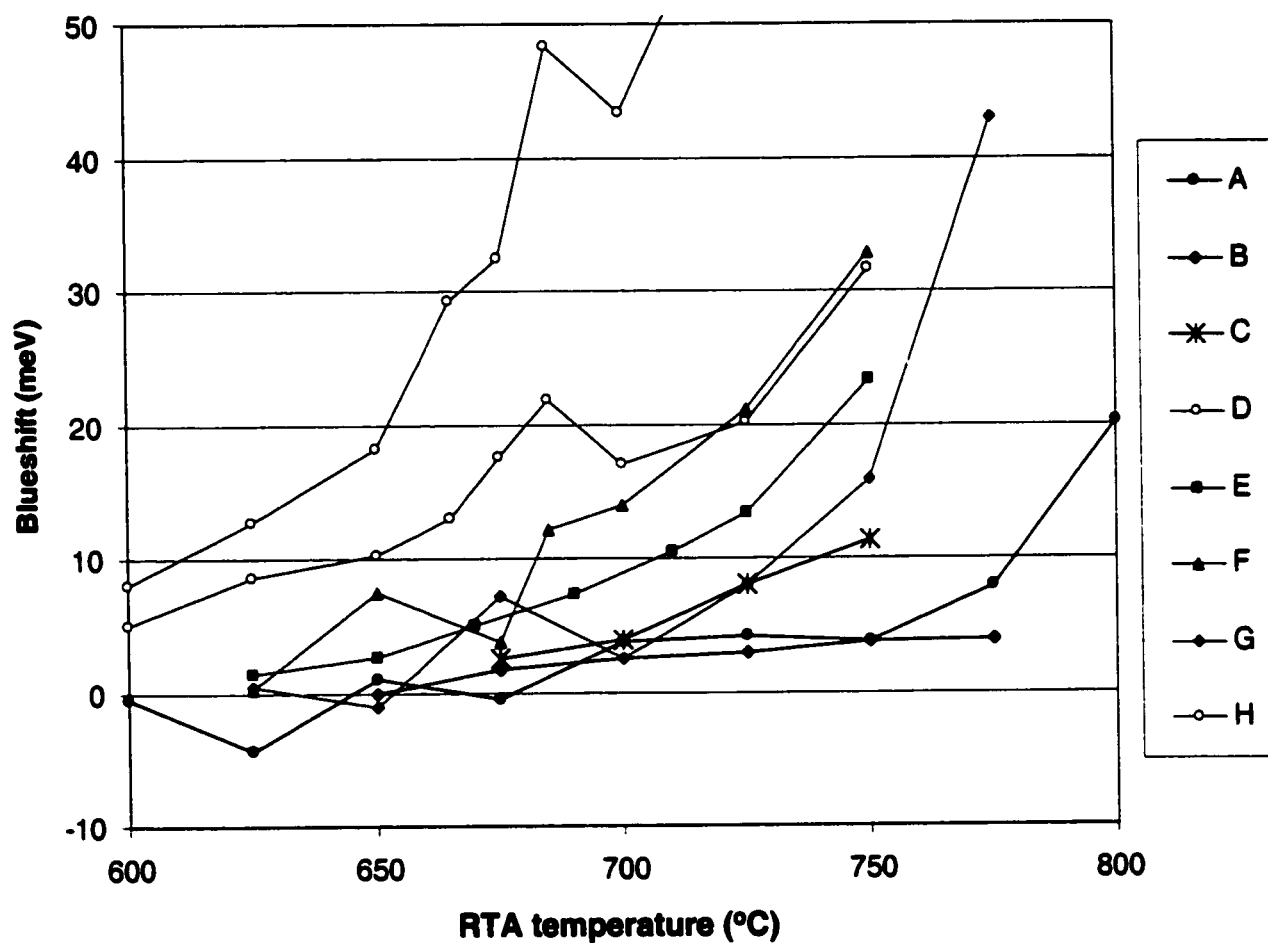


Figure IV-1: Knee curves from several different layer structures, illustrating the variability which has been observed for InGaAs(P)/InGaAsP structures.

and avoid sample degradation when annealing III-V semiconductors. Thus, a review of key aspects of the annealing procedure will be covered in this section, emphasizing key physical concepts, and including several experiments which justify the selected procedure.

The Oven

The rapid thermal annealer (RTA), made by AG Associates, is a small oven which heats the samples radiantly from the light given off by high-voltage tungsten halogen lamps. A schematic is given in figure IV-2. There are two banks of lamps, one above and below the sample chamber. The chamber walls are made of high purity quartz, and the sample is held in the center of the chamber using a quartz tray. Several small samples can be placed at the same time on a carrier wafer which is supported by the tray. Two different AG associates ovens were used during this thesis. The first oven (oven 1) is run under temperature control, that is, the lamp intensities are automatically adjusted in real time in order that the sample follow a desired temperature recipe. The oven allows for linear ramp-ups in temperature from 10°C/s to 300°C/s, and holds steady state value to within $\pm 7^\circ\text{C}$ for up to 300 s¹. The overall design of the second oven (oven 2) is identical to oven 1, but the controller was slightly older and did not allow real-time temperature control. Recipes were developed that were sufficiently similar to those of oven 1, providing temperature stability of $\pm 5^\circ\text{C}$; temperature profiles of the two ovens are compared in figure IV-3. It will be specifically mentioned whenever samples that are directly compared with one another were annealed in different ovens. For a few minutes after loading the samples, as well as during the anneal cycle, ovens are purged with a non-reactive gas (electronics grade N_{2(g)} was used here). Ramp-down rates are in the range of 20-80°C/s (temperature dependent and non-controllable). Outside the chamber, water and air-cooling systems keep the rest of the unit cool.

Temperature measurement of the carrier wafer can be accomplished using either a pyrometer or a thermocouple (TC). The pyrometer (which is integrated within the

oven) is located just outside of the chamber, and “looks” at the bottom surface of the carrier wafer. It calculates the sample temperature based on the intensity of radiation at a set wavelength (using blackbody theory). Each wafer type to be annealed must be calibrated (using a second measure of temperature such as a TC), where the value for emissivity (of the wafer surface, as viewed by the pyrometer) is adjusted to achieve a correct temperature reading. Pyrometer temperatures are only valid for temperatures above $\sim 800^{\circ}\text{C}$ (or $\sim 400^{\circ}\text{C}$ for extended range pyrometers). The measurement is inherently sensitive to changes to the surfaces of carrier wafers and chamber walls (such as oxidation or build up of deposits). The pyrometer also requires a separate water-cooling system, with chiller water maintained at a steady temperature $\pm 0.5^{\circ}\text{C}$. Although it is possible to have good control over these parameters, they are distinct disadvantages for the use of the pyrometer, and combined with further issues to be described below, led us to favour the TC for temperature measurement.

The oven is equipped for chromel-alumel (type K) TCs, and both the cantilever type and embedded junction type are used in this thesis. For the cantilever type, the bare wires are held in place using quartz holders and ceramic tubing, and the junction contacted the bottom of the carrier wafer by making use of the spring force of the cantilevered wires, as shown in figure IV-2(b) and (c). These TCs, where the junction is exposed to the chamber gas, give accurate measurements for temperatures below $\sim 750^{\circ}\text{C}$, but the junction will degrade at higher temperatures. The TCs with their junction embedded (fabricated by Sense Array) into a carrier wafer or into a carbide susceptor are stable to temperatures of 1050°C^2 . The bare wires are protected using soft weave ceramic tubing. For both types, the two ends are connected to chromel and alumel leads integrated within the oven door. The voltage across these leads is converted to a temperature by circuitry internal to the oven.

Several tests were performed to assess the reliability of the temperature control. The first test involved a calibration of the pyrometer. The oven was set to control

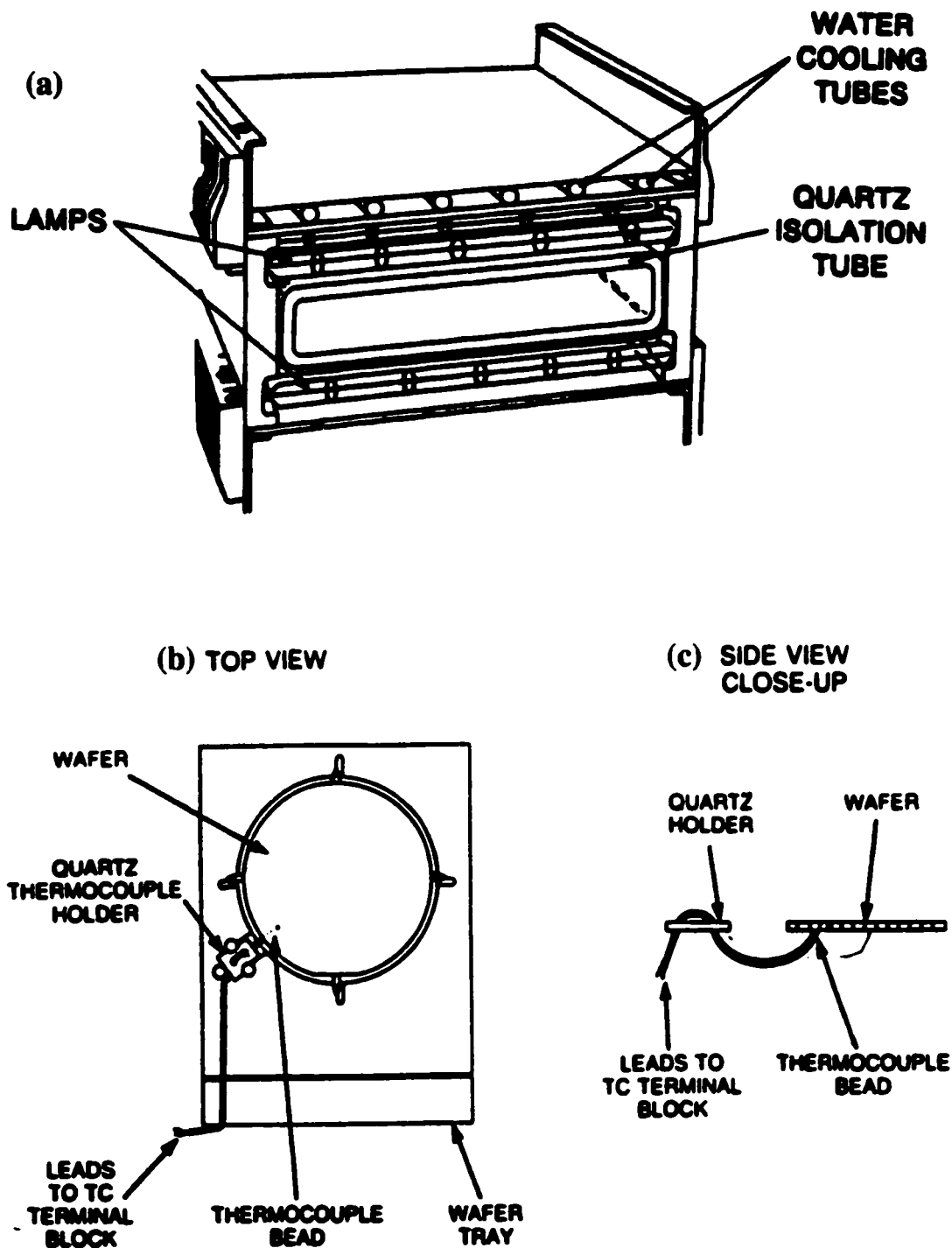


Figure IV-2: Schematics of (a) the chamber of the rapid thermal annealer and (b) quartz tray with cantilever thermocouple assembly. A carrier wafer or susceptor is supported by the pins of the quartz tray, which is supported on the door (not shown) and slid into the center of the chamber. (c) Side view of the contact between the cantilever thermocouple junction bead and the carrier wafer.

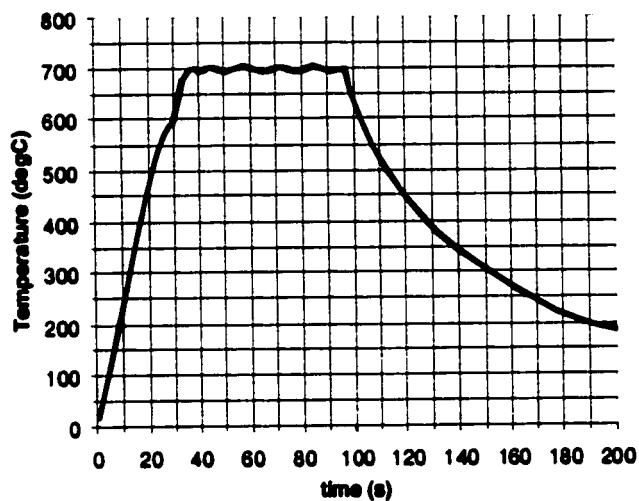
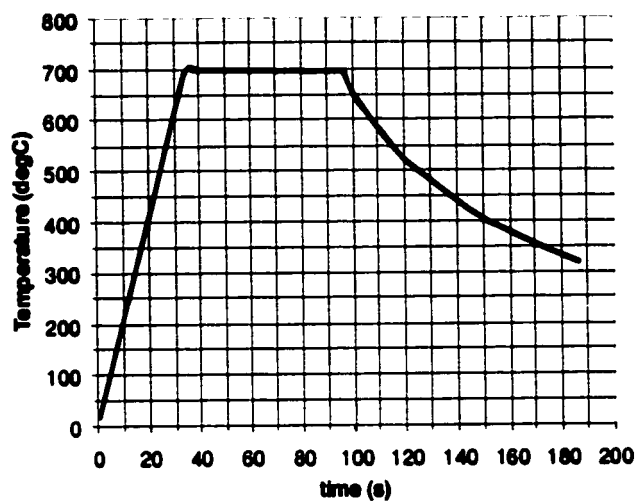


Figure IV-3: RTA temperature profile for a recipe of 700 °C for 60 s (a) oven 1 and (b) oven 2. Ramp-up rates are ~20 °C/s for both profiles.

lamp intensity based on the pyrometer temperature while following a recipe calling for stepwise increases in temperature (i.e. maintaining a constant temperature for a set period of time and then incrementing the value by 50°C). The TC was also installed, providing a second measure of the temperature. To calibrate, the value of emissivity is adjusted until both instruments agree on the same temperature. The two curves in figure IV-4(a) agree quite well in temperature (and thus an emissivity value used here, 99, for the pyrometer reading is correct). However, it can be seen that there is a discrepancy with time between the TC and the pyrometer, in that the TC measures a decrease in temperature during each stage, but temperature is suppose to remain steady. Thus one of the two means of measurement was exhibiting a drift with time. Similar results were also found in subsequent runs using a cantilever thermocouple instead of the embedded thermocouple. Given that the outer walls of the oven became warmer (by ~5-15°C) after processing, we concluded that there was a slow heating of the oven as a whole, such that components that were suppose to remain at constant (cool) temperatures via air and water cooling mechanisms, were warming up. It is likely that the inner components, such as the quartz walls of the chamber were warming-up with time, which would affect the pyrometer, and thus it was concluded that the pyrometer had a drift with time. TC measurement was deemed to be more reliable for anneals of longer than 10 s.

It was also found that pre-conditioning the oven was an important step to take, i.e. executing a trial version of an intended recipe before any samples are placed in the oven. There are two advantages to this: a) it confirms that the oven is operating correctly before samples can be ruined, and b) this seemed to greatly increase the reproducibility, as confirmed by results in figure IV-4(b). In this experiment, the oven was again controlled by the pyrometer, with TC providing a second measurement. The TC was a cantilever-type, contacting the bottom of a Si wafer. The same recipe is run several times, in this case the recipe requires the oven to hold for 300+ seconds at a fixed temperature (the actual value is 650°C, although an incorrect emissivity will mean the two instruments will read different

temperatures). It is obvious from the graph that the temperature, as measured by the TC, is very different during the first run than during subsequent runs (run 7 and 9 are shown), even though the same recipe was used for all the runs. The exact mechanism for this behaviour is not known, but may again be related to a warming-up or change in properties of certain elements of the oven³. But once a trial run is performed all subsequent anneals were consistent. Also, the reproducibility for annealed samples (to be discussed below) improved when the same total time was allotted for each anneal (including unloading one sample, loading the next, running a purge of the chamber and starting the next recipe), which allows the oven to cool to the same temperature between each run³.

To truly understand the interplay between radiation, chamber geometry, temperature measurement technique, type of sample, and the actual sample temperature requires a fair bit of expertise. A good review of the issues is provided by Timans⁴ (although more concerned with Si device requirements) and yearly symposia organized by the Materials Research Society.

Annealing of III-V Samples

When annealing any material, it is important to control the sample surface and the surrounding atmosphere. When annealing III-V materials, surface degradation can be a real problem, especially as temperature increases, due to the rate at which the group-V species (As or P) leaves the surface. P is especially volatile - for example, the equilibrium P_2 and P_4 partial pressures above an InP sample can be a significant fraction of an atmosphere for temperatures above $\sim 600^\circ\text{C}$ ⁵. Thus it is essential to protect the surface of the sample by minimizing the loss of P or As. This can be accomplished in several ways:

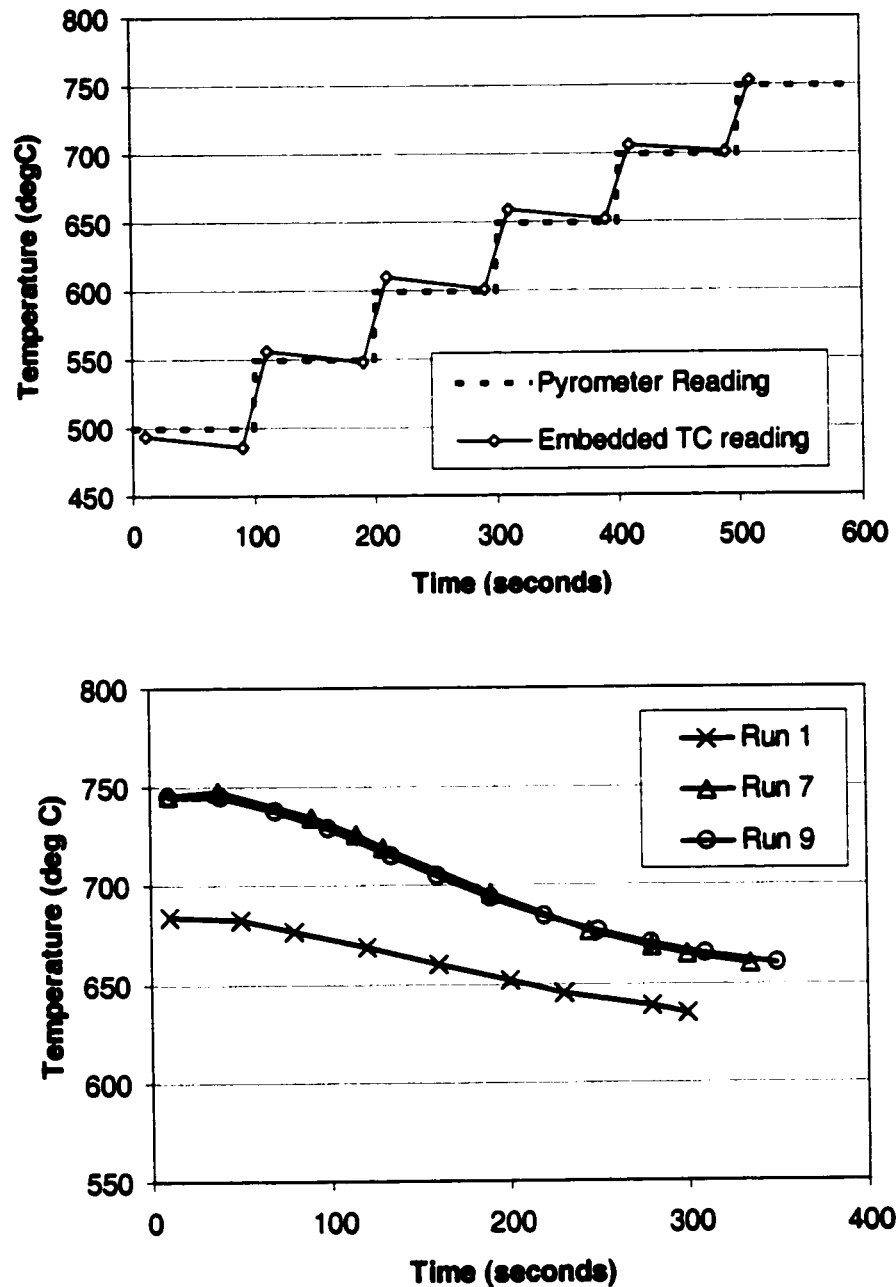
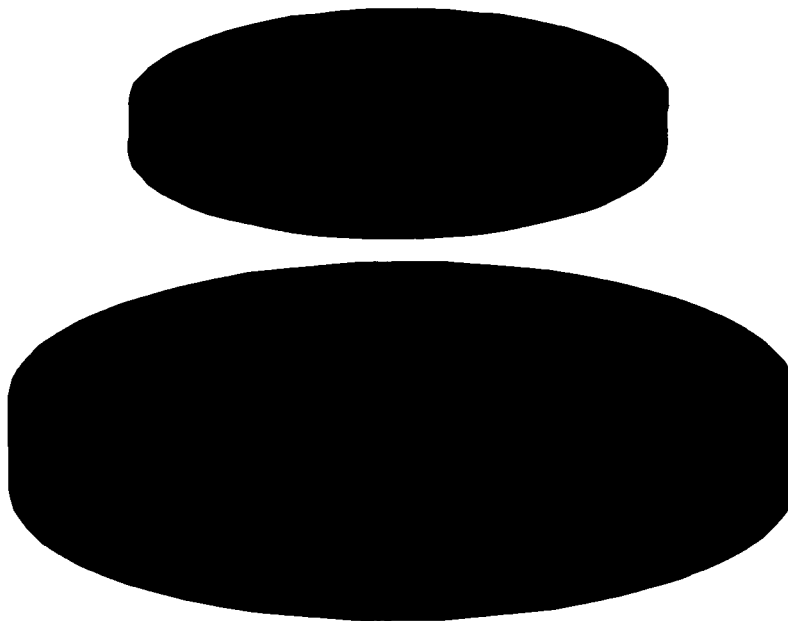


Figure IV-4: RTA tests (a) pyrometer calibration in oven 1, where the oven is run under pyrometer control, with secondary check of temperature performed by chromel-alumel TC. TC junction is embedded in 2" Si wafer which is placed within a carbide susceptor, and emissivity was set to 99. (b) Test of the repeatability – the oven is run under pyrometer control, with secondary check of temperature performed by cantilever TC in contact with the bottom of a 4" Si carrier wafer, and emissivity was set to 50. More than 10 sequential runs of the same recipe were performed, and runs 1, 7 and 9, are shown here.

(a)



(b)



Figure IV-5: (a) schematic of the graphite susceptor used to enclose wafers during annealing (b) schematic of the non-contact method for providing group-V overpressure using a proximity cap and border material.

- a) encapsulating the sample with a non-reactive material, such as a dielectric
- b) introducing a P or As containing gaseous compound (such as a metal-organic) into the chamber
- c) using a thermally stable material (such as a Si substrate) as a proximity cover, the purpose of which is to minimize the volume that must be filled with group-V vapour by the sample.
- d) using a III-V substrate as a proximity cap, which will perform volume minimization as above, but also provide an equal amount of group-V vapour itself.
- e) using a susceptor which is charged with an excess of group-V (during previous anneals, sacrificial III-V substrates have been inserted into the susceptor, and the group-V vapour is driven into the susceptor walls).

There are advantages and disadvantages to each method. The encapsulant will protect the sample's surface, but may induced stresses during the anneal due to thermal expansion mismatch, and the deposition and/or removal of the encapsulant may alter the surface. Option b) allows for controlled variation in the group-V overpressure, but logistically is usually only available for anneals performed within the growth chamber, since many precautions are required when dealing with arsine and phosphine. Use of a proximity cap c) and d) is a simple and commonly used method in research; using a III-V material provides a better group-V overpressure than Si which is especially important for anneals above ~650 °C, but the III-V substrates degrade with use and need to be replaced on a regular basis⁶. It is option d) that has been used for all the processing in this thesis. GaAs proximity caps were used for 5-10 anneals, while InP proximity caps could be used 2-5 times before a visual degradation of the surface occurred. Option e) was also explored at the beginning of the research. The susceptor is a pill-boxed shaped container made of graphite, within which the sample is placed (illustrated in figure IV-5 (a) and further explained below). The porous nature of the material means that it can be charged with excess group-V by annealing a sacrificial III-V substrate within it. This

excess group-V then provides the overpressure for samples during a subsequent anneals. It was found that a sacrificial substrate was only good for one charging, and that the susceptor had to be recharged every 1-2 anneals. Thus this method is a very inefficient use of sacrificial wafers in comparison to using them to directly cap a sample. A very useful reference for annealing of III-V's can be found in Pearton et al.⁵.

Since the vapour pressure of P is several times larger than that of As (i.e. an As terminated surface is more stable than a P terminated surface), it may be preferable to terminate an epitaxial structure with InGaAs. An upper InGaAs cap is common in device structures due to the ease of making good ohmic contacts to it. Logically, one would use a GaAs proximity cap over InGaAs, and an InP proximity cap over InP, although Pearton suggests that As overpressure could be used to protect InP⁷. An investigation was performed to determine whether a significant difference existed between using a InP or GaAs proximity cap when the structure is InP terminated. This was of particular interest because GaAs substrates cost less than InP substrates. The experiment involved an InGaAs/InP QW structure annealed at 685°C for 90 s. The blueshift resulting from the thermal anneal, and its uniformity, were similar in both cases (see table IV-1), indicating that the composition of the proximity cap does not strongly affect the interdiffusion (although the small value of blueshifts measured here reduce the ability to judge differences). However, the intensity of the 300K PL using HeNe excitation was reduced by a factor of 5 when using the GaAs cap over the InP terminated surface. This is attributed to the generation of non-radiative defects at the sample's surface as it loses P. A similar study done by Glew et al. in reactors with P or As overpressure for InP and InGaAs terminated wafers, respectively, indicated that the type of surface termination did not affect the intermixing⁸.

Table IV-1 Results from room temperature PL maps for anneals of an InGaAs/InP MQW using different proximity caps (growths were terminated with InP).

	proximity cap	PL blueshift (nm)	PL intensity (arb. units)
sample 1	GaAs	6 ± 1	0.9 ± 0.2
sample 2	InP	6 ± 1	4.3 ± 0.3

Ideally, an RTA will heat-up and quench samples very rapidly, such that there is no influence of the ramp-up and down times on physical processes. However, very rapid heating and cooling may induce thermal stresses on large diameter wafers, due to the differences in the heat loss at the edges of the sample compared with the center⁹. Although the samples in this thesis were much smaller and thus these stresses should not be an issue, relatively slow rates were employed such that the results would be transferable to full wafers. Thus values of the order of 20°C/s were employed for ramp-up, while the ramp-down, which is quite non-linear, also averaged ~ 20°C/s during the first 100°C drop, as was shown in figure IV-3. These values are still reasonably fast (significantly faster than older furnace technology) and only a small fraction of the total thermal energy given to the sample is due to time spent during the ramp-up and ramp-down phases of the recipe. It is common practice to place wafers within a susceptor, as shown in figure IV-5(a), to minimize temperature differences across large wafers (non-uniformities in the lamps' radiation and due to differences in cool-down rates between the wafer's center and edge). The susceptor acts as a black box radiator, absorbing the lamp's radiation and then re-emitting towards the samples. Some anneals performed for this thesis were performed with a silicon carbide coated graphite susceptor, large enough to contain two 2" wafers (the sample and proximity cap), while other anneals were performed without a susceptor. The additional mass of the susceptor had only a small effect on the ramp-up and ramp-down stages of annealing. For both types of anneals, care was taken to place the samples in the center of the chamber.

In order to further reduce thermal gradients across small samples^{9,10}, as well as prevent loss of group-V species at the sample's edges, additional III-V sacrificial material was used to surround the samples during anneals, as illustrated in figure IV-5(b). With use of a border, the uniformity of a shifted sample was typically governed by non-uniformity in the starting material, and only the first 0.5 mm in from the edge showed any difference in resultant blueshift or change in intensity, as is shown in figure IV-6, for an InGaAs/InP sample shifted by 27 nm. Although the composition of the border was not important, its thickness was found to be an important parameter. If the border is thinner than the sample, the proximity cap will be supported by the sample. Any variations in the distance between the two nominally contacting surfaces (such as that caused by a dust particle) could cause a hot spot and/or tilt the proximity cap, resulting in a non-uniform blueshift¹¹. Good blueshift uniformity and similar PL intensities were obtained for border thickness equal to or larger than the sample (in the range of 100 to 250 μm thicker). The additional volume between the sample and proximity cap, which must be filled with group-V overpressure when the border is thicker, can be provided by less than one monolayer of III-V material, if no gas exchange is assumed. This is of course an inaccurate assumption, since we count on there being gas exchange during the purging with $\text{N}_{2(g)}$. Thus, the deficiency of the proximity cap method is that we have poor control over the gas environment above the sample.

Reproducibility

When taking into account all of these considerations, a reasonable reproducibility between different runs was found. This is illustrated in figure IV-7, which contains comparisons of the blueshift as a function of RTA temperature for samples annealed at different times in oven 1. A different 5x5 mm sample is used for each temperature. Figure IV-7(a) shows results on an InGaAsP/InGaAsP structure: one set of data was performed by an NRC colleague, circa 1995, using the pyrometer and placing samples in the susceptor with small GaAs proximity cap above, while the three other sets was performed by the author in 1997 and 1998 using a cantilever thermocouple, with the samples in the susceptor, and with GaAs

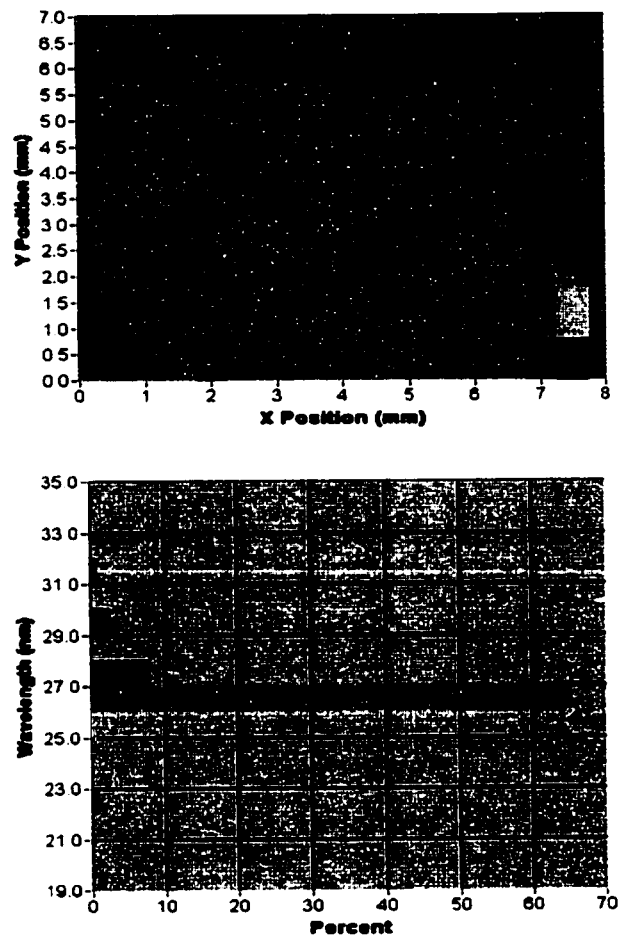


Figure IV-6: PL map showing the variation in blueshift across a 6x7 mm sample. The map is taken by subtracting the PL map of the sample in its as-grown state from the PL map of the same sample after an anneal of 700°C for 90 s. The histogram indicates a blueshift of 27 nm with less than 1 nm standard deviation.

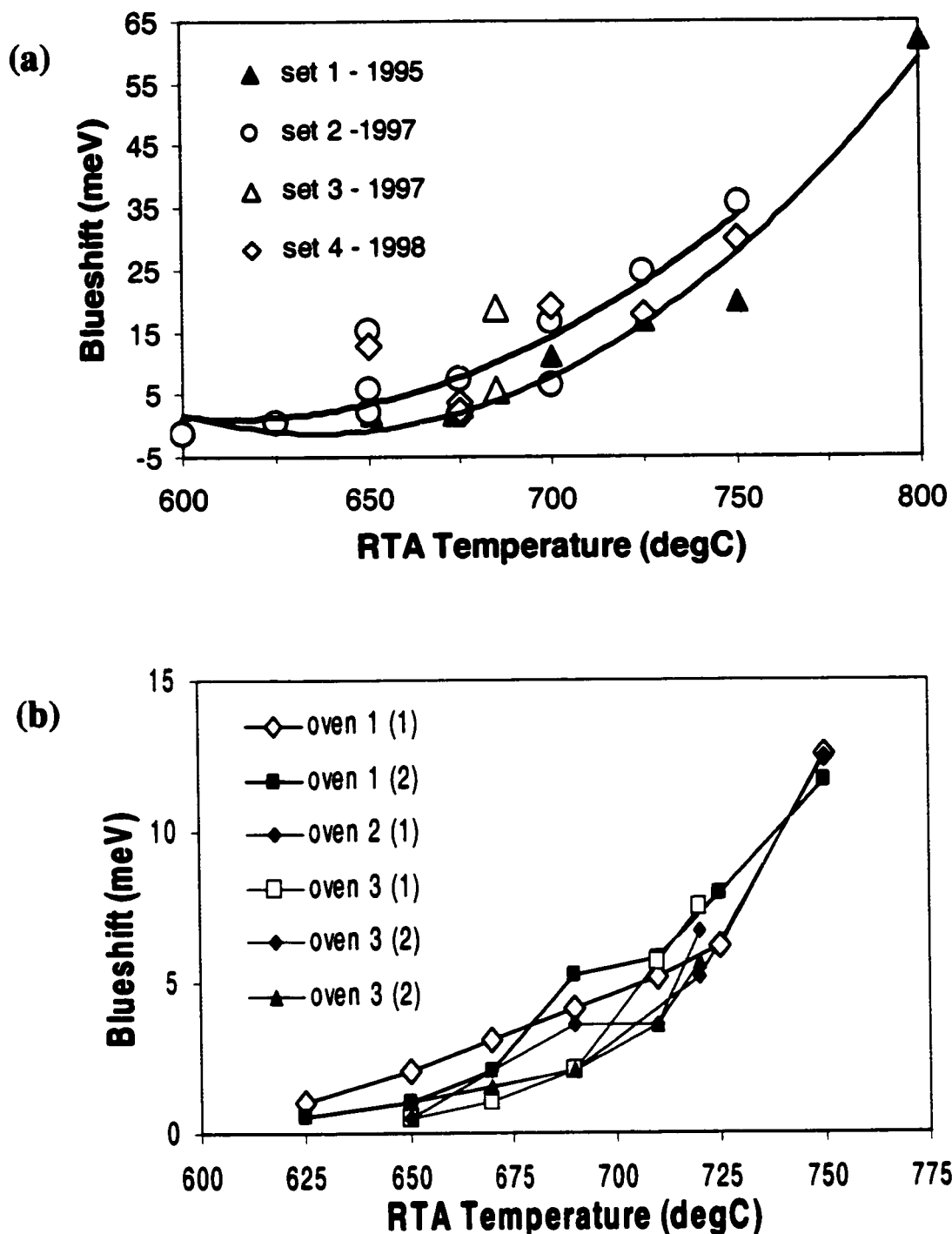


Figure IV-7: The reproducibility of knee curves is illustrated using two different layer structures (a) structure F: anneals are performed in oven 1, where a red line guides the eye for set 1, and a black line guides the eye for sets 2-4 combined; (b) structure E: anneals performed in three different ovens and using two nominally identical wafers (the number in brackets indicates different growth runs from the same MOCVD reactor). Structures are detailed in table IV-6.

surrounding and covering the sample (entire volume of susceptor was filled with sacrificial GaAs). Red and black lines provide guides to the eye for set 1 (1995 data) and sets 2-4 combined, respectively. Two points are worth noting about the results. First, the multiple data points at a given temperature in data sets 2 indicate that there is a variability of ± 5 meV. However, this is likely due to variations in the wafer itself, which showed variations in emission wavelength of ± 7 meV, and tied to the fact that single point PL was used in the analysis (use of PL mapping results, which determine the average of a whole sample, reduces the variability of calculated blueshift). Second, data set 1 generally shows less blueshift than sets 2-4, which could be due to a small offset of ~ 5 meV between TC and pyrometer, differences in the N_2 purge gas flow rate, or simply because samples for each set were taken as a whole from different regions of the wafer.

A later series of tests was run to confirm the equivalence of three different AG Associates RTA ovens, as shown in figure IV-7(b). Anneals in ovens 1 and 2 were done using TC measurement, and by placing samples on a Si carrier wafer. The material is an InGaAsP/InGaAsP structure and had a peak wavelength uniformity of ± 3 meV. The results show excellent agreement and reproducibility, with variations of the blueshift of only ± 2 meV. Figure IV-7(b) also contains results from anneals performed by an external collaborator (oven 3) using their AG Associates RTA. Samples were held in a susceptor and temperature was measured using a pyrometer. The procedure for acquiring these knee curves was somewhat different from ours - their approach involved annealing the sample at the lowest temperature, performing a PL measurement, and then re-annealing the same sample at a higher temperature to obtain the next data point of the series. The data values indicate the total shift from the as-grown peak. There is good agreement between different sets of their data, and it is surprising how well the data agree, given the difference in procedure. One might expect that samples annealed by the external collaborator would exhibit a larger shift since their blueshift values represent a total accumulated shift from several anneals, but perhaps such an effect is masked by an offset in temperature of a few degrees. Overall, the reproducibility and agreement is very

good. The data also illustrates the repeatability and uniformity of a multi-wafer MOCVD reactor. Data sets include different quarters from wafers grown in different growth runs.

Cleanliness

It is important to have samples as clean as possible for annealing. A simple three solvent clean followed by de-ionized water rinse and nitrogen blow dry was used for the samples after any possible contamination, such as mounting for 4K PL and implantation. The three solvents used, in order, are trichloroethylene, acetone, and isopropyl alcohol. The order is important in order that a solvent is soluble in the next liquid. When the order was altered for one sample from a large set of samples, the result was unexpectedly large blueshift, as shown in Figure IV-8. In this case, only the trichloroethylene was used, followed by a quick rinse in DI water. Since trichloroethylene is not soluble in water, a film of solvent and/or grease was likely left on the sample surface.

Proximity caps were used straight from the manufacturer's box, and were in an "epi ready" state (clean for epitaxial growth). Native oxides are in fact present on samples and/or proximity caps, although they are expected to be only 1-2 monolayers on GaAs and InP.

C – Growth Comparison Study

Introduction

Since the previous section proved that the RTA procedure has an acceptable reproducibility, the next stage is to determine the reproducibility of growth. To this end, a study was undertaken to compare the behaviour of several nominally identical wafers, including wafers which were grown by three different epitaxial techniques: metal-organic chemical vapour deposition (MOCVD), chemical beam epitaxy (CBE), and gas-source molecular beam epitaxy (GSMBE). Results of the thermal behaviour of the wafers are presented in this section, while the implantation-induced QWI is presented in the next chapter. It will be important to

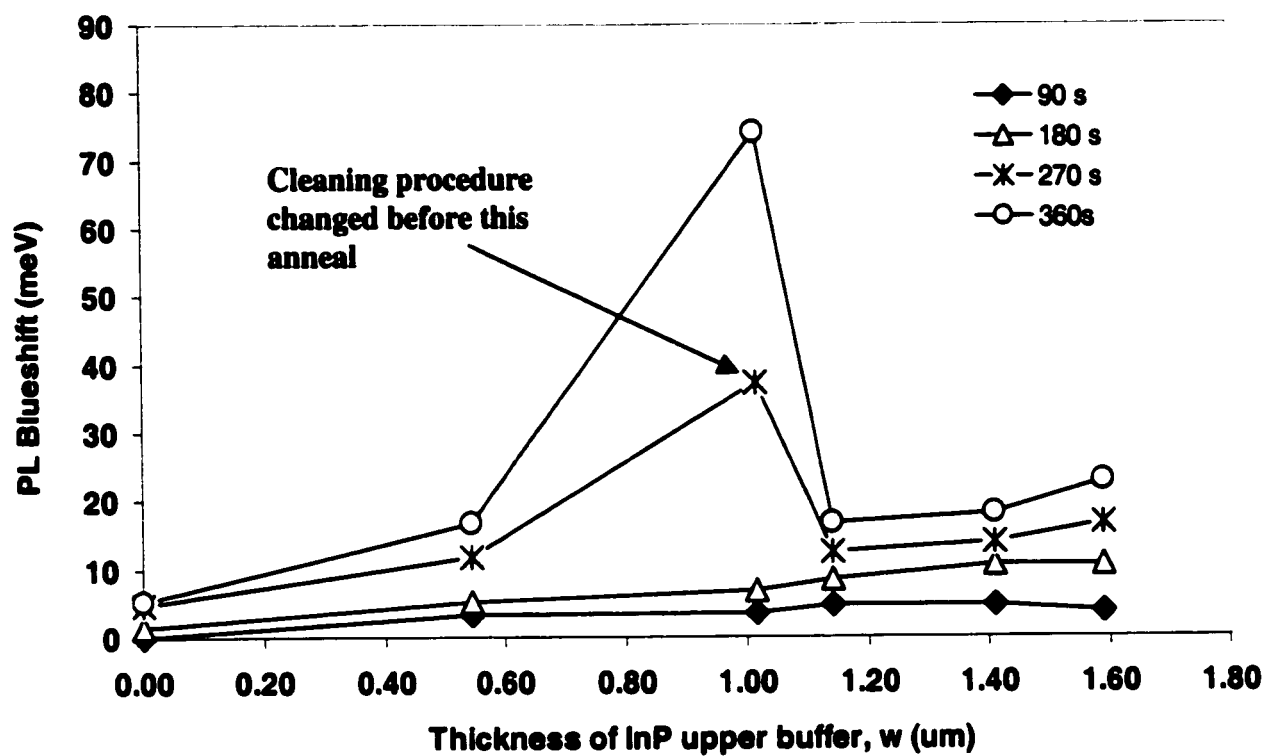


Figure IV-8: Example of how a surface film can affect QWI results. In this case the standard cleaning procedure was not followed for one of the samples halfway through a multi-anneal experiment.

understand any minor differences between wafers that may exist in their as-grown state. In the next few paragraphs, the key differences between the different growth mechanisms will be discussed, which is followed by analysis of the as-grown wafers.

Comparison of Growth Techniques

In chemical vapour deposition, gases containing the required chemical elements are made to react in the vicinity of the substrate on which the layer is to be grown. The gas pressure inside the chamber is relatively high ($\sim 10^{-2}$ to 100 torr) and the chemicals reach the surface by diffusion and viscous mixing. For growth of III-V alloys using MOCVD, metal-organic compounds like trimethyl gallium [$\text{Ga}(\text{CH}_3)_3$] and trimethylindium [$\text{In}(\text{CH}_3)_3$] are used as sources for the group-III, and a carrier gas (H_2) is passed through the liquid before entry into the chamber. The group-V sources are typically hydride gases such as arsine and phosphine, input directly into the chamber. Some of the chemical reactions, by which the group-III atom dissociates from the MO molecule and bonds with a group-V atom, occur in a boundary layer of gas above the substrate. Substrate temperatures are relatively high $\sim 600^\circ\text{C}$ in order to enable the chemical reactions.

In an MBE reactor, elemental beams of molecules [atoms, dimers, tetramers] are sent towards the substrate. The beams are created in a Knudsen cell, where the vapour from heated elemental solid source is released into the chamber. The chamber is held at a high vacuum, $\sim 10^{-6}$ torr during growth, such that the molecules can travel without collision towards the substrate. The substrate temperature is relatively low, to ensure that molecules stick to the substrate. There are no good *elemental* sources of P, making growth of InP by MBE rare. However, gas source MBE (GSMBE) allows for growth of InP by using hydrides gases as the group-V source (arsine can also be used for as the As source). The hydrides are cracked before the chamber, that is, heated such that they decompose leaving group-V monomers and dimers. Since the growth kinetics are controlled by the arrival of the group-III (as is true in all three growth techniques) the introduction of gaseous

group-V sources does not change the process as a whole, and thus the acronym MBE is still deemed to be applicable.

The third method of epitaxial growth, CBE, is a blend of the other two techniques. It uses most of the gas delivery systems of MOCVD in combination with the high vacuum chamber of MBE. The group-III portion of the system is similar to MOCVD, but no carrier gas is used. Instead, the group-III liquid is slightly pressurized, and the ensuing vapour pressure is directed to the chamber. Triethyl sources are more commonly used instead of the methyls sources due to a slightly different reactivity, which is better suited to CBE's slightly lower substrate temperatures. The group-V hydride gases are pre-cracked, as is done for GSMBE. Chemical reactions are initiated at the substrate surface, which is held at a reduced temperature in comparison to MOCVD (primarily because the group-V gas is now pre-cracked). Chamber pressures are around $\approx 10^{-4}$ torr during growth.

All three techniques have some advantages and disadvantages. Because MBE is a simple case of atoms diffusing along and bonding with a crystal surface, it is the simplest to model, and combined with the ability to do in-situ characterization of the growth surface, it has been popular in research laboratories. However, aging affects and limited availability of the elemental solid sources, as well as relatively slow growth rates, are its downsides. MOCVD systems are less expensive and have less downtime since they have no high vacuum, which also makes it easier to build large multi-wafer systems, and these all combine to make MOCVD very popular in industry. However, because complex gas flows occur within the chamber, it is very challenging to model, and instead precise growth depends upon empirical calibration runs. CBE systems are relatively newer and the least studied, but combine many of the advantages of both "parent" systems. The gas delivery allows for multi-wafer scale-up, which is much more challenging for GSMBE systems. Since the chamber is under vacuum, in-situ analysis is possible, and rapid removal of reactants from the chamber reduce memory effects, while the surface chemistry makes more efficient use of the group-V sources (which have

environmental concerns). CBE does however, have the strongest dependence on growth temperature, which can be both an advantage and a disadvantage¹². Higher incorporation of carbon and oxygen tend to occur in CBE growths (especially for GaAs/AlGaAs layers)¹³.

All three means of epitaxy are, in general, capable of producing high quality multi-quantum well heterostructures with excellent electrical mobility and abrupt interfaces (CBE^{13,14,15}; MOCVD¹⁶; GSMBE^{17,18}). Independent control of the flow rate of each source combined with precision timing allows for growth of alloys of desired composition and thickness. From the results published in the literature, quality, as measured by electrical and optical means, can be more dependent on the understanding and control of the reactor rather than the type of reactor. But since the sources used and mechanisms of growth are different, we theorized that there may be minor differences in the material (such as incorporation of impurities or native defects), which could result in differences in the thermal stability. One parameter that is potentially connected to defect incorporation is the growth temperature¹⁹ (T_{growth}) which is highest for MOCVD growth (since cracking must take place at the sample surface) and lowest for MBE (where a high sticking coefficient of the atoms is desired). The role of growth temperature within CBE growth was investigated in this thesis by including a wafer in which growth temperature of all the layers was specifically lowered by 20-25°C.

A further review of all three growth techniques, including a detailed explanation of CBE growth, is given by Davies et al.²⁰, while Veuhoff¹² does a nice comparison between MOCVD and CBE, and Pashley²¹ covers MOCVD and MBE.

Analysis of As-grown Wafers

The layer structure used in the study was a lattice-matched laser structure, as detailed in table IV-2, which was designed to emit at 1.53 μm . The nominal compositions for the QWs and barriers are $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ and $\text{In}_{0.74}\text{Ga}_{0.26}\text{As}_{0.57}\text{P}_{0.43}$, respectively. In total, three MOCVD wafers, three CBE wafers and one GSMBE

wafer are studied. The three MOCVD wafers differ only in their growth position – the wafers are herein labeled as 1L, 1T and 2T where the number indicates their run number, and L and T indicate a leading or trailing position within the gas flow of the two wafer reactor. Complete characterization of all three MOCVD wafers has not been done, but the wafer-to-wafer consistency is known to be very good for this MOCVD reactor. The three CBE wafers differ in more meaningful ways - doping and growth temperature, as will be detailed below. In the p-i-n doped wafers, the p-dopant in the upper buffer layers was Be for CBE and GSMBE wafers, and Zn for MOCVD wafers, while Si was the n-dopant in the lower buffer layers of all of the wafers. Two additional CBE wafers were undoped, with one grown at standard temperature and one grown at slightly reduced temperatures.

In this section, we review SIMS, PL, XRD, and TEM characterization of the wafers to confirm their exact layer structure. The doping, as verified by SIMS, had significant variations from the targeted values. In particular, p and n doping in the CBE wafer was lower than specified, while in the MOCVD wafers, there was a significant amount of p doping in the QW region, due to the commonly occurring Zn diffusion into the active region during growth of the upper cap (Zn exhibits a large concentration dependent diffusion rate^{22, 23}). The variations in thicknesses of the layers, as per TEM, were slightly greater than one would normally expect, but generally are acceptable. The one exception is that the uppermost InP layer in the CBE p-i-n wafer is thicker than was requested.

All wafers were grown on sulfur doped (n-type) substrates from the same manufacturer (Acrotec) in order to remove any effect that different substrates may have, although a quick test revealed no dependence on substrate manufacturer - the thermal-only blueshift of a sample from the GSMBE p-i-n wafer used in this study was compared with a second GSMBE p-i-n wafer grown on an InPact sulfur-doped substrate. Samples from both these wafers shifted by the same amount (10.8 ± 1 versus 11.7 ± 1 meV) after one anneal of 90 s at 700°C. This is not unexpected, since the key issue when comparing different substrates is the

Table IV-2 Layer structure for reactor comparison study, including key differences between wafers on a layer-by-layer basis.

Material (all lattice matched to InP)	Target doping (cm ⁻³)	Target Thickness	SIMS Measured Doping in p-I-n wafers (cm ⁻³)				TEM Measured Thickness in μm or nm (± 5 nm)				CBE Growth Temperature for I-I-I wafers (°C)	
			MOCVD p-I-n (1L)	CBE p-I-n	GSMBE p-I-n	MOCVD p-I-n (1T)	CBE p-I-n	GSMBE p-I-n	CBE Std I-I-I	CBE Std I-I-I	CBE Std I-I-I	CBE LT I-I-I
InGaAs	1×10^{19}	0.2 μm	Zn 2.2×10^{19}	Be 1.4×10^{19}	Be 7.6×10^{18}	0.218	0.162	0.201	0.130	0.130	515	490
InP	1×10^{18}	1.38 μm	Zn 1.0×10^{18}	Be 5.0×10^{17}	Be 1.4×10^{18}	1.227	1.750	1.234	1.432	1.432	485	465
InGaAsP	5×10^{17}	0.010 μm	Zn smoothly varying from 1.0×10^{18} to 2.0×10^{18}	Be 2.7×10^{17}	Be 1.4×10^{18}	0.011	0.010	0.011	0.010	0.010	485	465
InP	5×10^{17}	0.2 μm		Be 2.7×10^{17}	Be 6.5×10^{17}	0.188	0.296	0.221	0.221	0.221	485	465
InGaAsP	Undoped	50.0 nm				71.2	66.9	68.8	58.1	58.1	515	490
4x InGaAsP	Undoped	20.0 nm		$\sim 5 \times 10^{15}$ Be and Si	$\sim 5 \times 10^{15}$ Be and Si	20.8	18.2	20.6	17.6	17.6	515	490
5x InGaAs	Undoped	6.0 nm				6.2	5.5	6.3	5.5	5.5	515	490
InGaAsP	Undoped	70.0 nm				71.9	66.2	71.2	61.2	61.2	515	490
InP	1×10^{18}	1.5 μm	Si 5.0×10^{18}	Si 1.3×10^{18}	Si 1.3×10^{18}	not measured				485	485	465

Table IV-3 Summary of PL and XRD analysis of wafers in the reactor comparison study.

wafer	300 K PL peak wavelength ($\mu\text{m} \pm \text{nm}$)	4 K PL peak wavelength ($\mu\text{m} \pm \text{nm}$) ^a	XRD strain ^b	PL + XRD => well width ^c (nm) $\pm 0.2 \text{ nm}$	TEM well width (nm) $\pm 0.5 \text{ nm}$	TEM period (nm) $\pm 0.5 \text{ nm}$	XRD period (nm) $\pm 0.5 \text{ nm}$
MOCVD p-i-n (1L)	1.528 ± 10	1.416 ± 6	- acceptable L.M. of QW/B - overall strain is tensile	5.9 / 5.5	not done	not done	27.0
MOCVD p-i-n (1T)	1.532 ± 8	1.423 ± 8	not done	not done	6.2	27.0	not done
CBE p-i-n	1.532 ± 3	1.417 ± 5	- Excellent L.M. of QW/B - Very minor tensile strain in InGaAs cap	5.8 / 5.0	5.5	24.0	25.0 ^d
CBE Std i-i-i	1.540 ± 5	1.421 ± 3	- Excellent L.M. of QW/B - Minor compressive strain in InGaAs cap	6.2 / 5.2	5.5	22.7	21.0 ^c
CBE LT i-i-i	1.530 ± 5	1.417 ± 3	- Good L.M. of QW/B - significant broad strain in bulk layers (InGaAsP cladding?)	5.6 / 5.0	4.6	26.0	25.0
GSMBE p-i-n	1.564 ± 1	1.457 ± 5	- acceptable L.M. of QW/B (maybe overall tensile?) - Significant broad tensile strain in bulk layers	7.8 / 7.7	6.3	27.3	27.0

- ^a error on 4K PL is the standard deviation of peak wavelength found between sample used in the experiment
^b L.M. of QW/B means lattice matching of QW/barrier layers and their interfaces.
^c first number is from 300 K PL peak wavelength + X-ray strain, second is from 4 K PL + X-ray
^d no satellite peaks were evident on the as-grown material, period was derived from an intermixed sample

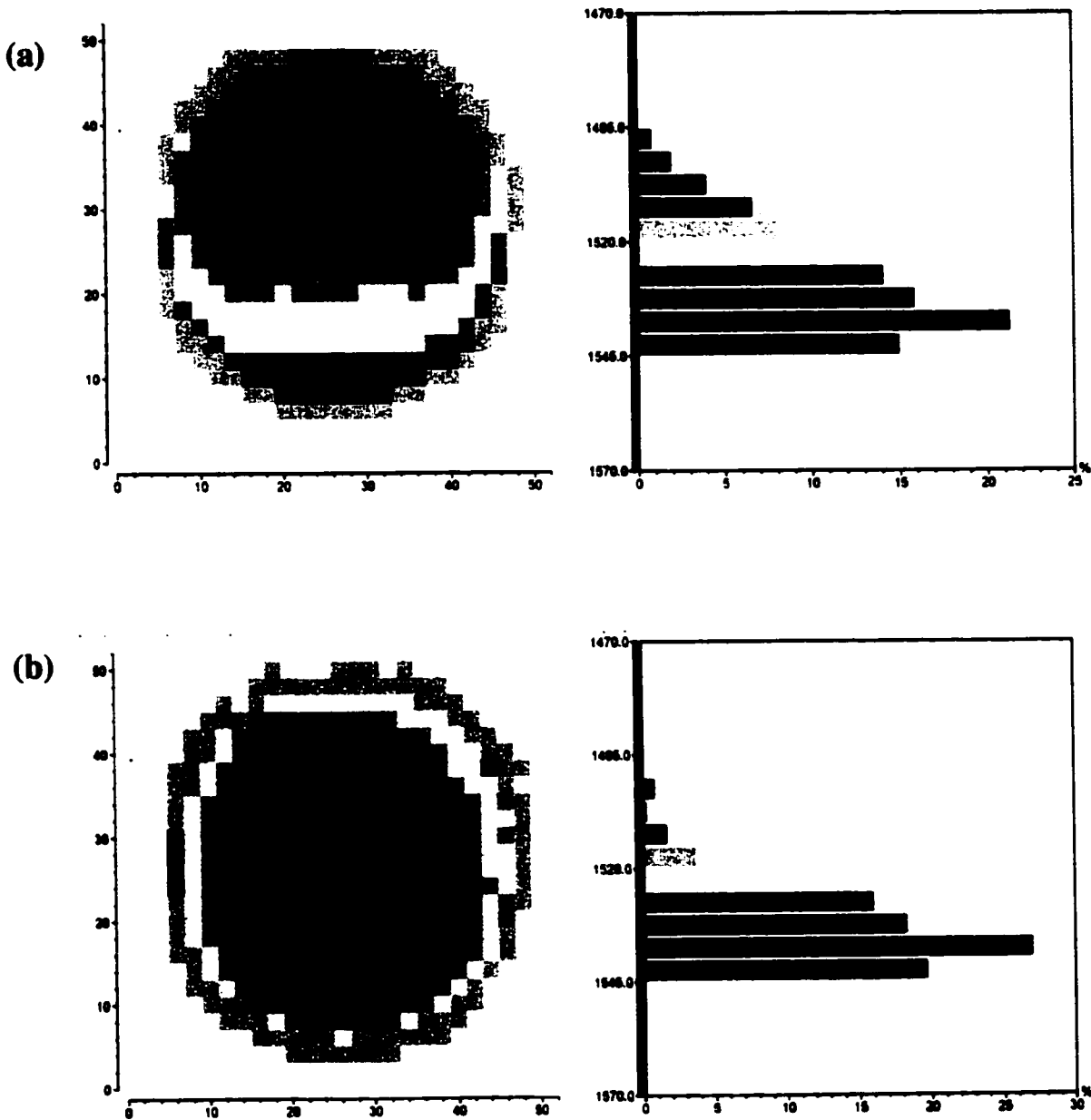


Figure IV-9: 300 K PL maps of the as-grown full wafer for (a) MOCVD p-i-n (1L) wafer and (b) MOCVD p-i-n (1T) wafer. Units of the histogram on the right hand side are nm, and each bin has a size of 5 nm.

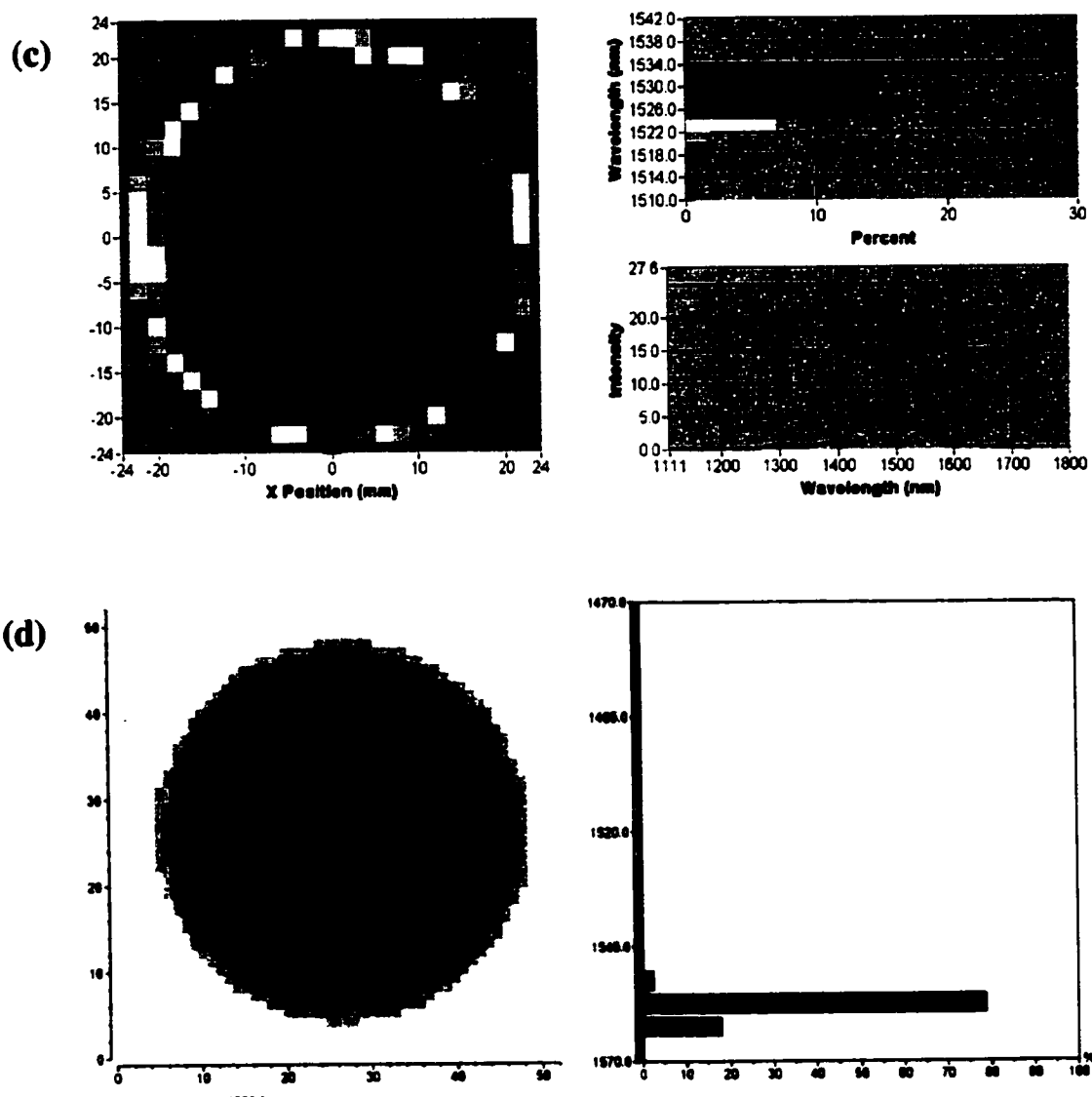


Figure IV-9 continued: 300 K PL maps of (c) CBE p-i-n wafer and (d) GSMBE p-i-n wafer. Units of the histogram on the right hand side are nm, and each bin has size of 5 nm.

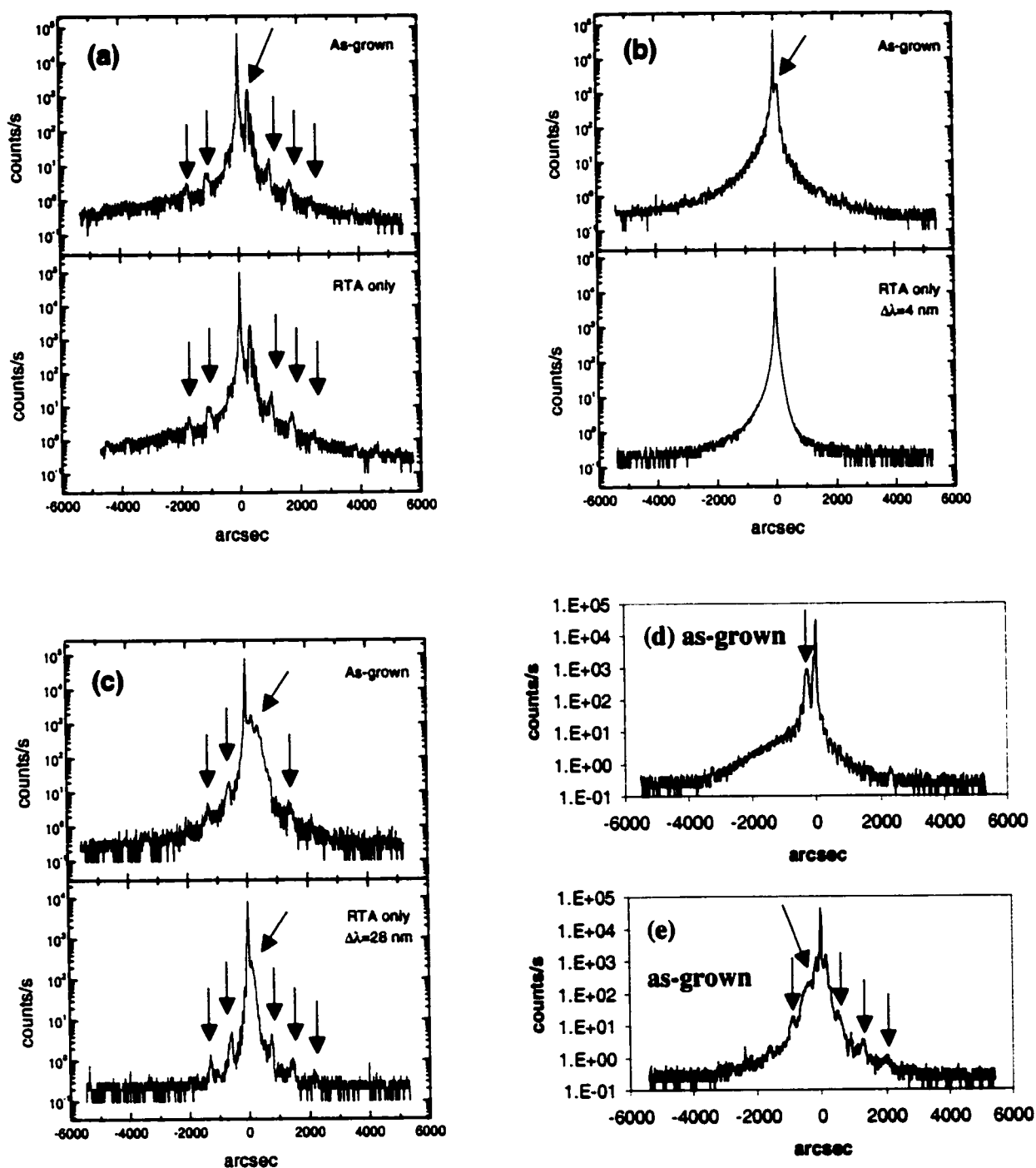


Figure IV-10: XRD spectra of the wafers (a) MOCVD p-i-n (1L); (b) CBE p-i-n; (c) GSMBE p-i-n; (d) CBE Std i-i-i; and (e) CBE LT i-i-i. Red arrows point to zero order diffraction peaks from the epitaxial layers, which were nominally suppose to be coincident with the central diffraction peak of the substrate (at 0 arcsec). Blue arrows point to higher order satellite peaks of the MQW stack. For (a) to (c) upper spectra are from as-grown samples, lower spectra are from samples annealed for 3x30s at 700°C. The InGaAs cap layer was removed for the lower spectra of (b) and (c).

dislocation or etch pit density^{24,25,26}, and both the Acrotec and the InPact substrates studied here were low etch pit density, which are the standard choice for optical components manufacturing. However, the substrate thickness was not the same for all wafers, the MOCVD growths used 500 μm thick substrates, while the CBE and GSMBE growths were on 350 μm thick substrates. This may have had an effect on some implantation results to be discussed in Chapter V.

A detailed list of the all the wafers is given in tables IV-2 and IV-3, including results of PL mapping, XRD, and TEM analysis. 300K PL maps, as shown in figure IV-9, generally indicated that the wafers are within specifications, with the exception that the GSMBE wafer emits at a longer wavelength than specified. The uniformity of the GSMBE wafers was excellent (± 2 nm), owing in part to the lack of temperature dependence of GSMBE growth. The uniformity of the CBE wafers was good (± 5 nm) with a radial symmetry, while the uniformity of the MOCVD wafers was inferior (± 10 nm), due to the fact the wafers were not rotated during growth.

XRD spectra of the principal wafers are shown in figure IV-10. All growths exhibited acceptable lattice matching of the MQW stack, as per the weakness of the satellite peaks in XRD spectra (the CBE wafer in particular has excellent lattice matching of the MQW stack). By knowing the strain in the QWs (and from the spectra we can assume lattice matched or near lattice matched composition for the QW), and using the measured PL transition energies, we can calculate the QW widths for each structure, as tabulated in table IV-3. The QW widths were within 0.3 nm of the targeted width (6.0 nm) for both the CBE and MOCVD wafers, while the QW of the GSMBE wafer was a bit wider at 7.8 nm. A larger well width should mean that this wafer will exhibit slightly less blueshift compared to the others, given identical processing. The measurements of the QW/barrier period by TEM and XRD exhibited excellent agreement with each other, and only small deviations from the targeted period of 26.0 nm. TEM measurements of the QW widths agreed quite well with the calculated values, but a discrepancy between the two values existed for the GSMBE and CBE LT i-i-i wafers. Some minor discrepancies may be

expected, since we are not taking into account strained layers in the QW/barrier interfaces in our calculations²⁷. However, the two wafers with the largest disagreement also showed a significant amount of strain in the bulk layers (red arrows on figure IV-10 (c) and (e)), while the broadness of these peaks indicate a variation in composition within the bulk layers. This may indicate an overall reduced quality of the growth in these two wafers.

Annealing Results

Wafers were cleaved into 5x5 mm pieces and each sample was annealed for 30 s at a different temperature. Samples were analyzed by PL at 4K and by PL mapping at 300K, followed by a cleaning and a repeat anneal for another 30 s at the same temperature. Figure IV-11 shows the resultant blueshifts for all the wafers after 30 s (a), the additional blueshift during the second and third anneal, (b) and (c), and the total blueshift during the $3 \times 30 \text{ s} = 90 \text{ s}$ (d). The thermal stability of the CBE p-i-n and the MOCVD wafers (1L and 1T studied here) was excellent – all exhibited less than 5 meV blueshift after 90 s of annealing for temperatures up to 750°C. The stability of the GSMBE p-i-n wafer was a bit more suspect, showing a significant blueshift for temperatures of 675°C and higher. Most of this shift occurred during the first 30 s anneal, indicating that there must be something in the epitaxial material which is not at thermal equilibrium, as will be further discussed shortly.

The CBE Std i-i-i wafer also showed acceptable stability (insignificant shifts below 700°C), however the shifts were larger than that of the CBE p-i-n wafer. This may indicate that the doping had an effect on the creation and/or motion²⁸ of defects. A further discussion on the effects of doping is contained in Chapter V, during the analysis of implantation-induced blueshifts.

The CBE LT i-i-i wafer undergoes an enormous blueshift, and similar to the GSMBE wafer, the shift is largest during the first 30 s of RTA compared with subsequent RTAs. This transient enhanced diffusion indicates that a non-equilibrium process is

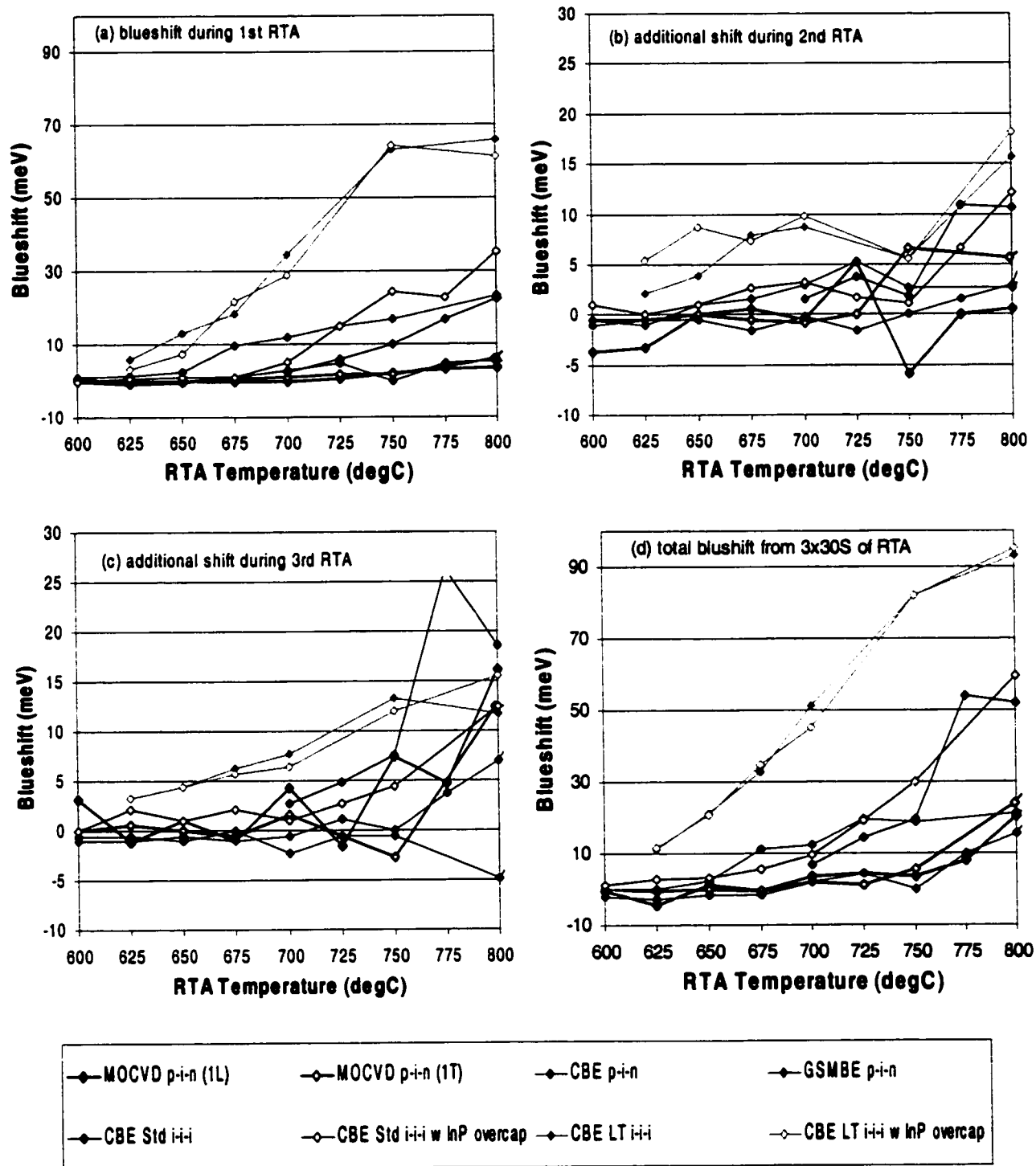


Figure IV-11: Knee curves for nominally identical wafers from growth comparison study (a) blueshift measured after 30s of annealing (b) additional blueshift from second 30 s anneal; (c) additional blueshift from third 30 s anneal; (d) total blueshift from 3x30 s of annealing.

occurring in these wafers. There are two likely non-equilibrium mechanisms: (a) excess defects presence in one or more of the layers, or (b) a change from non-homogeneous (non-stable) QWs to more homogenous ones. For case (a), the presence of a large number of excess point defects in the as-grown material will cause a surge in intermixing, and depending on the rate of diffusion of the defects, they could be in the QWs and/or in the bulk buffer layers. The broad strain peaks observed in the bulk peaks of the XRD spectra may be connected with a non-optimal growth. For case (b) the homogenization of the QW composition via diffusion along the plane of a QW, could result in an increase in the PL energy emitted. This is because the excited carriers will tend to find the regions of the QW with the lowest bandgap energy, and the emitted luminescence of the as-grown structure would be more representative of these regions. After in-plane homogenization, the luminescence would increase towards the average bandgap energy of the layer. However, the changes to the in-plane variations must have a length scale larger than the exciton radius in order for this effect to be observed, since composition variations smaller than the exciton radius will be averaged out by the exciton. Excitonic radii in InGaAsP alloys are ~ 20 nm in bulk²⁹ (and even larger in the InGaAsP QWs), but QWI interdiffusion lengths are found to be of the order of 1-2 nm, which is certainly smaller than the exciton radius. Additionally, TEM analysis on some of the samples studied here, as well as other InGaAsP QW samples, have shown in-plane variations of only 1.0 nm or less³⁰ in as-grown samples (some of which does get averaged out during QWI). Thus, we do not believe that (b) has caused the observed blueshifting. Additionally, the results presented in the next section provide clear evidence that possibility (a) did occur.

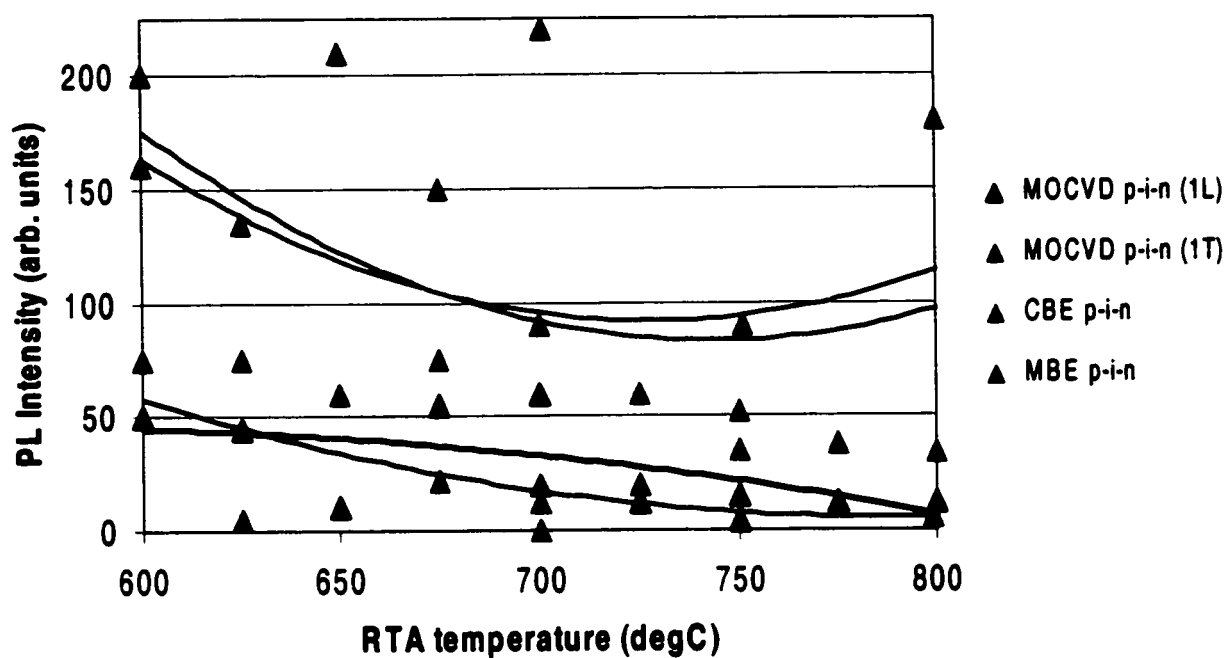
There are two additional curves (with open symbols) on each graph in figure IV-11; these samples had an extra 0.1 μm InP overcap on top of the standard InGaAs cap found in all other samples. In fact, several of the wafers originally had this extra InP layer, used to protect the sample during initial characterization, but it was removed by selective wet etch prior to these studies. But for a set of samples from each of the CBE Std i-i-i and CBE LT i-i-i wafers, it was left intact. During annealing, these

samples were protected with an InP proximity cap (versus GaAs for the InGaAs terminated samples). As can be seen in figure IV-11 (d), the presence or absence of the InP overcap does not significantly affect the blueshift for either of the wafers. Thus the differences in the “flavour” of the surface overpressure of group-V that has been provided to these samples has had no effect on the observed blueshift.

The measured PL intensity (obtained from the PL map data) after anneals totaling 90s are shown in figure IV-12. The PL intensity varied from one wafer to the next in the as-grown samples, therefore a comparison of the PL intensity of the processed wafers should not normally be done, however, there are three trends that are significant and fair to comment on:

1. The intensity of the p-i-n wafers was much weaker than the i-i-i wafers (this was true of the as-grown samples also), because the internal electric field in the p-i-n structures tends to pull carriers away from the QWs, thereby reducing carrier recombination rates. It does not necessarily reflect a difference in quality of the wafers. At the laser excitation intensities used in these experiments, a sufficient number of carriers are produced to overcome the internal electric field and thus create flat band conditions. The power used is not much above this threshold, and thus PL intensity for these samples will be sensitive to overall doping of the structure.
2. The PL intensity generally decreases as the RTA temperature increases, which may be due to damage at the surface, indicating that our method of group-V overpressure may not be sufficient for the protection of the surface as the RTA temperature is increased. The dependence is obvious for the i-i-i wafers, but not readily apparent for the p-i-n wafers, presumable because of issues mentioned above.
3. For the CBE LT i-i-i wafer, the presence of the InP overcap did not seem to affect the PL intensity after annealing, which seems to indicate that group-V overpressure for an InP terminated samples can be well controlled, as long as

(a)



(b)

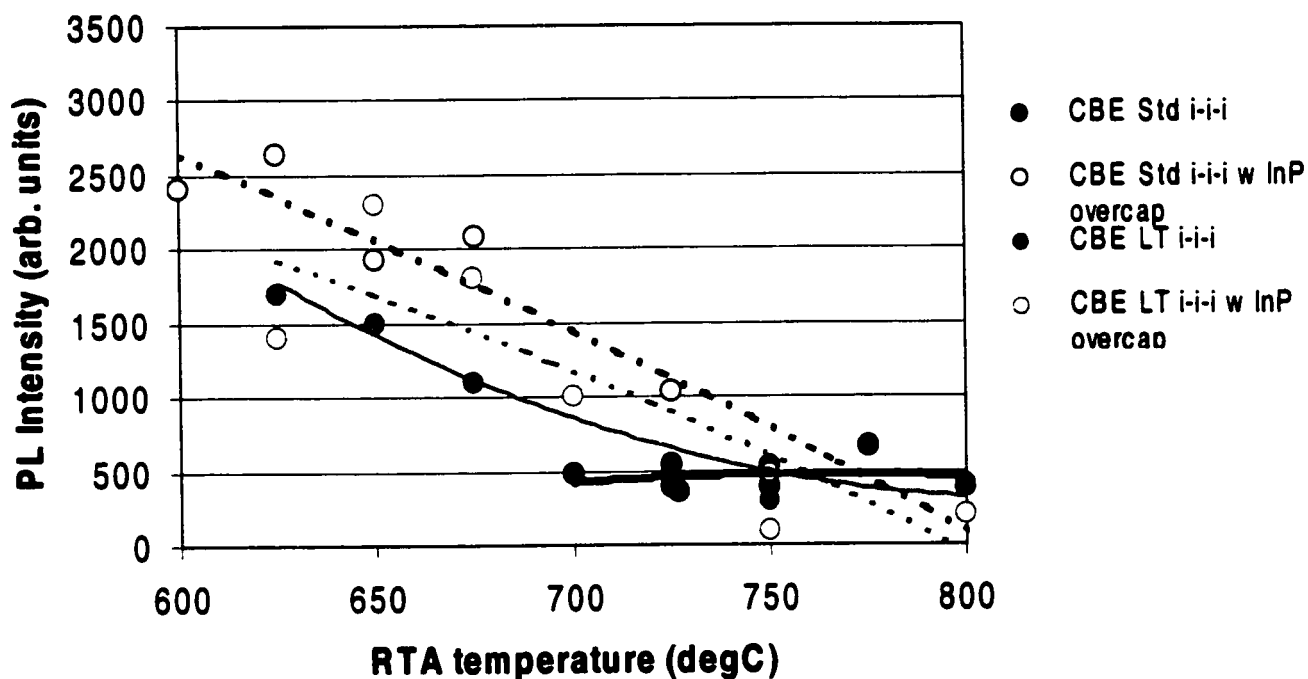


Figure IV-12: Intensity of the PL peak after 3x30s anneals (a) for p-i-n wafers and (b) for i-i-i wafers. Lines are included to help guide the eye.

an InP proximity cap is used. The data from the CBE Std i-i-i wafer is less complete and therefore it neither supports nor contradicts the behaviour of the LT wafer.

SIMS profiles of three p-i-n wafers, shown in figure IV-13, indicate that some diffusion of the p-dopants has occurred during an anneal at 700 °C for 3x30 s. The MOCVD p-i-n 1L wafer has the most diffuse p-dopant profile, but this Zn diffusion occurred during growth, and it is difficult to say whether more diffusion occurred due to the anneal. The dopant diffusion due to annealing is the most evident in the GSMBE p-i-n wafer. Recall that this wafer was the only wafer to exhibit interdiffusion of the QWs, thus there may be a correlation between dopant diffusion and amount of interdiffusion. It is difficult to say whether any dopant diffusion has occurred in the CBE and MOCVD p-i-n 1L wafers due to annealing. The QW blueshift in these samples is small, but one would expect that samples that were significantly blueshifted (due to grown-in defects or implantation, for example) would likely exhibit more dopant diffusion. Even then, it is not expected that the dopant motion is very severe, since in a previous study on material that was significantly blueshifted (via implantation) no changes occurred in the laser threshold current, the differential quantum efficiency³¹, or diode reverse current. However, dopant diffusion of the order observed here could have a measurable affect on modulation-doped structures.

The diffusion profiles for the p-dopant in all three wafers appear to be non-Fickian^{32,33} in the following manner: at the InP/InGaAsP interfaces, there is some depletion of the dopant within the InP³⁴ and accumulation of it in the InGaAsP (denoted by green arrows), presumably due to a higher solubility of Zn in InGaAs(P)³⁵, although SIMS artifacts could also cause unusual profiles at an interface, and should not be ruled out.

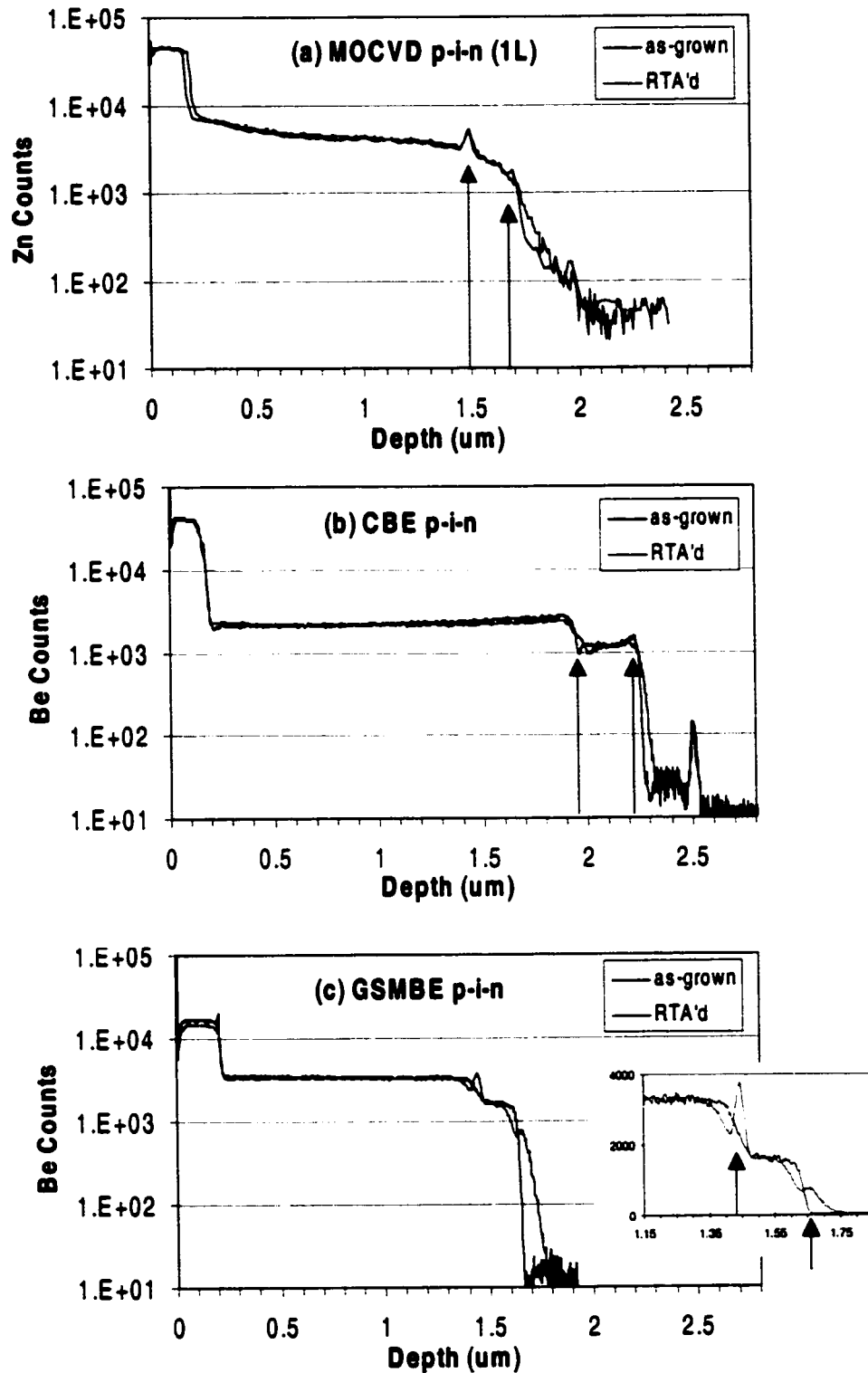


Figure IV-13: SIMS depth measurements of the p-dopants for three p-i-n wafers both before and after an anneal of 3x30 s at 700 °C. Light green and dark green arrows indicate the position of the InGaAsP etch stop layer, and the start of the nominally undoped InGaAsP active core, respectively. The inset of (c) shows a blow-up of the GSMBE profile in the vicinity of the etch stop and MQW.

Summary

In summary, this study has shown that CBE material can be of equal quality to MOCVD in terms of the thermal behaviour of the QWs. This will allow for transfer of QWI results between CBE growth and MOCVD growth. The GSMBE material exhibited less stability, and this was attributed to non-optimal growth resulting in an excess of point defects. Multiple anneals were necessary to make this conclusion. The instability may be related to the lower growth temperature of the GSMBE versus CBE and MOCVD, although the quality of this GSMBE material may be improved with adjustments to the growth parameters. The dramatic blueshift that occurred in CBE material when the growth temperature was dropped by 20-25°C indicates that subtle differences between like structures can have important consequences. A further look at the dependence on CBE growth temperature will be covered in the next section of this chapter.

A possible correlation between doping and blueshift was observed when comparing the CBE p-i-n and i-i-i wafers, and this should be studied in more detail in the future. Finally, small amounts of dopant motion may have occurred during the RTA, whose effects on device operation should be assessed.

D – Low Temperature Growth

Introduction

In the previous section we saw how the thermal behaviour of material can vary with growth temperature, and we postulated that it is due to an excess of grown-in defects. We will now specifically study them (a) in order to learn more about them and possibly learn how to avoid them, (b) information gained from the grown-in defects may be transferable to the implantation-created damage (as analysis proceeded it appeared that the type of intermixing taking place was similar to that of implantation-induced intermixing, and thus the same defect might be the mediator of intermixing in both cases) (c) introducing defects during growth may be an alternative to the use of implantation, and thus it could be a new means of QWI.

This has previously been suggested by others, but only in the case of GaAs-based structures grown at very low temperatures by GSMBE^{36,,37}.

This section further explores the effects that grown-in defects have on QWI. Most of the analysis is on a new pair of CBE grown wafers, which comprise an undoped lattice-matched structure with InGaAs/InP QW/barriers. In the LT wafer, the growth temperature of only an upper InP buffer is lowered (thus the QWs and barriers in both wafers are identical in all respects). The advantages of this structure over the previous laser-like structure are three-fold:

1. The use of ten QWs improves the signal strength in XRD and optical transmission analysis, allowing us to learn much more about changes to the QW following intermixing.
2. We know the exact location of the grown-in defects (uniformly distributed in the upper InP buffer), and thus we can model their motion to the QW. We will assume that there is only one type of intermixing-causing defect in the LT layer. This is a particular advantage over studies on implantation, which creates a complex and poorly understood distribution of many types of defects.
3. The XRD spectra of this new LT wafer is very good, as shown in figure IV-14 (b), exhibiting good lattice matching of the bulk layers and typical satellite peaks relating to minor lattice mismatch at QW/barrier interfaces (in comparison, the two wafers with thermal instabilities in previous section had unsatisfactory amounts of broad strain in the bulk layers).

Additional Std and LT wafers which had only bulk InP (no QWs) were also used in this study when performing Hall measurements and PL analysis of the bulk properties. Researching the topic of grown-in defects has been very fruitful, and results have been published in three papers, which will be briefly summarized here, and subsequently included to form part of the material of this chapter. Many of the references for this study are listed within the papers. Additional analysis of optical transmission results follows the papers, including a discussion on different

intermixing models. XRD analysis was also performed on the same samples as in these papers, providing further evidence in support of the conclusions drawn in the papers – this work is included after the papers.

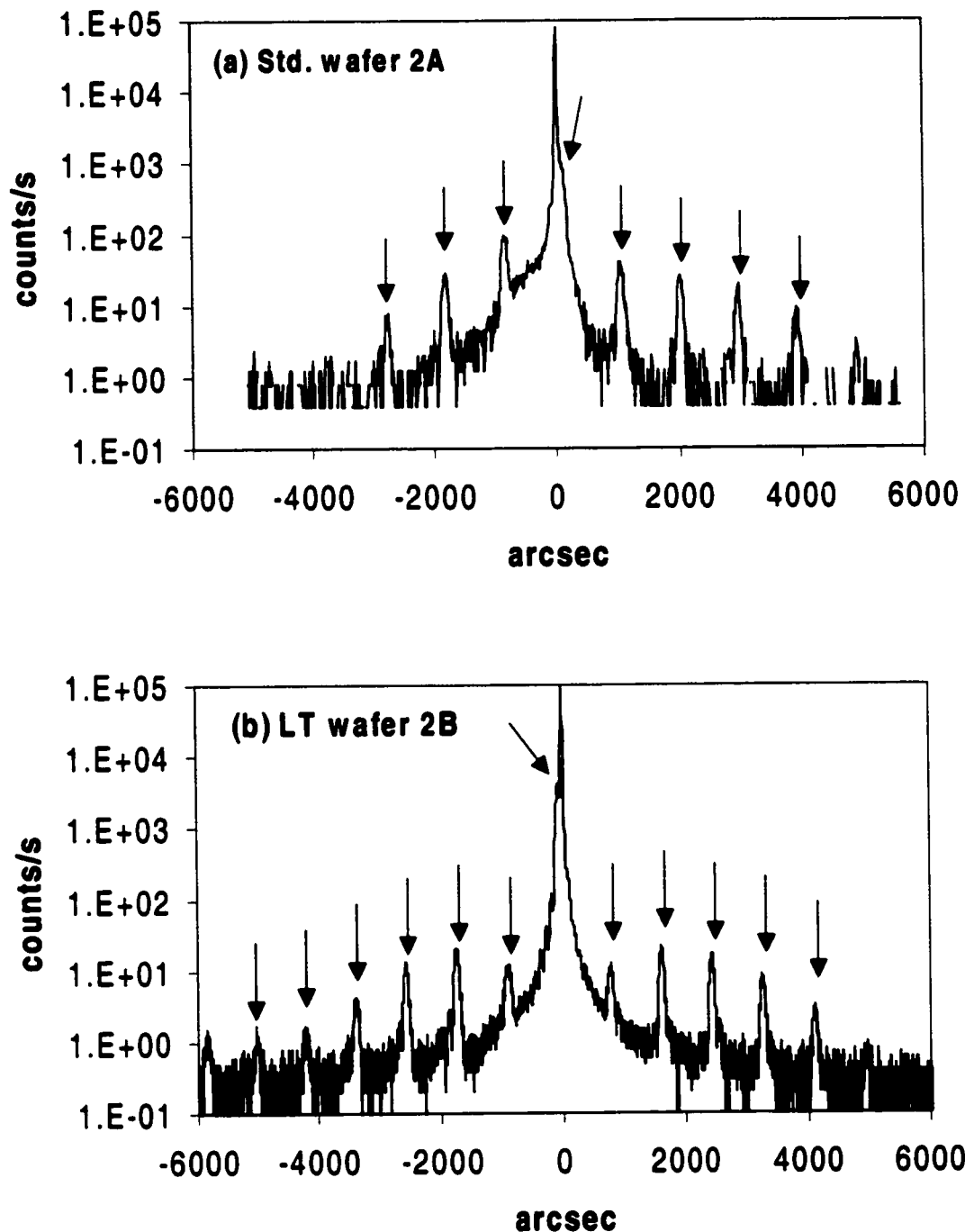


Figure IV-14: XRD spectra of as-grown samples for the LT growth study. Red arrows point to zero order diffraction peaks from the epitaxial layers, which were nominally lattice matched to the central diffraction peak of the substrate (at 0 arcsec). Blue arrows point to higher order satellite peaks of the MQW stack, due to small lattice mismatch at the interfaces between the QW and barrier layers. The position and intensity of all of these fall within acceptable characteristics for lattice matched structures.

Paper 1 (JAP)

J. E. Haysom, G. C. Aers, S. Raymond, and P. J. Poole; A Study of Quantum Well Intermixing Caused by Grown-in Defects; J. Appl. Phys. 88, 3090, 2000.

Knee curve results illustrate how small variations in T_{growth} can affect QWI (results from the CBE Std and LT i-i-i wafers from the previous section are included in addition to knee curves from the new InGaAs/InP Std and LT wafers). Normal incidence optical transmission is also performed on the samples, which gives the energy of both the heavy and light hole transitions for a set of samples shifted up to 188 meV. By analyzing the splitting between the two states as a function of intermixing (blueshift of the hh), we determine that tensile strain must be developing in the center of the well. Comparing the results with output from the intermixing theoretical calculations, we determine that the ratio of the group-V to group-III interdiffusion lengths (k) has a value between 2 and 4. Most aspects of this paper (experiments, analysis, writing, etc.) were performed by the author of this thesis. Epitaxial growth was by P.J. Poole.

Study of quantum well intermixing caused by grown-in defects

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We show that the degree of thermally induced quantum well intermixing is dependent on the growth quality of epitaxial layer structures. Two different undoped quantum well/barrier structures are studied: an InGaAs/InGaAsP 1.5 μm laser-like structure, and an InGaAs/InP structure. In both cases, the temperature of growth of one or more layers is altered and results compared with a control wafer. Wafers with material grown at the lower temperature display blueshifts of up to 80 meV in the QW emission energy during the early stages of rapid thermal annealing. Wafers grown at temperatures that are more standard exhibit excellent stability. We examine shifts of both the heavy hole and light hole transitions as a function of intermixing via transmission measurements, and conclude that interdiffusion occurs primarily on the group V sublattice. © 2000 American Institute of Physics. [S0021-8979(00)04417-0]

Quantum well intermixing (QWI) is a post-growth processing technique that allows for the monolithic integration of different optoelectronic devices. It is used to alter the band gap in selected areas of a quantum well heterostructure, via the deliberate interdiffusion (intermixing) of atoms at the quantum well/barrier interfaces.¹ One method of performing this interdiffusion in a selective manner is to use shallow ion implantation followed by a rapid thermal anneal (RTA).² In this technique the implantation of nonimpurity species (into regions above the QWs) creates a surplus of lattice defects. It is the motion of these defects through the QWs that enhances the interdiffusion of the QW/barrier material. The temperature of the RTA must be hot enough to allow these defects to diffuse from the damaged region through the QWs, and also repair the implantation damage. However, if it is too hot, a large equilibrium generation of lattice defects occurs in non-implanted regions, resulting in unwanted intermixing. Thus, it is important to know the thermal behavior of as-grown material in order to properly select the RTA conditions. Other QWI techniques, such as the use of patterned dielectric cap(s) during RTA to enhance or suppress the creation of defects at the surface, and direct write laser annealing also require understanding of the thermal stability of the starting material.

In this communication we examine how the thermal stability of InP-based heterostructures depends on the epitaxial growth temperature, including an examination of the dynamic nature of the intermixing, the associated strain development and its effects on optical transitions.

All material in this study was grown by chemical beam epitaxy (CBE) in which the temperature of the substrate was measured by a pyrometer. The first structure studied (wafers 1A and 1B) was a 1.5 μm laser-like structure consisting of five InGaAs quantum wells separated by InGaAsP barriers, and surrounded by InP. The growth temperature (T_{growth}) for

all layers of wafer 1B were lower by 20–25 °C than for the growth of wafer 1A, as listed in Table I. The second structure (wafers 2A and 2B) consists of ten InGaAs quantum wells, with InP barriers, and InP cladding. For wafer 2B, the growth temperature of only the upper InP cladding was reduced (by 35 °C) in comparison to wafer 2A, as listed in Table I. All layers were nominally undoped and lattice matched, and grown on S-doped InP substrates. Photoluminescence (PL) maps performed at 300 K showed good uniformity for all wafers.

Wafers were cleaved into 5×5 mm pieces for annealing, and one sample per wafer was annealed at a given temperature for several 30 s anneals. Anneals were performed using thermocouple temperature control and N₂ purge gas, and samples were surrounded and capped using sacrificial GaAs material to protect the edges and top surface from desorption of As. PL maps were performed on each sample before the first anneal and after each subsequent anneal. From these measurements, we derive the thermally induced blueshifts of the PL peak as a function of temperature and time, as shown in Fig. 1.

In Fig. 1(a), the high thermal stability of wafer 1A is obvious, showing no shift for RTAs of 700 °C or lower, while wafer 1B undergoes significant blueshifting within the first 30 s of RTA, even at a temperature of 650 °C. This severe blueshifting does not continue to the same degree during subsequent thermal treatment, with small additional shifts of 5–10 meV occurring during the second and third 30 s RTAs. This enhancement of the intermixing during the early stages of annealing can be explained by the presence of nonequilibrium defects, created in the material during growth. This population of grown-in defects is transient. During the anneal, as they move through the material, their numbers quickly diminish due to absorption or trapping at various possible defect “sinks,” such the substrate and the sample surface.

The impact of grown-in defects in the QWs has been reported by Gillin³ in an InGaAs/GaAs structure grown by molecular beam epitaxy (MBE), where he shows that an in-

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TABLE I. Layer structure for wafers used in the study, including the temperature of the substrate during growth and nominal layer thicknesses.

Layer	Thickness (nm)	T_{growth} (°C)	
		Wafer 1A	Wafer 1B
InGaAs cap	200	515	490
InP upper buffer	1380	485	465
InGaAsP etch stop	100	485	465
InP upper buffer	200	485	465
InGaAsP cladding	70	515	490
InGaAs QWs $\times 5$	6	515	490
InGaAsP barriers $\times 4$	20	515	490
InGaAsP cladding	70	515	490
InP lower buffer	1500	485	465
		Wafer 2A	Wafer 2B
InGaAs cap	30	505	505
InP upper buffer 2	1600	505	470
InP upper buffer 1	25	505	505
InGaAs QWs $\times 10$	5	505	505
InP barriers $\times 9$	17	505	505
InP lower buffer	300	505	505

creased diffusion at short anneal times can be correlated to T_{growth} of the QWs. Unfortunately, two variables were changing at the same time in his structures, T_{growth} and composition. In this study, since the compositional structure of each wafer pair is nominally identical, the measured blueshifts are directly comparable, with T_{growth} being the only difference between wafers.

Wafers 1A and 1B, differed in the T_{growth} of all layers. Even if we assume that grown-in defects are distributed evenly throughout these layers, it is still unclear whether it is just defects at the QWs, or defects in other epitaxial layers that play a role in the intermixing. This detail was investigated using wafers 2A and 2B, which differ only in the T_{growth} of the upper InP cladding layer. The PL blueshifts of wafers 2A (2B) are qualitatively similar to wafers 1A (1B). Wafer 2B exhibited significant blueshifts, especially during

the first RTA, while wafer 2A was very stable to temperatures up to 750 °C. From the data, it is evident that the thermal stability of the QWs can be affected by epitaxial layers that are spatially separated from the QWs. As a further test, the low T_{growth} buffer layer was removed from a sample of wafer 2B and during a subsequent anneal the sample was found to be very stable. Other authors^{4,5} have also seen this phenomenon in AlGaAs/GaAs structure where the T_{growth} of a nearby GaAs layer was 200 °C. We have performed multiple anneal studies on many other InP-based wafers, including *p-i-n* doped structures and MBE and MOCVD growths occasionally observing decreased thermal stability. We therefore believe that the possibility of grown-in defects can be a concern for any InP-based structure.

We have performed normal incidence transmission measurements at 5 K on samples from wafer 2B. Spectra of the absorbance, obtained using a similar *n*-type substrate as the reference, are shown in Fig. 2(a). In the as-grown sample (spectrum i) we attribute the low energy peak to the QW $n = 1$ electron to heavy hole transition (hh), and the next resonance to the QW $n = 1$ electron to the light hole transition (lh). A weak resonance at ~ 1.17 eV in all spectra, due to an $n = 2$ electron to $n = 2$ heavy hole transition, becomes sharper with intermixing, as expected from theory since the $e2$ level becomes bound after ~ 60 meV of blueshift. All resonances are fairly weak since only a small amount of material (ten QWs) is available for absorbing, however it is evident that the energy difference between the hh and lh transition (the hh–lh splitting) has decreased in the slightly intermixed samples (spectra ii and iii) to the point where the hh and lh overlap in spectra iv. In the more highly intermixed samples (spectra v and vi), the slope of the band edge has changed, leading us to believe that the lh (which is expected to be a weaker resonance) may now be the lowest transition.

The interdiffusion process was modeled assuming independent Fickian behavior for the groups III and V sublattices.⁶ We define the ratio of the group V to group III diffusion lengths as k ; local strain develops when k is not equal to 1. The compositional profiles from this model were used to calculate the hh and lh energies.

Experimental values of the hh–lh splitting, derived from the absorbance measurements, are plotted as a function of the hh shift, in Fig. 2(b), together with theoretical curves for different values of k . The data indicate that $k > 1$, and that k is best described by a value between 2 and 4, although it is difficult to distinguish for $4 < k < \infty$. For a value of $k > 1$ the center of the QW becomes tensile, and the edges of the QW compressive. Our interpretation of the hh and lh positions of the more heavily intermixed samples (v and vi) is more contentious, since the tensile strain development at the center of the QW is strong enough that off-zone center contributions to the transition may need to be considered. It is also feasible that for these samples (which were annealed at 725 and 750 °C, respectively) the k value may represent a combination of intermixing due to nonequilibrium defects as well as a (smaller) contribution due to equilibrium generation of defects, since for RTA temperatures of 725 °C or more, we observe consistent (but small) shifts in all wafers. Neverthe-

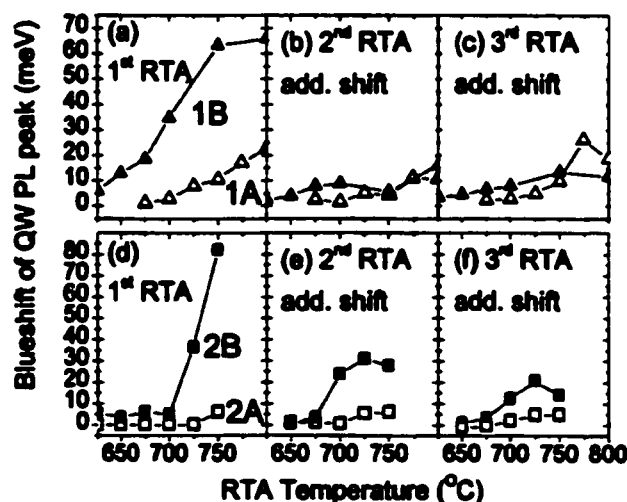


FIG. 1. Blueshift of the QW photoluminescence peak energy as a function of RTA temperature for wafers 1A and 1B (a)–(c), and wafers 2A and 2B (d)–(f). (a) and (d) show the shift that occurred during the first 30 s RTA, while (b) and (e), (c) and (f), show the additional shift that occurred during a second, and third 30 s RTA.

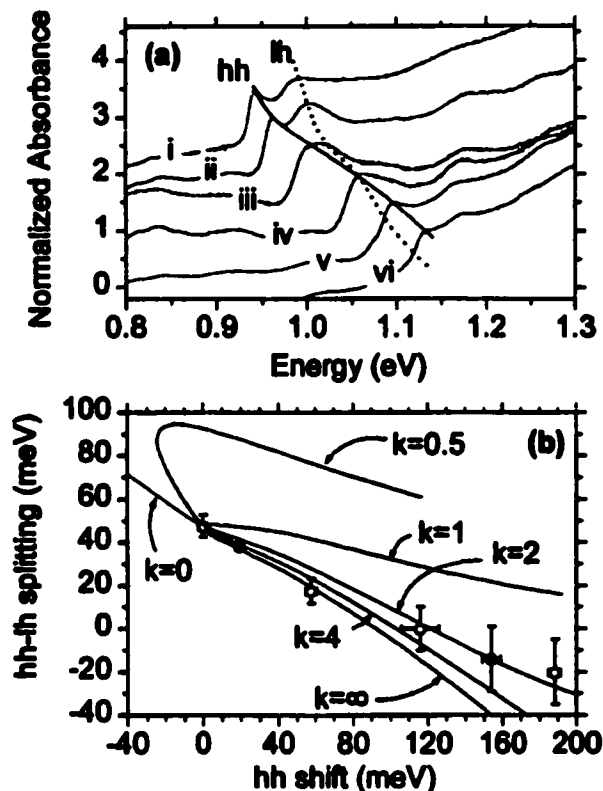


FIG. 2. (a) Normalized absorbance spectra for samples from wafer 2B (i) as-grown, (ii) annealed at 650 °C for 360 s, (iii) annealed at 675 °C for 360 s; (iv) 700 °C; (v) 725 °C; and (vi) 750 °C. (b) Measured values and theoretical curves for the energy difference between the QW heavy hole (hh) and light hole (lh) transitions as a function of the hh transition energy. Curves are calculated using error function intermixing assumptions using a range of values for k (defined as the ratio of diffusion lengths of the group V sublattice over the group III sublattice).

less, the reduction in the splitting in spectra i–iv of Fig. 2 clearly indicate $k > 1$. It is important to note that results from ion implantation-induced intermixing (where the ions are implanted above the QWs)^{7,8} and from dielectric cap intermixing⁹ also indicate that $k > 1$. This suggests that many different techniques used to induce intermixing may be mediated by the same mobile defect.

In conclusion, nonequilibrium concentrations of defects may be grown in to epitaxial layers if the growth temperature is reduced by a small amount. These defects appear to be highly mobile, and cause an initial surge of intermixing, even when located in layers separated from the QWs. By performing multiple anneals one can confirm the presence or absence of these defects, which is an important consideration for any diffusion study. For investigations that rely solely on the thermal treatment of samples, the background defect concentration must be understood to avoid erroneous results. The interdiffusion due to the grown-in defects occurs predominantly on the group-V sublattice. The diffusion dynamics of these defects will be discussed in a forthcoming paper.

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Paper 2 (IPRM)

J. E. Haysom, P. J. Poole, G. C. Aers, S.J. Rolfe, S. Raymond, I. V. Mitchell, and S. Charbonneau; Quantum well intermixing caused by non-stoichiometric InP; oral presentation and paper at the 12th International Conference on Indium Phosphide and Related Materials, Williamsburg, Virginia, May 14-18, 2000.

This paper discusses the identity of the grown-in defects using SIMS analysis of impurities, PL analysis of defect states and Hall conductivity results, as well as a significant review of relevant literature. The paper concludes that the LT material is rich in P, and likely contains P antisites that account for the increased n-type conductivity. We propose that the P antisites would convert during the annealing, releasing P interstitials that preferentially intermix the group-V sublattice of the QWs. Most aspects of this paper (experiments, analysis, writing, etc.) were performed by the author of this thesis, while Hall and SIMS measurements were performed by P.J. Poole and S.J. Rolfe, respectively, and epitaxial growth was by P.J. Poole.

QUANTUM WELL INTERMIXING CAUSED BY NON-STOICHIOMETRIC INP

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We study the thermal stability of InP-based quantum well hetero-structures in which the temperature of growth of one or more layers is slightly reduced in comparison to standard growth. We examine the enhancement of quantum well intermixing (QWI) using repeated isothermal anneals, and show that the enhancement is a transient effect due to a surplus of mobile defects grown-in to the low temperature (LT) layers. These defects are related to a surplus of group-V atoms, and are thought to be phosphorus interstitials. The resultant interdiffusion occurs at different rates on each sublattice, thereby causing an enhancement of local strains, as observed by X-ray diffraction.

I - Introduction

Interdiffusion between the atoms of a quantum well (QW) and barrier leads to a change in the compositional profile and thus to the quantum well electronic potential. Usually this results in a blueshift (increase in energy) of the lowest transition, as well as changes to other optical properties such as the refractive index. This phenomenon is generally referred to as quantum well intermixing (QWI). As a post-growth means of selectively tuning the bandgap, it holds great promise for many opto-electronic applications, in particular the monolithic integration of photonic devices. There are many different QWI techniques, but in general they all accomplish two things: create a surplus of lattice defects in selected areas of the wafer, and then diffuse those defects through the QWs during a high temperature anneal. The temperature of this RTA must be hot enough to allow these defects to diffuse, but not so hot that a large equilibrium generation of lattice defects occurs throughout the entire wafer (whereby *selective* adjustment to the bandgap would be lost). Thus, for any QWI study it is important to understand the thermal behaviour of the as-grown material.

In this paper we examine how the thermal stability of a hetero-structure can depend significantly on its epitaxial growth conditions, and demonstrate that a surplus of defects originating in the material during growth leads to a dynamic enhancement of the QWI. We discuss the possible identity(ies) for the grown-in defects, and examine the type of intermixing that takes place.

II - Thermal Behaviour

All material in this study was grown by chemical beam epitaxy (CBE). The first structure under study (wafers 1A and 1B) consists of five InGaAs quantum wells separated by InGaAsP barrier material, and surrounded by epitaxial InP. The growth temperature for all the epitaxial layers of wafer 1B were lower by 20 to 25°C than for the growth of wafer 1A, as listed in Table I. The second structure (wafers 2A and 2B)

consists of ten InGaAs quantum wells separated by InP barrier material, and again surrounded by InP cladding. For wafer 2B, the growth temperature of *only* the upper InP cladding was reduced by 35°C in comparison to wafer 2A, as listed in Table II. All layers were nominally lattice matched to InP, undoped, and the substrates for all the wafers were S-doped LEC substrates. Photoluminescence (PL) maps (performed at 300 K using a 980 nm excitation with a power of 20 mW) showed good uniformity for all wafers.

Table I: Layer structure for wafers used in the study, including the temperature of the substrate during growth and nominal layer thickness.

Layer	Thickness (nm)	T _{growth} (°C)	
		Wafer 1A	Wafer 1B
InGaAs cap	200	515	490
InP upper buffer	1380	485	465
InGaAsP etch stop	100	485	465
InP upper buffer	200	485	465
InGaAsP cladding	70	515	490
InGaAs QWs x 5	6	515	490
InGaAsP barriers x 4	20	515	490
InGaAsP cladding	70	515	490
InP lower buffer	1500	485	465
		Wafer 2A	Wafer 2B
InGaAs cap	30	505	505
InP upper buffer 2	1600	505	470
InP upper buffer 1	25	505	505
InGaAs QWs x 10	5	505	505
InP barriers x 9	17	505	505
InP lower buffer	300	505	505

Wafers were cleaved into 5x5 mm pieces for annealing, and one sample per wafer was annealed at a given temperature for several anneals. PL maps were performed on each sample before the first anneal and between each subsequent anneal. Samples were surrounded and capped using sacrificial GaAs

material to protect the edges and top surface from desorption of As. The thermally induced blueshifts of the PL peak are shown in Figure 1. By looking at the blueshifts that occur during the first 30 s RTA, as well as the *additional* blueshifts that occur during subsequent RTAs, it is obvious that the control wafers (1A and 2A) are very stable for RTA temperatures $\leq 725^\circ\text{C}$. However, wafers with LT layers (wafers 1B and 2B), undergo a significant amount of blueshifting, even at RTA temperatures of 650°C . This blueshifting is largest during the first 30 s RTA, and does not continue to the same degree during subsequent RTAs, showing that it is a transient effect. Thus we believe this QWI to be due to a surplus of defects that are present in the LT layers from growth. During the RTA, these defects diffuse through the epitaxial material, and the population quickly diminishes as the defects are absorbed or trapped at various sinks. The transient behaviour of grown-in defects has also been reported in GaAs-based structures^{1,2,3,4}, but to our knowledge this is the first conclusive correlation between growth temperature and QWI for InP-based structures. The results of wafer 2B are particularly interesting, demonstrating that there is defect motion from an LT buffer layer to the QWs. We further confirmed this using an additional sample from wafer 2B, in which the entire upper cladding was removed by selective wet etch, such that the uppermost QW is exposed at the surface. This sample showed minimal (3 meV) blueshifting after an RTA of 90 s at 725°C . The layer structure of wafer 2B, in which the QW are spatially separated from a LT layer, has also allowed us to study of the defect motion and determine their diffusion rates⁵. Furthermore, the results on this structure also suggest that the study of thermally induced QWI can be used as a method to test for the quality of growth of *any* epitaxial layer.

III - Defect Identification

Nominally intrinsic InP typically exhibits n-type conductivity, with a carrier concentration that increases as growth temperature is reduced^{6,7,8,9}. Carbon also increases in concentration as growth temperature is reduced,^{6,9} but is expected to be an acceptor and thus cannot account for the negative carriers. Thus the donor identity for the n-type conductivity is at present unconfirmed, but expected to be a native defect.⁹ Characterization of our LT InP shows results that are in agreement with these findings, as described below. Secondary ion mass spectrometry (SIMS) is performed on the upper buffer layer of wafers 2A and 2B, while Hall conductivity and PL measurements are performed on additional wafers of bulk epitaxial InP grown at the same conditions as the upper buffers of wafers 2A and 2B (from hereon referred to as standard InP and LT InP).

Hall conductivity by the van der Pauw method at 300 K shows an increase by a factor of three in the n-type carrier concentration in the LT InP ($8.3 \times 10^{15} \text{ cm}^{-3}$ compared with $2.4 \times 10^{15} \text{ cm}^{-3}$). And SIMS suggests a 2-3 times higher concentration of carbon in the upper InP layer of wafer 2B in comparison to wafer 2A ($\sim 1 \times 10^{18} \text{ cm}^{-3}$ compared with $\sim 4 \times 10^{17} \text{ cm}^{-3}$), while oxygen levels in both wafers were the same at $\sim 7 \times 10^{17} \text{ cm}^{-3}$. All other likely impurities (Mn, Mg, Si, S, Sn,

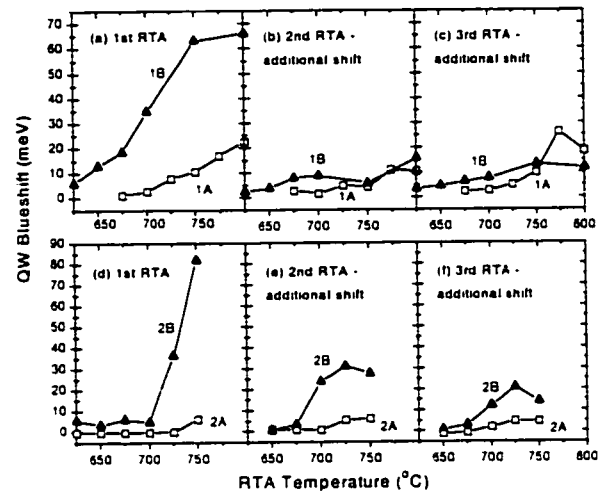


Figure 1 – Blueshift of the QW photoluminescence peak position as a function of RTA temperature for wafers 1A and 1B (a)-(c), and wafers 2A and 2B (d)-(f). Figures (a) and (d) shows the shift that occurred during a first 30 s RTA, while figures (b) and (e), (c) and (f), show the *additional* shift that occurred during a second, and third, 30 s RTA.

Se, and Be) were below the SIMS detection limits in all epitaxial layers of both wafers. We do not believe that the increased carbon in the LT InP is the mobile defect responsible for the QWI, since C is known to have slow diffusion rates¹⁰. Instead, we believe that the highly mobile defects that cause the intermixing are native defects, likely connected to the native donor which cause the increased n-type carrier concentration.

Results of 4K photoluminescence on bulk InP are also consistent with this understanding. Broadband spectra (0.7 to 2.0 eV) were collected using a Fourier Transform Infrared Spectrometer (FTIR) with InGaAs Detector. We have also measured high-resolution spectra of the exciton band (1.412 to 1.422 eV), collected using a 0.75 m double-grating spectrometer with photomultiplier tube at a resolution of 0.08 meV. By comparing the relative intensities of various peaks in both the standard InP and the LT InP, we will show that there are similar concentrations of *shallow* donors and acceptors in both wafers, with the exception that there is more of the shallow carbon acceptor in LT InP.

Looking first at the broadband spectra (Figs. 2a and b), the ratio of intensities of the donor to acceptor transitions (D-A) to the intensity of excitonic band (X-band) is much larger in the LT InP than in the standard InP. By performing PL as a function of temperature and excitation power (not shown here), we have concluded that the D-A peak of the LT InP is comprised of two D-A transitions: one at 1.376 eV identified with the acceptor carbon and the second weaker peak at 1.379 eV relating to an unknown acceptor commonly labeled (thought to be Mg)^{11,12}. The carbon D-A dominates in the LT InP, while in the standard InP, the carbon D-A is still present but at a comparable intensity to the Al peak. Electron band to acceptor (e-A) transitions for these same acceptors were weak,

but were discernable at slightly elevated temperatures (~ 15 K) when the donor is thermally ionized. In both wafers, we conclude that peaks at 1.332 eV are one-phonon replicas of the D-A transitions. No other peaks, such as luminescence from deep centers¹³, were observed in either wafer, even using high excitation powers and a cooled Ge detector. Turning to the excitonic bands of the two wafers (Figs. 2c and d) we can identify in both wafers: the free exciton (X) at 1.4181, the transition associated with an exciton bound to neutral donor (D^0, X) at 1.4166, as well as the associated higher order $n=2, 3$, and 4 transitions, a doublet from the exciton bound to a neutral acceptor (A^0, X) at 1.4143 and 1.4145 eV, as well as possible weak transitions around 1.415 eV associated with the donor to hole D-h transition or exciton bound to an ionized donor (D^+, X). The positions of all of the above peaks of the X-band are ~ 0.1 meV lower than reported values,¹⁴ due to minor arsenic incorporation.^{6,8} Comparing the X-bands of both wafers, we see that the ratio of the intensities of the (A^0, X) to X is much larger in LT InP, while the ratio of the (D^0, X) to X is nearly equal in the two wafers. This confirms that the difference between the two materials is due to number of shallow acceptors (carbon), while the concentrations of shallow donors are similar in both materials.

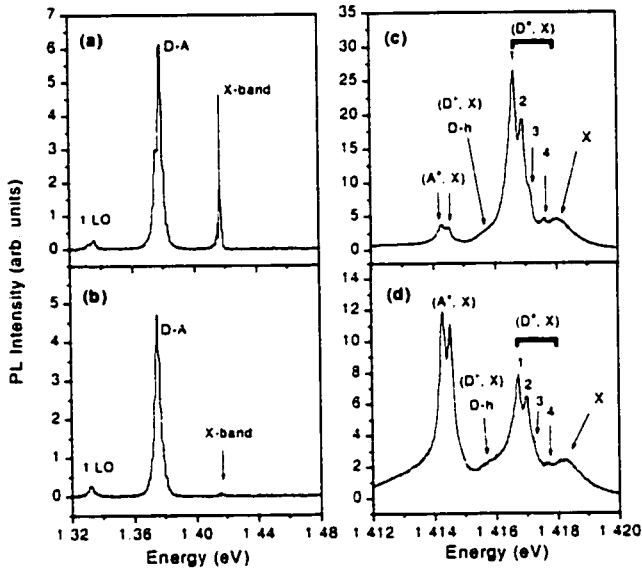


Figure 2 – Photoluminescence spectra of standard InP (a), (c) and LT InP (b), (d). Broadband spectra are shown in (a) and (b) while high resolution spectra of the excitonic band are shown in (c) and (d).

There has been a considerable interest in the properties of very low temperature growth (170 to 350°C) of GaAs and InP. Although the structural properties of both materials are similar, the electrical properties of LT GaAs and LT InP differ remarkably. Structurally, both have a non-stoichiometric increase in the group-V concentration, accommodated primarily by antisites of group-V atoms on group-III sites (As_{Ga} or P_{In})¹⁵ with also substantial concentrations of vacancies on the group-III sublattice (V_{Ga} or V_{In}).^{15,16} In LT GaAs, the antisite defect EL2 (either As_{Ga} or $As_{Ga} + As_i$ pair)^{17,18} is a deep double donor, while the V_{Ga} is a

compensating triple acceptor, resulting in semi-insulating properties. In contrast LT InP exhibits an n-type conductivity which increases as T_{growth} is decreased, to the point where it shows metallic-like conductivity at $T_{growth} \leq 285^\circ C$.¹⁹ Although the antisite defect is again dominant, its first ionization state is within the conduction band ($E_c + 0.12$ eV) which is auto-ionized and provides these n-type carriers (it's second ionization state is a deep donor at $E_c - 0.23$ eV).²⁰ For InP, the concentrations of the antisite-related defects have been examined on LEC substrates^{21,22} and epitaxial layers grown in the range 170 to 350°C.²³ Unfortunately for epitaxial material with T_{growth} values above 350°C, the signal strength became too weak to measure. The role of group-V interstitials in LT material has also been analyzed (As_i or P_i)²⁴ but it is not well understood, due in part to the apparent isoelectric nature of the interstitials²⁵ which reduces the number of techniques which can be applied. Given the electronic structure of P_{In} and P_i , it is not surprising that we did not see PL emission from them in PL. So although we cannot prove its existence, PL and SIMS seem to rule out the possibility of impurities, and conductivity measurements are consistent with known characteristics of P_{In} .

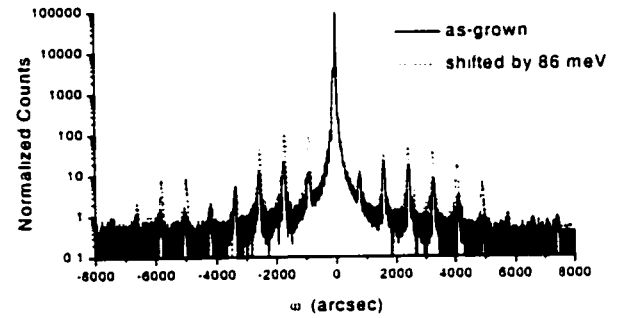


Figure 3 – High-resolution X-ray diffraction spectra of two samples from wafer 2B: as-grown (solid line); a sample which blueshifted by 86 meV after an RTA of 270 s at 725°C (dotted line).

IV – Interdiffusion on the group-V sublattice

High resolution X-ray diffraction (HR-XRD) shows that there is an increase in the strain modulation between the QWs and barrier material after intermixing (Figure 3). This can occur if the interdiffusion of the group-V sublattice occurs at a different rate than the interdiffusion on the group-III sublattice²⁶. We define k as the ratio of the interdiffusion length on the group-V sublattice to the interdiffusion length on the group-III sublattice. A blueshift in the photoluminescence can occur for both $k < 1$ and $k > 1$, but in the case of $k < 1$, the bandgap redshifts for small amounts of interdiffusion, then eventually blueshifts for larger interdiffusion lengths. Since all of our samples only show blueshifting, $k < 1$ seems unlikely. In a related paper²⁷, we have performed optical transmission analysis and obtain energies for the first and second transition in both as-grown and intermixed samples, which then allowed us to confirm that the interdiffusion in these samples occurred predominately on the group-V sublattice ($k > 1$). It is then not unreasonable to propose that the QWI-causing defect is group-

V in nature. In fact, some experimental evidence supports fast interdiffusion of the group-V sublattice is controlled by group-V interstitial^{28,29,30}. We propose that the *mobile* QWI-causing defect is P_i , which either exists in the as-grown LT InP or is released by a change to the P_{in} -related defect during annealing^{31,32}. For example, as a lone antisite, it could convert to P_i and a V_{in} , or if it is a $(P_{in} + P_i)$ defect pair, the P_i could be released. The antisite itself is not expected to have a fast enough diffusion rate to account for the QWI, whilst interstitials are³³.

V - Conclusion

Non-equilibrium concentrations of defects may be grown into epitaxial layers if the growth temperature is reduced by small amount. These defects cause an initial surge on intermixing, even when they are located in layers other than the QWs. In other words, they are highly mobile. An increased concentration of carbon was found in LT InP, but it was concluded that this would not be the defect responsible for the QWI. Instead, we propose that the defect is related to an excess of phosphorus. We have shown that the intermixing is predominately on the group-V sublattice, and we further argue that the phosphorus interstitial is a very likely candidate for the mobile QWI-causing defect. Further study will aid in resolving these issues.

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Paper 3 (SSC)

J. E. Haysom, P. J. Poole, R.L. Williams, S. Raymond, and G. C. Aers; Diffusion of defects in InP studied using quantum well intermixing; Solid State Commun. 116, 187, 2000.

This paper studies the motion of the defects from the LT InP buffer to the QWs by using a set of samples with a varying thickness of the LT layer removed by slow wet etch. QWI is essentially used as a probe for the defect motion - using a simple model, the amount of interdiffusion can be related to the number of defects passing through the QW. Experimental data of the interdiffusion length (Δ_i) as a function of thickness of the LT layer and anneal time are fit with profiles that depend only on the defect diffusion rate and the location of sinks. The diffusion coefficient of the defects is found to be of the order of 10^{-10} cm²/s. All the experimental aspects of this paper were performed by the author of this thesis, while the modeling was performed by G.C. Aers after joint discussions. Epitaxial growth was by P.J. Poole.



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Diffusion of defects in InP studied using quantum well intermixing

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Abstract

The diffusion rate of grown-in defects in InP is studied by determining the flux of defects from a source layer to underlying quantum wells (QWs). The grown-in defects are caused by epitaxial growth at lower than optimal temperatures, and are located in an upper InP buffer. We study the photoluminescence blueshift of the QWs as a function of the thickness of the buffer and as a function of anneal time. Modeling correlates the intermixing of the quantum wells to the concentration of defects at the wells. Possible locations of defect sinks and the identity of the grown-in defects are also discussed. © 2000 Published by Elsevier Science Ltd.

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Quantum well intermixing (QWI) is a well-known method for post-growth modification of bandgaps in quantum well heterostructures. It has many potential applications in opto-electronic devices and photonic device integration. Also, studies of QWI can yield more fundamental materials information, such as rates of diffusion and the role of defects in diffusion. However, currently there are large discrepancies in the literature for interdiffusion rates in III–V semiconductors. This is due in part to variations in the annealing conditions (temperature, atmosphere) which will favor certain diffusion mechanisms, but may also be due to differences in the starting material itself. For example, it has been shown that QWI in GaAs is often enhanced by non-equilibrium concentrations of defects in the as-grown material, especially during the early stages of high temperature annealing [1–3].

In a previous paper we demonstrated that the incorporation of grown-in defects increases as the growth temperature of epitaxial InP is reduced, and that the defects exhibit significant mobility, thereby causing intermixing in underlying QWs [4]. Using absorption measurements, we also

showed that intermixing occurred primarily on the group-V sublattice, and the ratio of the interdiffusion lengths of group-V versus group-III sublattice (defined as k) was in the range of 2–4. This is a similar value to that seen in many of our studies on shallow ion-implantation-induced QWI on similar InGaAs/InP structures [5,6], and that other authors have reported for dielectric cap disordering [7]. Given that the resulting interdiffusion in these different techniques appears to be very similar (predominantly group-V sublattice interdiffusion of underlying QWs for similar time and temperature of annealing), we speculate that it is the same group-V defect [8] which diffuses and causes the intermixing in all cases.

Since the effects of implantation are complex, changes to any one variable (such as dose or energy) will likely affect the concentration and distribution of the defects and the local microstructure. Thus it has been difficult to gain knowledge about the defects which cause the intermixing. In the case of grown-in defects, although we are uncertain as to their concentration and exact identity, we *can* assume that they are uniformly distributed throughout the low temperature (LT) layer and thus by controlling the thickness of this layer we can linearly vary their numbers. In the present paper, we study the dynamics of motion of the grown-in defects by studying QWI as a function of LT layer thickness.

The material in this study was grown by chemical beam epitaxy. The structure consisted of ten 5.0 nm InGaAs QWs

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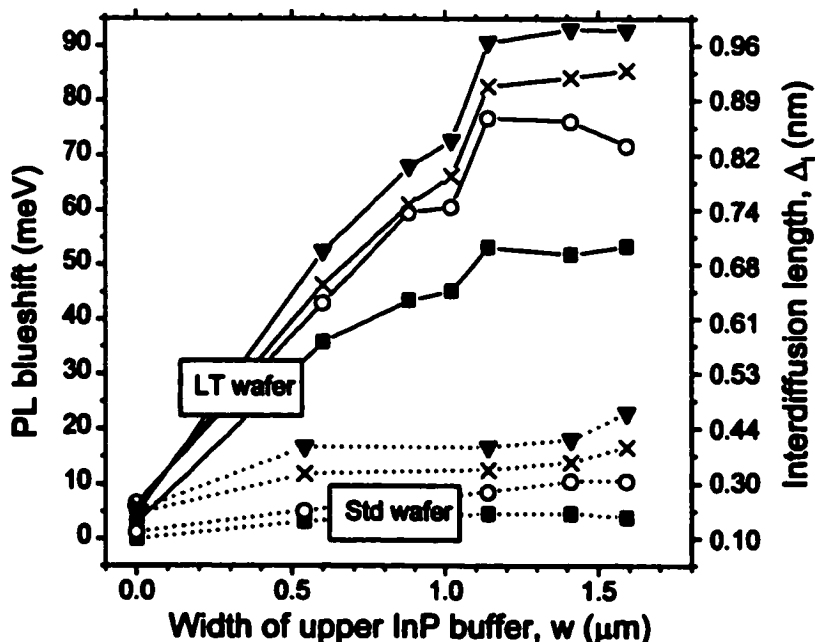


Fig. 1. Experimental values of PL blueshift as a function of width of upper InP buffer layer for the low-temperature grown wafer (LT wafer) and the standard growth temperature wafer (Std wafer). Anneals were done at 725°C for total times of 90 s (solid squares), 180 s (open circles), 270 s (crosses), and 360 s (solid triangles). Right-hand axis gives the interdiffusion length corresponding to a given blueshift.

separated by 17 nm InP barriers, and grown on a small layer of InP on a S-doped LEC InP substrate, while above the QWs was an upper buffer of 1.64 μm of InP, and a 30 nm cap of InGaAs. Two wafers were studied: a standard (Std) wafer, where all layers were grown at the normal growth temperature of 505°C; and an LT wafer in which the growth temperature of the uppermost 1.600 μm of the upper InP buffer was reduced to 470°C. A 0.04 μm layer of standard growth InP separated the QWs from this LT InP. All layers were nominally undoped and lattice matched to InP. Photoluminescence (PL) maps performed at 300 K showed good uniformity for both wafers.

The following etch-back procedure was applied to samples from both wafers: (a) the upper InGaAs cap was etched-off using a selective wet chemical etch; (b) a silicon dioxide layer was used to mask half of each sample; (c) a portion of the upper InP buffer in the unmasked half of each sample was etched-off using a slow wet chemical etch for various times; (d) the dielectric mask was removed by wet etch; (e) the depth of the etch was measured using a profilometer. Samples were then annealed for 90 s at 725°C and the QW luminescence was measured using a 300 K PL map. The anneal + PL steps were repeated several times in order to track the shift as a function of anneal time for each sample. Anneals were performed using an N_2 purge gas with sacrificial InP material placed above and surrounding the samples to create an overpressure of phosphorus. Additionally, for two samples (one per wafer) steps (b)–(e) were omitted, and instead a fast and selective InP etch was used to

remove all of the upper InP cladding, such that the first InGaAs QW was exposed at the surface. During annealing of these two samples, sacrificial GaAs material was used.

From the profilometer measurements we determine the thickness of the remaining InP buffer, w . Using the PL measurements, we extract the blueshifts of the QW ground state (relative to the transition energy of the starting material) for each w and each anneal time, as shown in Fig. 1. For samples from the LT wafer with $w \sim 0.5 \mu\text{m}$, the total shift ($\sim 50 \text{ meV}$) is less than the samples with larger w , and the majority of this shift occurred within the first 90 s of annealing. For samples with a thicker LT layer, the shift during the first 90 s anneal is similar, but significant shifting continues during the subsequent anneals, as defects which were initially further away from the QW finally make their way to the QWs.

By making certain assumptions with respect to the interdiffusion of the QWs, the compositional profiles and the transition energies of interdiffused QWs can be calculated. For this experiment we have assumed independent Fickian behavior for the group III and V sublattices [9], with a k value of 2. This allows one to correlate the blueshift with the interdiffusion length $\Delta_i = (D_i t)^{1/2}$, where D_i is the interdiffusion constant and t is the anneal time. Here, Δ_i and D_i refer to interdiffusion on the group-V sublattice (values for the interdiffusion length on the group-III sublattice are simply Δ_i/k). The vertical axis on the right-hand side of Fig. 1 has the Δ_i equivalence for the experimentally observed blueshifts.

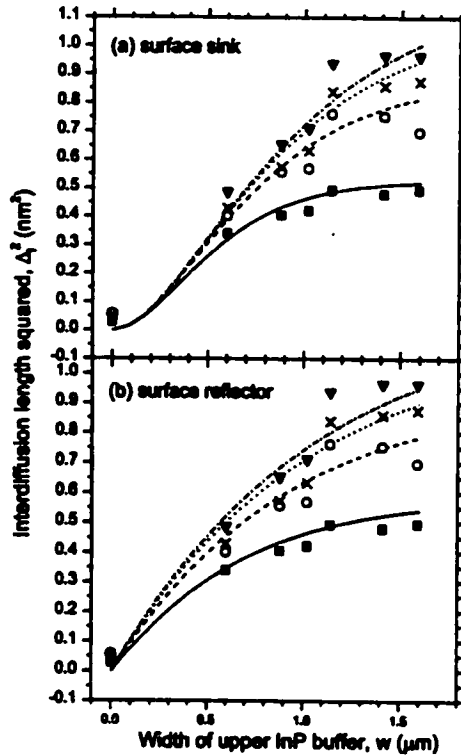


Fig. 2. Values of the square of the interdiffusion length derived from experiment (symbols) and theoretical curves (lines) for the low-temperature grown wafer. Data values for anneals of 90 s (solid squares), 180 s (open circles), 270 s (crosses), and 360 s (solid triangles), and the corresponding theoretical curves for 90 s (dash-dot-dash), 180 s (dotted), 270 s (dashed), and 360 s (solid).

Following Cibert and Petroff [10], Δ_i^2 is proportional to the time integrated concentration of defects at the QW, as expressed by

$$\Delta_i^2 = \beta D_d \int_0^t dt' N_d(D_d, t', w) \quad (1)$$

where β is an arbitrary constant used in the fitting, D_d is the diffusion rate of the defects and N_d is the concentration of defects at the QW. We assume that the defects are uniformly distributed throughout the as-grown LT layer, while their distribution after annealing can be described by a solution of the diffusion equation. It is then straightforward to compute the time integral of N_d for a given distance away from the LT layer (we assume one infinitely thin plane in the center of the QW stack). The variables t and w are set by the experiment, while D_d and β are adjusted in an iterative manner to determine the best fit to the experimental values of Δ_i^2 .

Within this solution, some assumptions must be made concerning the location of defect sinks which diminish the number of defects. Initially, we will assume the surface is a perfect sink (such that all defects that reach the surface are

trapped there) and that there is also a uniform distribution of sinks in the bulk, which is incorporated using an effective diffusion length for a defect (distance traveled before annihilation), Δ_d . In order to get a satisfactory match to the experimental curves in terms of both shape and accuracy for all four anneal times, it was necessary to include this bulk defect loss. The curves shown in Fig. 2(a) were obtained with $D_d = 3.5 \times 10^{-11} \text{ cm}^2/\text{s}$ and $\Delta_d = 0.72 \text{ } \mu\text{m}$. If instead we assume the surface acts as a perfect reflector instead of a sink and use values of $\Delta_d = 3.5 \times 10^{-10} \text{ cm}^2/\text{s}$ and $\Delta_d = 2.3 \text{ } \mu\text{m}$, the resulting theoretical curves have a slightly different shape but provide an equally good fit, as shown in Fig. 2(b). We consider that the surface is unlikely to be a perfect sink because of the observed correlations between surface processing (such as plasma exposure [11] and sputter deposition [12]) and QWI. If the surface was a perfect sink, most of the defects generated in such processing would not reach the QWs. The perfect reflector is the extreme opposite of this possibility. Future experiments will examine the role of the surface.

As mentioned previously, the model assumes a single plane positioned approximately in the center of the 10 QW stack. Varying the position of this plane by $\sim 112 \text{ nm}$ (half the thickness of the QW stack) results in small variations in the predicted interdiffusion length. Thus we expect there to be a small distribution in the resultant blueshift in the 10 QWs, with QWs nearer the LT layer blueshifting slightly more. Considering the most interdiffused sample, we calculate a 20 meV variation in the blueshift between the first and last QW when using the surface sink model, while the surface reflector model gives a spread of only 6 meV (the spread is less in the reflector case because the bulk loss is reduced). Experimentally, this variation between QWs would result in an increased PL linewidth after interdiffusion. Increases in the linewidth in the PL peak (measured at 4 K) are observed — full-width-half-maximum linewidths change from 9 meV in the as-grown to 14 meV for the most interdiffused sample. If we assume that the linewidth of PL emission from each interdiffused QW is 9 meV (the same as the as-grown), and create a superposition of 10 such peaks, each blueshifted by a slightly different amount, then the resultant peak will have a linewidth of 14 meV if the total variation in the blueshift of approximately 12 meV. This value of 12 meV falls in between the above-predicted model-dependent values of 6 and 20 meV. The accuracy of this analysis is not sufficient to select for a given model, but it does provide a check that the modeling in general produces the right range of values.

It is of interest to note that the defect diffusion length ($\Delta_d \sim 1 \text{ } \mu\text{m}$) is much larger than the interdiffusion length ($\Delta_i \sim 1 \text{ nm}$). Or equivalently, when comparing diffusion rates, the defect diffusion rate is $D_d \sim 10^{-11} \text{ cm}^2/\text{s}$, while the interdiffusion rate is $D_i \sim 10^{-17} \text{ cm}^2/\text{s}$. This difference is expected: in the case of the defects, we measure an effective distance traveled by a type of defect, although it may not be the same specific atom from start to finish (i.e. the

defect will interact with the lattice and continuously regenerate itself during its motion) but for the interdiffusion we analyze for the exchange of *specific* atoms at the QW [13].

It has been proposed that the grown-in defects in this LT material are related to a phosphorus-rich stoichiometry, which either starts with, or during the anneal results in an excess of phosphorus interstitials [8]. There is recent evidence that the diffusion of the arsenic sublattice in GaAs is controlled by group-V interstitials, at least in the case of group-V-rich conditions [14,15]. The low atomic mass (size) of phosphorus also gives reason to expect it is able to diffuse readily as an interstitial. A surplus of phosphorus interstitials in our material could mediate QWI by the kick-out mechanism [14], in which an interstitial hops onto a group-V site, releasing the previous occupant (As or P) as a new interstitial. This is in contradiction to claims that the group-V interdiffusion is mediated by vacancies [16].

In conclusion, non-equilibrium concentrations of defects may be grown-in to epitaxial layers if the growth temperature is reduced by small amounts. These defects are highly mobile, exhibiting diffusion rates of the order of 10^{-11} cm²/s at 725°C. They diffuse freely through the epitaxial structures and cause intermixing predominantly of the group-V sublattice in underlying QWs. We argue that the mobile defect in this material is the same as the defect responsible for implantation-induced QWI, and that this defect is a phosphorus interstitial.

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Additional Modeling of Transmission Results

In Paper 1, the hh and lh transition energies for a series of samples were determined by optical transmission, and then analyzed to determine the k ratio for intermixing. The blueshifts of this set of samples was caused by annealing at different temperatures (herein referred to as knee curve samples). Here, we will repeat the transmission analysis on a second set of samples, where the blueshifts were caused by removing portions of the LT layer and then annealing at 725 °C (these are the samples from Paper 3, herein referred to as etch-back samples). The etch-back samples removes one potential complication inherent in the knee curve samples - variations in anneal temperature have the possibility of introducing more than one QWI-defect or interdiffusion mechanism with differing k ratio. Thus the transmission analysis is repeated here on the etch-back samples. The hh shift and the splitting between the hh and lh transitions for the etch-back samples are derived from the transmission spectra (not shown) and the results are plotted in figure IV-15. The previous data points from Paper 1 are also included on the graph.

The first thing to note is that the two sets of data agree with each other, confirming that $k > 1$ for all samples, independent of annealing temperature. This likely implies that a single interdiffusion mechanism is occurring over the range of anneal temperatures. The error bars are relatively large on all data points due to the width of the optical resonances in the transmission spectra. The error is especially large for the samples where the splitting is small (it is difficult to determine hh and lh peak positions when the two peaks overlap - refer to figure 2 of Paper 1). If similar experiments were undertaken in the future, structures with more than 10 QWs would improve the strength of the resonance and therefore the accuracy of the peak position.

Second, the figure includes theoretical curves for both error function and square well interdiffusion models, each for a range of k ratios. For the cases of $k > 2$, the predicted differences between the two models is very small, and thus this type of data (making use of splittings between quantized energy levels) will not be able to

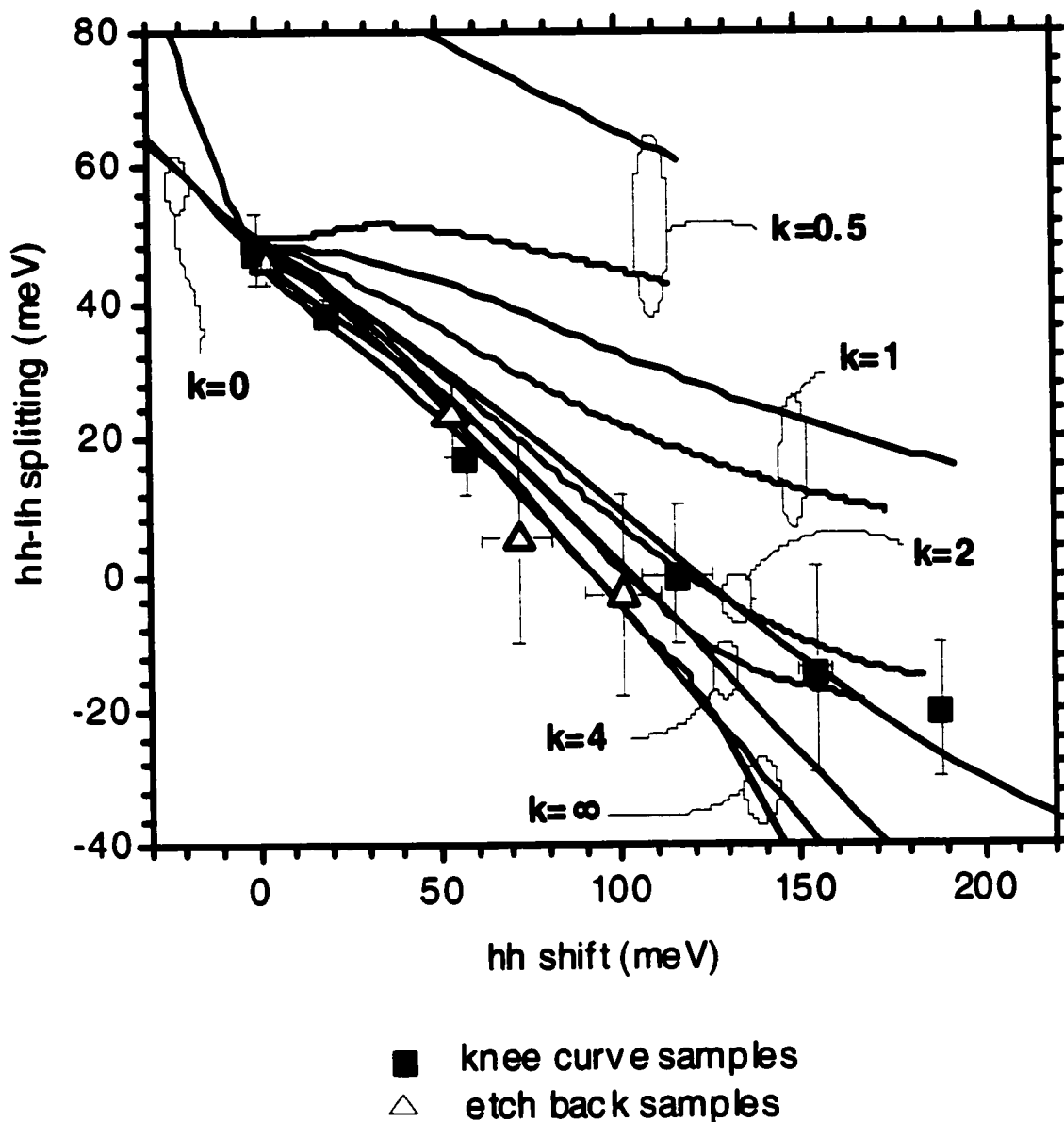


Figure IV-15: Plot of the energy difference (the splitting) between the hh and lh transitions versus the blueshift of the hh transition. Data points are given by symbols, while theoretical curves for error function and square well models are shown with black and blue lines, respectively. Theoretical curves, under both the above assumptions, are shown for several different k values, as indicated on the figure.

distinguish between interdiffusion models²⁶. This is likely because, due to their spatial spread, the QW excitons “see” an average composition for the entire well width, and thus the exact distribution of composition (along the z-direction) has a similar influence on all the quantization energies. This holds for diffusion lengths that are not too large, before the wavefunction distributions for the two interdiffusion models diverge significantly. Examples for blueshifts of 100, 150, and 190 meV are shown for both error function and square well models in figure IV-16 (similar plots for a blueshift of 75 meV in the same layer structure were shown in figure II-8). The wavefunction distributions are not significantly different between the two models for a blueshift of 100 meV ($\Delta_{i(V)}=1.0$ nm), again, because of a certain amount of averaging-out, but by 150 meV blueshift, the wavefunction profiles are significantly different. Thus, measurable differences between the two models using this analysis begin to appear for blueshifts in the range of 150 meV. But, as was discussed in Chapter II, the uncertainty in the modeling also increases in the regime of large blueshifts, so it may be inappropriate to apply this type of analysis to samples with shifts greater than 150 meV. Therefore, for $k>1$, any study relying solely on a comparison of the transition energies will not be conclusive in determining whether diffusion is Fickian or not. Direct physical or chemical characterization of the QW shape (either by itself or in combination with optical results) may be the only means of sorting out this issue. For example, the use of cross-sectional scanning tunneling microscopy in combination with PL blueshifts has been used to determine k ratios for implantation-induced blueshifts³⁸.

Third, independent of whether error function or square well interdiffusion is assumed, we are also insensitive to values of $4<k<\infty$. This is in part because k is a ratio of $\Delta_{i(V)}/\Delta_{i(III)}$. We are in a regime where $\Delta_{i(III)}$ is already quite small (the order of one lattice spacing) therefore small changes to its absolute value are relatively inconsequential to the QW profile, but will have a strong effect on the k ratio, since $\Delta_{i(III)}$ is in the denominator. For example, the interdiffusion lengths for several k ratio assumptions for a 100 meV blueshift of the hh (for this layer structure) are presented in table IV-6. Note that the value of $\Delta_{i(V)}$ is nearly constant

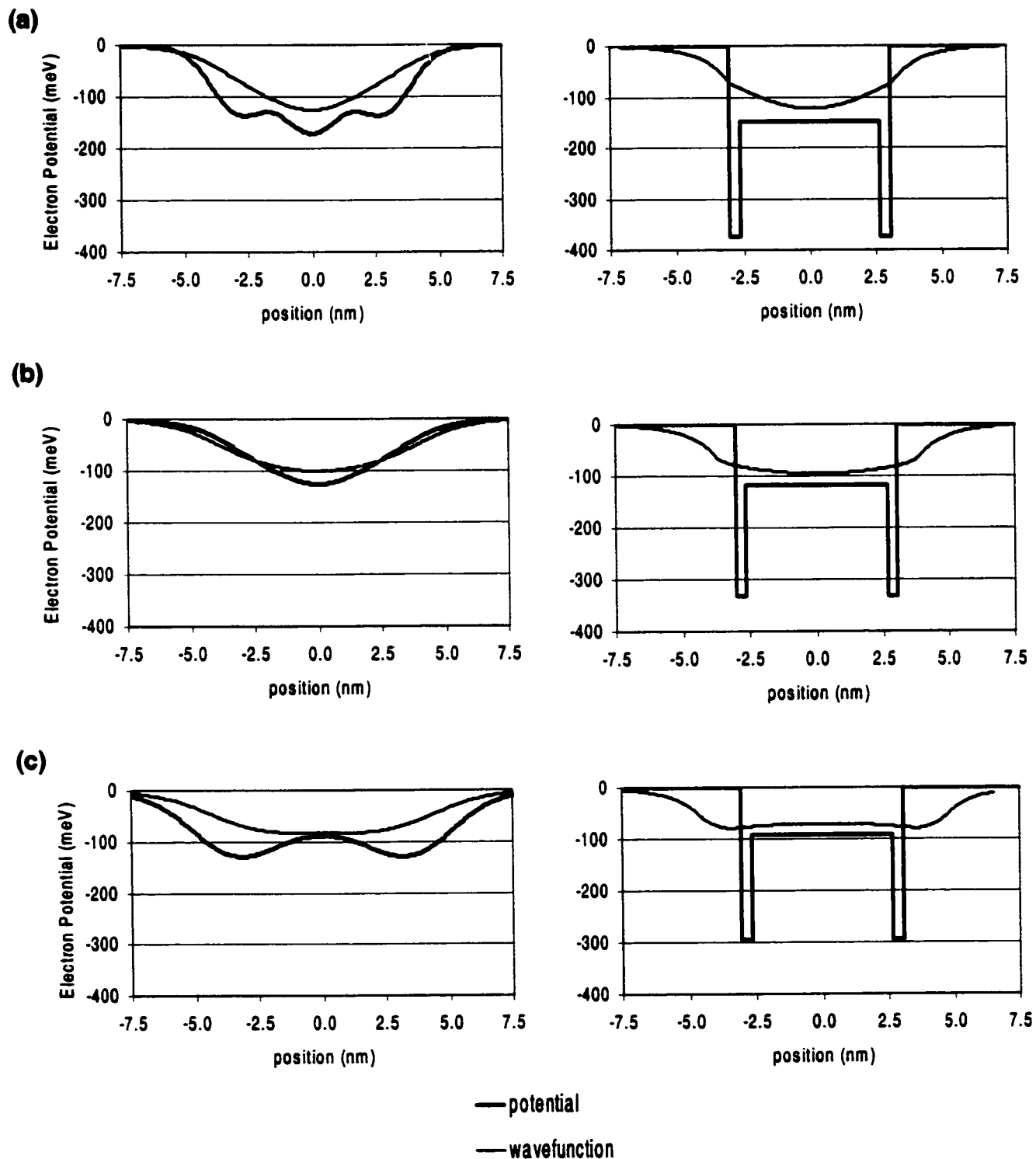


Figure IV-16: Modeled profiles for the electron potential (black lines) and electron wavefunction distribution (pink lines, arbitrary units) for an InGaAs/InP layer structure which has been blueshifted by (a) 100 meV, (b) 150 meV, and (c) 190 meV. Profiles for error function assumptions are shown in the left column, and square well assumptions in the right column.

for all k ratios, while the significant variations in the $\Delta_{i(III)}$ have almost no effect on the blueshift. This third point - the “insensitivity” to $k>4$ - is inherent in our definition of k, and will occur to a certain extent no matter what characterization technique is used.

Table IV-6 Interdiffusion lengths (error function) and well width changes (square well) of the group-III and group-V sublattices corresponding to a blueshift of ~100 meV under different assumptions for k.

Error Function	$\Delta_{i(III)}, \Delta_{i(V)}$ (nm)	ΔE_{hh} (meV)
k=2	5.50, 11.0	102.7
k=4	2.63, 10.5	100.3
k=20	0.53, 10.5	100.1
k=infinity	0.00, 10.5	100.1
Square Well	$\Delta_{L(III)}, \Delta_{L(V)}$	ΔE_{hh}
k=2	8.25, 16.5	100.8
k=4	3.75, 15.0	100.5
k=20	0.73, 14.5	100.7
k=infinity	0.00, 14.5	100.8

XRD Measurement and Modeling

Following a point made in the preceding section, XRD is one means of directly characterizing the interdiffused QWs^{39,40} that may allow us to determine whether the interdiffusion is Fickian or not, as well as analyze the k ratio. The transmission results in the preceding section show that the interdiffusion is described by $k>1$, which means that there will be local changes to strain profile across the QW/barriers, as was illustrated in figure II-5. This strain development can be analyzed using high-resolution XRD, as was discussed in Chapter III-D. Figure 3 in Paper 2 shows the experimental spectra for the as-grown structure of the LT wafer

and for a sample that has been shifted by 88 meV via 270 s annealing at 725°C (with an intact LT buffer layer). The intensity of the satellite peaks has increased dramatically in the shifted sample, which gives additional proof that $k \neq 1$ (recall that local strain variations will develop for $k < 1$ and for $k > 1$). This increased intensity of the XRD satellite peaks was observed in all interdiffused samples.

In order to determine whether $k < 1$ or $k > 1$, and possibly further quantify the conclusions, simulations of the XRD spectra for the intermixed sample were performed and compared with the measured spectra. This is accomplished by taking the output from the QWI program for the compositional profiles (using an assumed model and k ratio) corresponding to an interdiffused QW whose PL emission has blueshifted by 88 meV. These compositional profiles are then entered into the XRD simulation program which calculates the expected XRD spectra. Simulated spectra using an error function assumption and a range of k ratios are shown, and compared with the experimental spectra, in figure IV-17. Examining the results, none of the simulated spectra exactly match the experimental spectra, but several trends in the relative intensities of the peaks can be compared in order to qualitatively determine the best fit:

- (a) the relative heights of the -1 and the $+1$ satellite are in agreement when $k > 1$
- (b) the number of observable satellite peaks is too low for $k \leq 1.3$
- (c) the overall heights of the satellite peaks is too large if $k \geq 5$

Thus, it appears that the overall best match is for k ratios in the range of 1.7 to 2.5 for the error function model. The above exercise was repeated under the assumption of square well modeling, as shown in figure IV-18, and the following conclusions can be drawn from these simulated spectra:

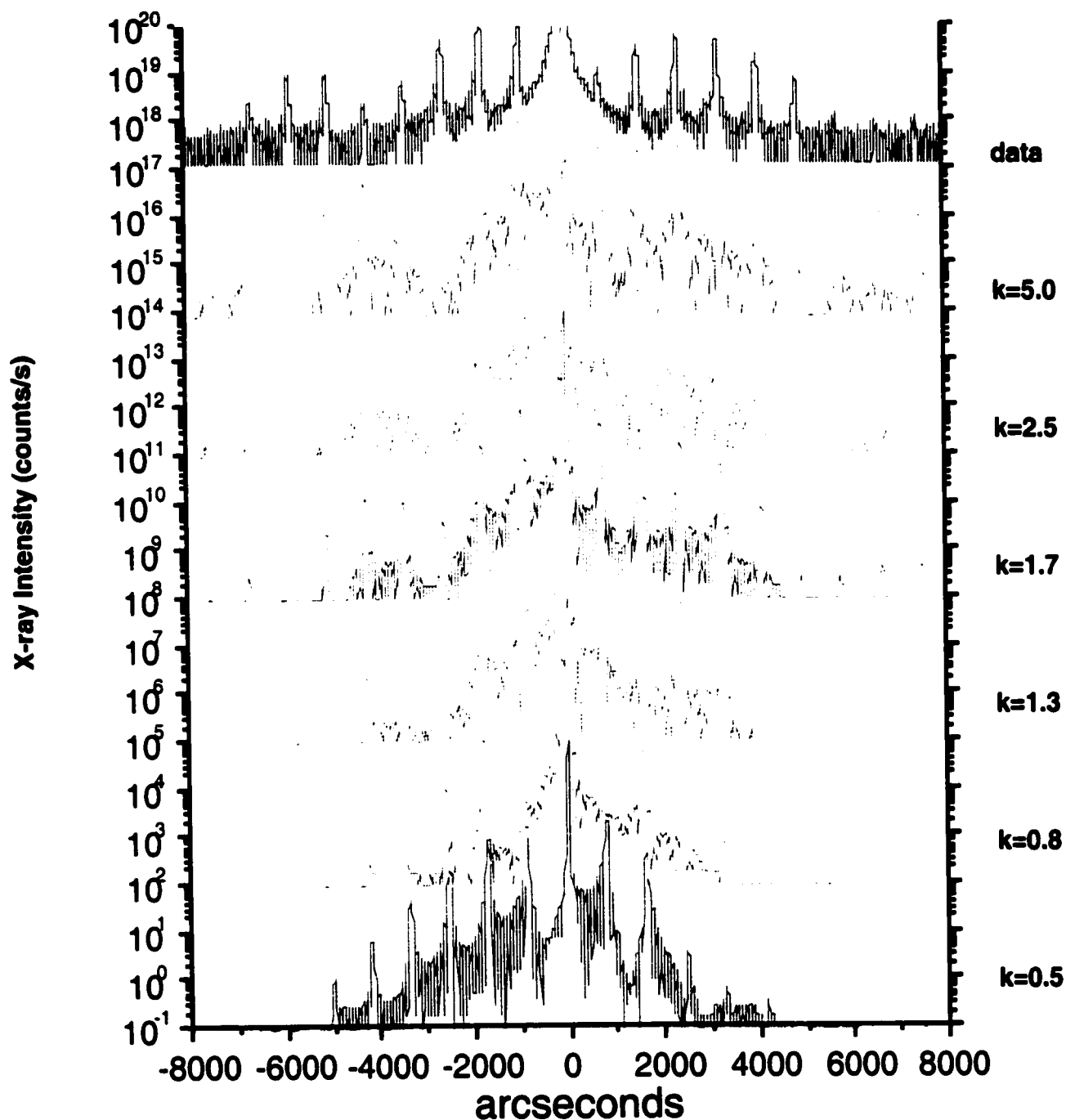


Figure IV-17: XRD spectra for sample which has shifted 88 meV, and for simulated spectra assuming error function interdiffusion and a range of different k values. Each spectra is offset by from the previous spectra by 10^3 .

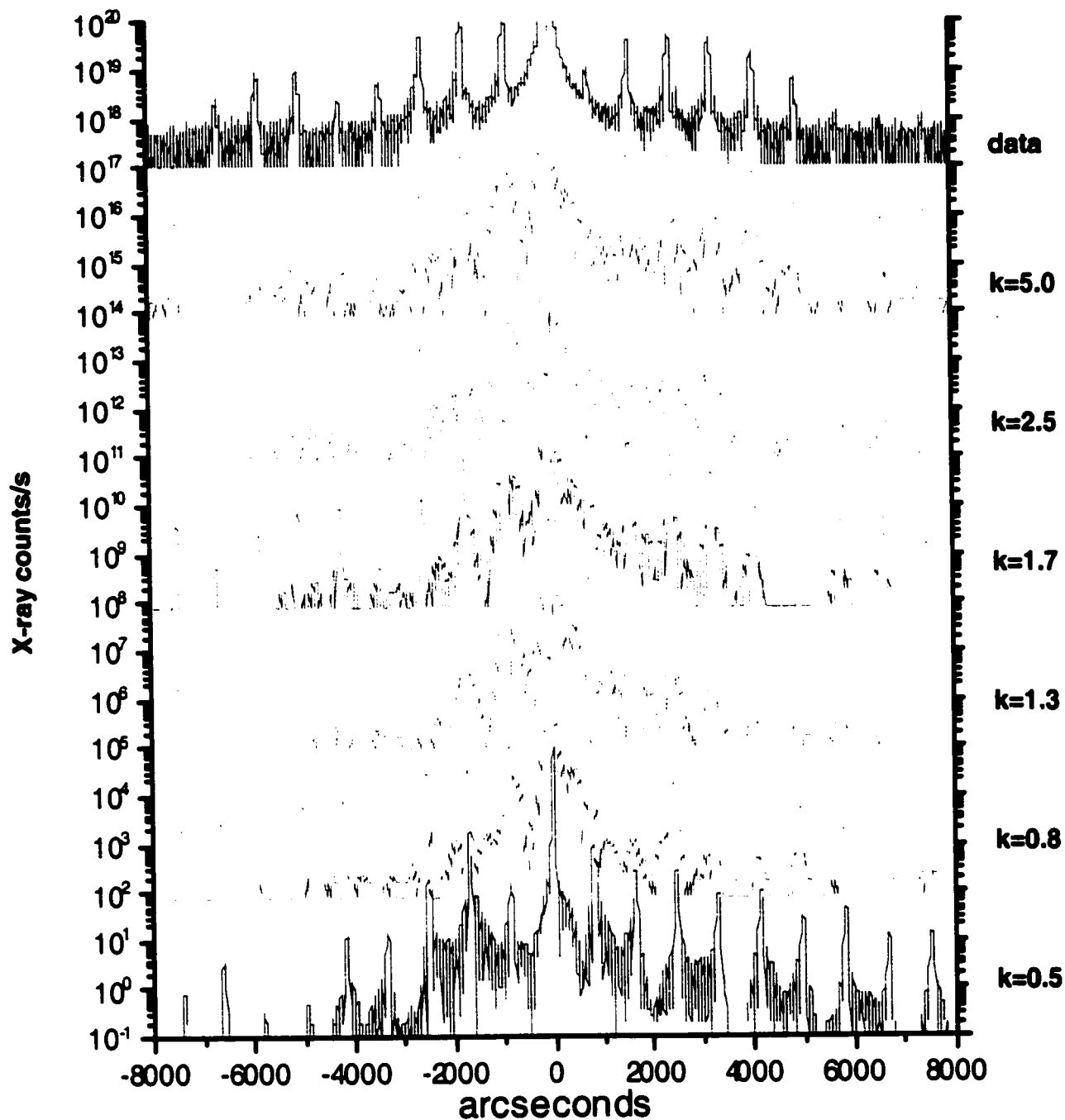


Figure IV-18: XRD spectra for sample which has shifted 88 meV, and for simulated spectra assuming square well interdiffusion and a range of different k values. Each spectra is offset by from the previous spectra by 10^3 .

- (a) the relative heights of the -1 to the $+1$ satellite are in agreement when $k > 1$
- (b) the magnitude of the peaks are too high in most of the spectra, indicating that the strain modulation in the square well model is too large⁴¹.

Overall, the match between the measured spectra and the simulated spectra is not as good with square well model as it was for the error function model, but still it can be concluded that for square well modeling, better matches are obtained with k in the range of 1.7. Thus we show agreement with the results from optical transmission that a k ratio in the range of 2 is a good descriptor of the interdiffusion.

Furthermore, these results indicate that XRD spectra may be quite sensitive to different intermixing models, thus allowing for a means of determining which model best describes the actual compositional profiles in interdiffused samples (as long as a sufficient amount of strain variation has occurred). For example, one of the features which results in a less than optimal fit for both models is the location of a minimum in the satellite peaks' intensities. In the data, one of the minima occurs at the -5 satellite peak, while in the error function (square well) model, this minima occurs at -3 (-4). This minima tends to correlate with the relative widths of the QW and barrier⁴¹, which, when modeling an interdiffused structure, will depend on the intermixing model used. The fact that in both simulations the minima occurs at too low an order may indicate that our description of the as-grown QW (which was the input into the QWI modeler as a perfect square well) needs some modification.

It seems likely that more detailed analysis could be pursued in order to develop conclusions with enhanced details to the ones drawn so far. Automated XRD fitting packages are available which iteratively adjust the composition and/or thickness of various layers in order to obtain better fits^{42,43} than can normally be achieved manually. However, in order to obtain a valid fit, it is important that the user inputs appropriate structure parameters, as well as the ranges within which these

parameters are allowed to vary. A certain expertise is required to do this well. In a more rigorous attempt to use XRD spectra for intermixing analysis, the first step would be to produce an accurate fit to the as-grown XRD spectra using such a program, including accounting for the strained interface layers between QWs and barriers. The second step would include these interface layers within the interdiffusion modeling (throughout this thesis a perfect square well has been assumed at this stage), and the third would be to re-enter the diffuse compositional profiles back into the XRD simulator, with some carefully thought-out limitations as to how much adjusting the simulator can make to the various parameters.

One reason that the above approach was not performed during this thesis is that the lack of ± 1 satellites in the as-grown structure could not be explained. Even when running the automated simulator and taking into account interface layers, this feature of the spectra could not be reproduced. It occurred for both the Std and the LT wafers in this study, but did not always occur in the CBE growths at NRC. Thus it would be best to work with a new wafer whose as-grown state could be acceptably simulated. It would also be best to work with a structure that has more QWs to improve signal-to-noise ratio of the high order satellites. In addition, if the period of the structure was increased, the satellite peaks would be more closely spaced, providing for more satellite peaks. The trade-off for both of these changes is that if the QW stack becomes too thick, uncertainty as to whether all the QWs are shifted by the same amount will increase. From the time when the research for this thesis was completed, co-workers have made advancements, using STM and XRD, to further describe the true compositional profiles of the as-grown QWs⁴⁴.

Further Discussion on Grown-in Defects

In Paper 2, it was proposed that the LT material contains P antisites, which cause the increased n-type conductivity, and which produce P interstitials during the annealing. These P interstitials would then be the defects that enhance interdiffusion of the QWs, or are the “QWI-defects”. However, the LT material also had increased carbon concentrations. Recent evidence indicates that C acts as

poor donor in InP⁴⁵. Thus, in our material, both the negative carrier concentrations (measured by the Hall effect) and the acceptors (measured by PL) could be due to C, but the QWI-defects cannot be C since C diffuses at very slow rates⁴⁶. Therefore, the QWI-defects must be native defects. Docter et al.⁴⁷ have shown, via SIMS, that GaAs and InP material grown at low temperatures by MBE have an excess of group-V atoms. This was only measurable for growth temperatures of 300°C and lower (since the measurement resolution was 0.1% excess P), although one can extrapolate that some excess P should still occur at the more moderate growth temperatures employed in this work. Other work has shown, using detailed glow discharge mass spectroscopy (which has a higher sensitivity than SIMS for many impurity elements), that nominally undoped InP had more n-type carriers than there were impurities present – thus there must be a native donor in the material⁴⁸. In the paper, the authors believed that the donor was a $V_{In}H_4$ complex⁴⁹, but the experimental evidence for its presence (3 scattered data points) is questionable. Other convincing experimental work has shown that the P antisite is found in epitaxially grown material and that it is a donor⁵⁰, which is also supported by theory⁵¹.

Further work is obviously required to investigate the various defect models. The LT growth here is significantly different than LT growth reported by other researchers, in that the growth temperature is only reduced by a few tens of degrees, and not the more common hundreds of degrees. It is also the only work on CBE grown material, which may result in some unique features. It is challenging to characterize the defects in our low temperature growth material because defect concentrations are low (expected to be in the mid- 10^{15} to mid- 10^{16} cm⁻³ levels, given the previous SIMS and Hall carrier concentration results in this thesis) making most signal intensities difficult to detect. A few advanced techniques which could be useful for such low concentrations include optically detected magnetic resonance (ODMR, which has been used to identify P antisites^{52,53}), localized vibrational mode spectroscopy⁵⁴, or a recently developed technique employing p-i-n diodes with layers with grown-in defects placed in the undoped layer⁵⁵.

E - Comparison of Different Structures

In section A, a series of knee curves for different structures indicated significant variability, and the possible causes for the variability were briefly mentioned. The next three sections of this chapter have shown that the observed variability in knee curves is not due to the RTA (section B), but can be due to grown-in defects (sections C and D). It has been shown that an error function profile and a k ratio of 2 are reasonable assumptions for modeling the interdiffusion, at least in the case of grown-in defects and lattice-matched, undoped QWs. We will at first assume that these assumptions are also valid for other structures. Armed with this information, we can now revisit the knee curves observed in figure IV-1 and convert the blueshifts for each curve into interdiffusion lengths, thus allow for fair comparison between different structures. Relevant details of the QW and barrier compositions for each of the structures are given in table IV-7.

For each sample the blueshift has been converted into an interdiffusion length by applying error function and $k=2$ modeling to all the structures, as shown in figure IV-19. To do this, the QW1 modeling program is run once for each structure, and for each run, the outputs of blueshift of the e1-hh1 transition as a function of group-V interdiffusion length are fit with a polynomial equation, with the exception of structure H (which has a tensile QW), where the e1-lh1 transition is used since the lh is the lowest hole state. The interdiffusion length for each sample is then calculated from the measured blueshift using the appropriate polynomial fit. Because these structures were designed for other projects, there is no systematic variation of one parameter, but the structures can be categorized by strain and by doping. Structures with unstrained QWs are shown in blue, compressive in pink and tensile in green. Also, p-x-n doped structures are represented with filled symbols (where x represent various doping configurations in the QW/B layers), undoped with open symbols, while the all n-doped structure (C) is shown with asterisks.

Table IV-6: key structure parameters for comparison of knee curves (nominal values).

Structure	overall doping*	QW				Barrier			
		strain	comp.	doping	L _z (nm)	strain	comp.	doping	L _s (nm)
A	p-i/i-n	0%	InGa _{0.47} As	i	5.5	0%	InGa _{0.28} As _{0.57} P	i	20.0
B	p-i/i-n	0%	InGa _{0.40} As _{0.88} P	i	9.5	0%	InGa _{0.15} As _{0.32} P	i	8.0
C	n-n/n-n	0%	InGa _{0.47} As	n	8.0	0%	InP	n	18.7
D	i-i/i-i	-1.5%	InGa _{0.21} As _{0.91} P	i	5.0	0%	InGa _{0.20} As _{0.43} P	i	16.0
E	p-n/p-n	-1.3%	InGa _{0.19} As _{0.81} P	n	5.0	0%	InGa _{0.25} As _{0.53} P	p	10.0
F	p-n/p-n	-1.0%	InGa _{0.18} As _{0.89} P	n	5.0	0%	InGa _{0.25} As _{0.53} P	p	10.0
G	p-i/p-n	-1.0%	InGa _{0.15} As _{0.82} P	i	3.5	0%	InGa _{0.15} As _{0.32} P	p	10.0
H	i-i/i-i	+0.5%	InGa _{0.54} As _{0.98} P	i	8.5	0%	InGa _{0.20} As _{0.43} P	i	16.0

* p-n/p-n indicates the doping in the upper cladding – QWs/barriers – lower cladding
 , negative strain is compressive

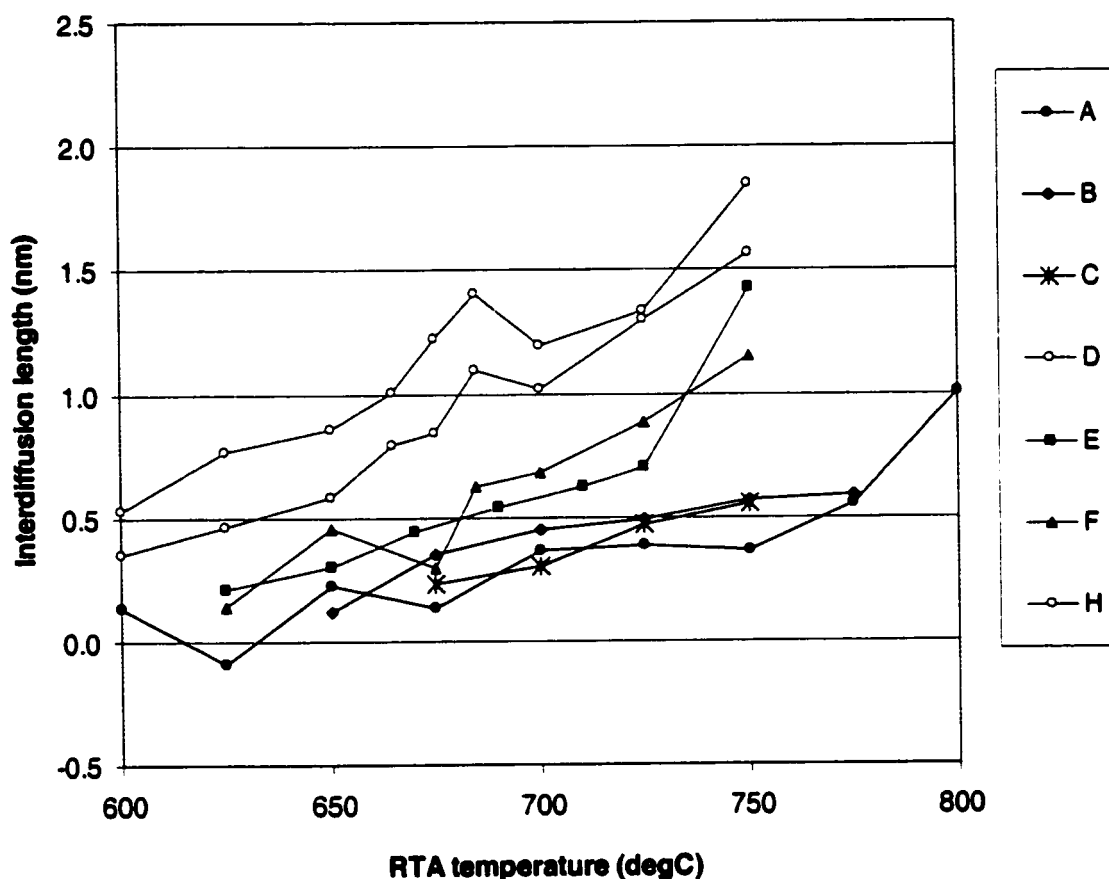


Figure IV-19: Plots of interdiffusion length of the group-V sublattice as a function of anneal temperature (for 90 s anneals) for eight different layer structures. Interdiffusion length is converted from the blueshift (plotted in fig. IV-1) assuming error function and $k=2$. Lattice matched structures are shown in blue, structures compressive QWs are shown in pink, and a tensile QW structure is shown in green; undoped wafers are shown with open symbols, and p-i-n doped wafers are shown with filled symbols, while the asterisks indicate an all-n doped structure (further details are contained in table IV-7).

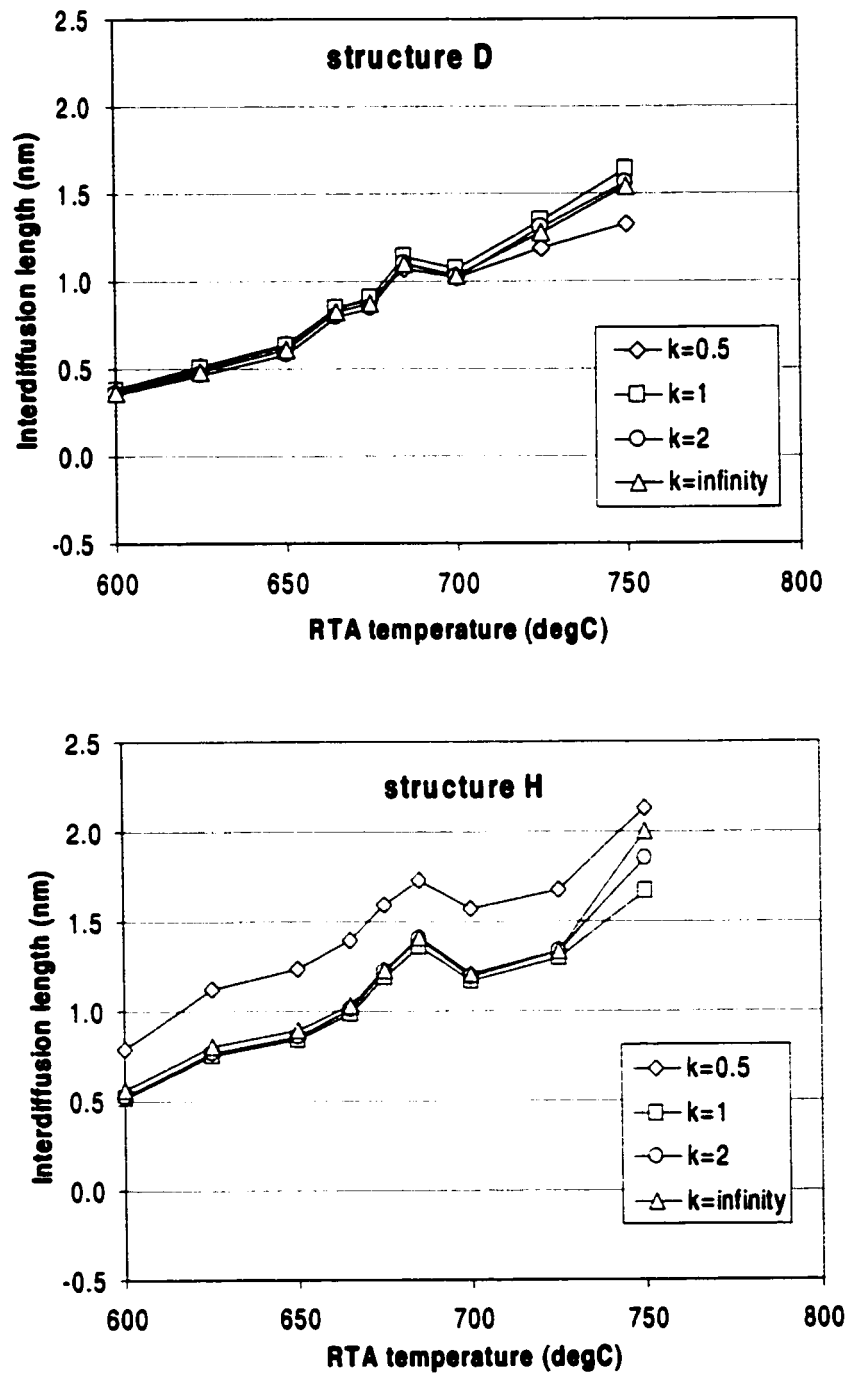


Figure IV-20: Plots of interdiffusion length of the group-V sublattice as a function of anneal temperature (90 s anneals) for two of the layer structures from figure IV-18. Interdiffusion length is converted from the blueshift (as plotted in figure IV-1) assuming error function and several different k ratios.

There is a definite trend in the results shown in figure IV-19. The three most stable structures (blue lines) have lattice matched QWs, followed by the four structures with compressive QWs, while the structure with the tensile QWs exhibits the most interdiffusion. This seems to imply that strained QWs are less stable than lattice-matched QWs. Unfortunately, only one anneal was performed on these structures, thus we cannot say whether the blueshifts in the strained structures are due to an equilibrium or a non-equilibrium phenomenon. If the cause is non-equilibrium in nature, it would imply that defect incorporation is more prevalent when growing strained layers¹⁹. If the cause of the enhanced interdiffusion in strained materials is an equilibrium effect, there are two possibilities to consider:

- (a) the equilibrium generation of defects depends on composition, and then this data implies that strained layers (both tensile and compressive) have larger generation rates, or
- (b) the number of defects and type of intermixing is the same, but the probability of atomic hopping increases in the strained layers. This type of explanation is only possible for an interstitial defect mechanism: motion of vacancies necessarily requires atomic exchange, whereas interstitial motion can travel significant distances without interacting with the lattice, and only cause atomic exchange if kick-out mechanisms are energetically possible.

Alternatively, we should consider the possibility that the variations between curves are due to inaccuracies in our modeling, i.e. our assumption that the k ratio is the same in all structures is flawed. A k ratio of 2 or larger was proven to be valid for lattice-matched structures, but it could be different for the tensile and compressive structures. Thus the modeling has been repeated for structure D (compressive) and structure H (tensile), using alternate ratios of k . Results, as shown in figure IV-20, indicate that different k ratio assumptions have only small effects on the resultant position of the curves, and thus approximations in modeling are not the cause for the observed differences between structures. Additionally, the work of others indicates that $k=1.5$ for strained layer structures^{56,57}.

Thus we are left with the equilibrium or non-equilibrium strain dependent arguments presented above. There is conflicting information⁵⁸ in the literature as to whether strain is⁵⁹ or is not a factor^{60,61} in interdiffusion. Since local strain development has been shown to occur during interdiffusion, it is unlikely that it is a driving force for interdiffusion. More work, in particular with a specifically designed series of growths should be undertaken to study the effects of strain. The quality of the material must be confirmed, in part by performing a series of multiple anneals to assess whether shifts are or are not equilibrium in nature.

At a first glance, it appears that there might be a dependence on doping, since the two curves for undoped samples (open symbols, structures D and H) have shifted the most. However, recall that in section B, the standard growth CBE p-i-n and CBE i-i-i wafers had similar knee points (the temperature below which no blueshifts occur) although a small difference in magnitude of blueshift did occur above the knee curve. These structures are the same as structure A presented in figure IV-19, thus the difference in doping is unlikely to be the reason why structures D and H shift so much.

F – Conclusions

Several aspects relating to thermally-induced QWI have been studied in this chapter. The annealing temperatures required for QWI are higher than growth temperatures and most other typical processing steps, and this puts tough requirements on many aspects of the research. First, reproducible annealing is a key requirement for all diffusion studies, and this demands consistency and attention to detail. Tests and analysis of annealed material, such as the experiments described in section B, should be done to gain confidence and eliminate sources of error. Control of the group-V overpressure must be carefully considered; the proximity cap method used here may have led to some surface degradation, manifested in a decrease in PL intensity with anneal temperature.

The quality of growth is a second variable that must be assessed, and studies in this chapter have shown that subtle changes in epitaxial growth can influence QWI. Multiple anneals are required to determine whether the blueshifts are due to grown-in defects. Such experiments could be used as a new metric for measuring the quality of epitaxial growth (in addition to standard characterization such as PL, XRD, Hall conductivity, etc). For example, in the last section, a comparison of one-anneal knee curves from six different structures indicated that strained layers tended to have a lower thermal stability than lattice matched structures, but further research, using multiple anneals and specifically designed layer structures, is required to conclude whether the cause of the enhanced QWI is due to the strain itself (as-grown material in equilibrium) or due to a tendency for less optimal (non-equilibrium) growth of strained layers.

The variation in QWI with growth conditions can also be used advantageously as a new means of purposeful and selective QWI. It was demonstrated that by growing a buffer layer with grown-in defects above the QWs, and then selectively etching it away in some regions, one can intermix regions selectively. This was accomplished using CBE growth at reduced growth temperatures. Detailed analysis also allowed for some new insights to be drawn on the mechanisms of the QWI - it is believed that the defects in this LT grown InP are related to excess P, which then releases P interstitials that act as the mobile defects which enhance QWI. Their diffusion coefficient was found to be in the range of 4×10^{-10} to 4×10^{-11} cm²/s, the exact value depending on what assumptions are used with regards to the role that the semiconductor's surface has in defect annihilation. It was also determined using both optical transmission and XRD that the intermixing caused by LT growth occurs predominately on the group-V sublattice, with a k ratio between 2 and 4 being an appropriate description. This is the same sort of value that has already been measured for QWI caused by implantation^{38,44} and dielectric cap disordering³⁹. Since the RTA conditions and resultant changes to the QW are similar to those observed for implantation-induced QWI (shallow P⁺ implantation), we suspect that it is the same QWI-defect in both LT growth and implantation which mediates the

intermixing. The LT growth is a simpler system than implantation to study and understand, and it may even be attractive for manufacturing as well – since it alleviates the need to purchase and operate an ion implanter. Further discussion on the types of defects expected in the case of implantation is included in the next chapter.

Finally, it was shown that analysis of the relative energy shifts between hh and lh states was useful for determining the ratio of group-V to group-III interdiffusion lengths (k) but was not capable of determining whether the intermixing was Fickian or not. Instead, direct characterization of the compositions, although challenging, will be beneficial. A brief look at using XRD to model the intermixing indicated that no matter which intermixing model is employed, k ratios between 2 and 5 can be concluded, and secondly, it may be possible to differentiate between different shapes of QWs if more rigorous modeling of the XRD spectra is undertaken.

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Chapter V – Implantation-Induced Intermixing

A – Introduction

Ion implantation can be used as a means of introducing excess defects into selected regions of a wafer, which will enhance intermixing in those regions during a high temperature anneal. Implantation-induced QWI, as studied in this thesis, involves the implantation of P ions into InP buffer layers located above the QWs. Some of the lattice defects caused by the implantation are quite mobile, and diffuse down through the underlying QWs and enhance their interdiffusion during a subsequent anneal. This chapter will be devoted to a more detailed study of this process. Overall, we will cover a similar set of issues as were discussed in the previous chapter (but now on implantation instead of thermal behaviour), including optimization of processing parameters, comparison of material grown in different reactors, reproducibility, and analysis of the identity and motion of defects. Section B will cover the basic concepts of implantation and discussion of implantation as applied to QWI. This section contains a significant review of the literature on implantation in order to build pictures of the nature of the defects which cause QWI. Section C will cover the implantation portion of the growth comparison study, where the repeatability of the implantation-induced QWI is proven, and the anneal time and temperature are studied to determine best conditions of annealing of implanted material. The motion of the implantation-created QWI-defects is analyzed, and the nature of the QWI-defect is discussed in light of a measured activation energy.

In practical application, the spatial distribution between implanted and non-implanted regions, must be known, and this is addressed in section D, which contains a study of the lateral selectivity of the technique. The motion of the defects are again analyzed using these results. Section E presents a study of the effect of intermixing on changes to refractive index, and showcases one example of how this property can be used advantageously in order to fabricate a novel buried waveguide device. The studies in these latter two sections has been particularly successful,

and resulted in the publication of two papers. The papers are included herein to directly form part of this thesis.

A summary of the findings on implantation-induced QWI is given in Section F.

B – Implantation Damage and Intermixing

Basic Physics of Implantation

During the process of ion implantation, atoms are ionized, accelerated in an electrostatic field and implanted into a solid. The penetration depth of the ions depends on the accelerating voltage, the mass of the ion, atomic mass of the solid, and other parameters (the implanted atoms are referred to as ions, and the host atoms called atoms). The concentration profile of the ions can be approximated as a Gaussian distribution, with an average projected range R_p and a standard deviation ΔR_p , following the theory of Lindhard, Scharff and Schiott (LSS theory)¹. Simulated depth profiles for several different implantation energies are shown in figure V-1.

For high energy implants (the order of 100 keV to 10 MeV), when the ion first enters the solid the slowing-down is mainly by electronic stopping (due to interaction with the electrons of the target), and the ion moves in an almost straight path. When the ion has slowed down sufficiently, the collisions with nuclei become more probable, and finally dominate the energy loss. Following a collision, when atoms of the target gain significant recoil energy, they will leave their lattice positions and produce a cascade of further collisions in the lattice. The process is schematically illustrated in figure V-2. These collision cascades are the main cause of damage production during ion implantation. The amount of damage and its distribution depend on the ion, the energy, the dose, and the target temperature. As dose is increased, the damage tracks will begin to overlap, and finally, above a critical dose (dependent upon the implant conditions), amorphization will occur². Lateral straggle, ΔR_L is defined as the distance that ions will penetrate laterally under a mask edge. It is typically the same order as the straggle in the depth direction, ΔR_p .

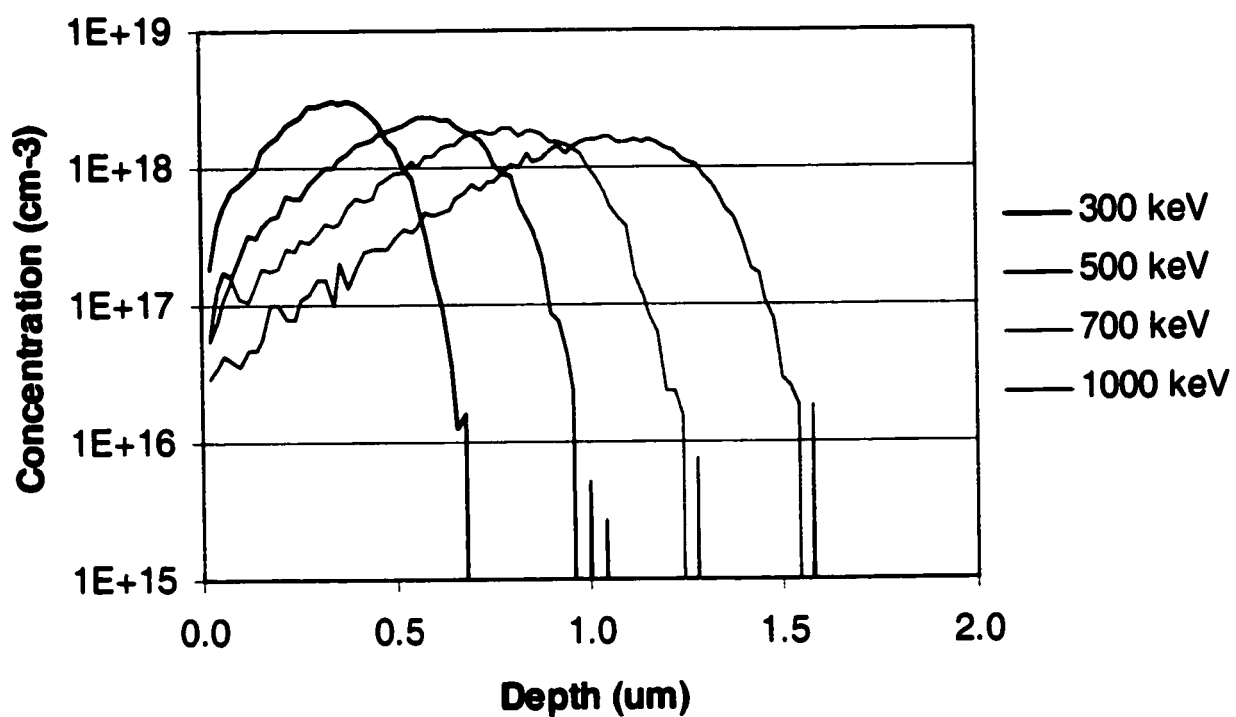


Figure V-1: Ion depth profiles obtained from SRIM for 300, 500, 700, 1000 keV P⁺ ions into InP. Concentrations are for an implanted dose of $1 \times 10^{14} \text{ cm}^{-2}$.

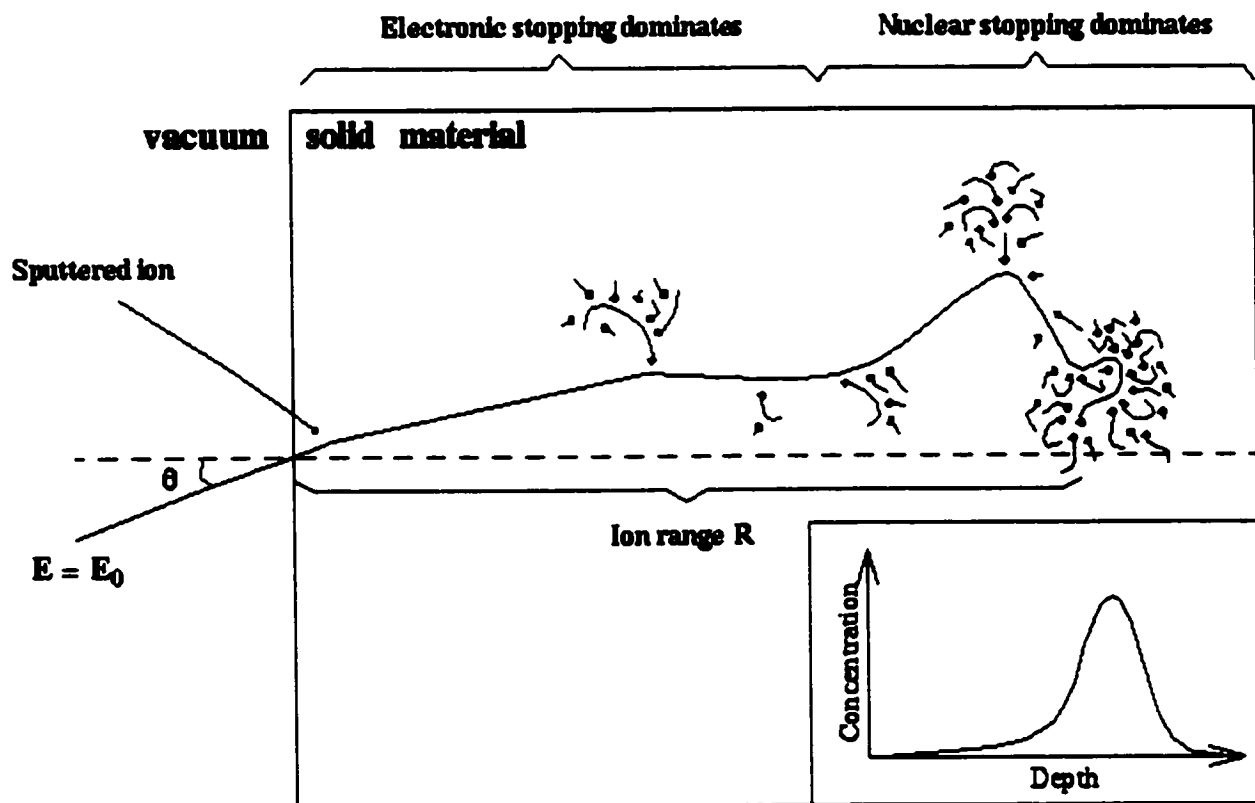


Figure V-2: Illustration of the slowing down of an implanted ion in a solid material, including the production of collision cascades. The inset shows a typical depth distribution for the implant damage.

It is caused by nuclear collisions which cause the atoms to recoil in all directions, and is accounted for within standard theory. The effects of channeling cause deviations from the theoretical distribution³. Channeling, which occurs when the ion trajectory is parallel to a lattice planes of a crystal, allowing the ions to travel between crystal planes where they experience very few nuclear collisions. The penetration range is significantly increased when this occurs, and small variations in the incident angle can lead to dramatic differences in the magnitude of channeling, and therefore in the penetration depth. For this reason, it is common practice to minimize channeling by specifically tilting a crystalline solid into a non-channeling angle⁴. Even then, it is still possible for some of the recoiled atoms to acquire channeling trajectories and thus penetrate deeper than will be predicted using amorphous assumptions⁴.

Defects Created by Ion Implantation

The simplest lattice defects created are Frenkel pairs. Divacancies and trivacancies can be produced when neighbouring atoms are displaced, or through migration of single vacancies. Similar interactions between other point defects, or between a point defect and an impurity atoms will also occur. Dislocations and other defect clusters (including amorphous zones) can be formed from the accumulation of simple defects. The portion of the ion energy loss which is electronic results in a heat spike along the ion track which helps the point defects diffuse and annihilate. This process is known as dynamic annealing. Tracks left by light ions (primarily stopped via electronic processes) have only a small amount of damage, while heavier ions tend to cause more nuclear collisions. Since ions require a certain energy for the production of the damage, the ion distribution is always slightly deeper than the damage distribution (~200 nm for the implant parameters used in this work).

There is still much to be learnt with respect to the damage found in implanted III-V semiconductors. Textbooks on implantation typically contain an introductory discussion of the damage in III-V compounds (again usually on GaAs, while InP

typically receives only a few short paragraphs). Even in the simpler and more studied silicon, it is not a priori clear how the as-implanted population of vacancies and interstitials develops into more complex defects. The binary nature of the GaAs and InP lattices makes damage removal more complex than in elemental semiconductors. This is partially due to deviations of stoichiometry, caused by the unequal displacement of lattice constituents with differing masses (lighter atoms recoil further). A majority of papers focus on the electrical properties of the material following implantation (for doping or isolation) plus annealing, which gives useful but incomplete information on all the induced changes. A brief summary of annealing behaviour is given below for GaAs⁵. InP shows similar trends in terms of the generalized thermal behaviour of the defects, although annealing temperatures tend to be ~100°C lower, and the defects' electrical properties are not always identical. The main defects created in InP act as donors, whilst those in GaAs act as deep centers.

Table V-1: The general stages of defect annealing in GaAs. InP is expected to have similar trends, but with temperatures about 100°C lower, as summarized from Pearton⁵.

Temperature	Stage
150-200°C	recrystallization of amorphous layers begins, leaving twins, stacking faults and other defects
400-500°C	the above defects anneal out, leaving dislocation loops
600°C	short range diffusion of dopant atoms from interstitial sites to lattice sites (activation) begins
700°C	dislocation loops grow and annihilate
750°C	point defect clusters begin to anneal out
>750°C	optimal dopant activation of acceptors
≥850°C	optimal dopant activation of donors

Implantation Applied to QWI

The implantation-induced QWI, as studied in this thesis, involves the implantation of P ions into InP buffer layers located above the QWs. It is this implant damage that is used as a source of mobile defects which enhance interdiffusion in underlying QWs. During the RTA stage of the QWI process, defect reactions will cause removal of some defects, agglomeration of others, as well as release of mobile defects which cause the QWI which we will call QWI-defects. The agglomeration occurs in particular at the ion's end-of range, leading to occurrence of dislocation loops⁶, which may have an interstitial nature⁷. Currently, the identity of the QWI-defects are not known, although they are expected to be point defects, either vacancies or interstitials, because they exhibit fast diffusion rates (to be further discussed below). It is the motion of these defects through the QW that enhances intermixing compared with un-implanted material which is annealed under the same conditions.

QWI using ion-implantation has been studied by Charbonneau et al. since ~1990, with work on InP beginning in ~1993. The results showed that shallow implantation of P⁺ ions provides a means of modifying an active region buried ~2 μm below the surface while causing minimal degradation of other important parameters. Two important results were that laser device lifetimes and waveguide absorption losses below the bandgap were not altered by the intermixing. This meant that the implantation damage left after the RTAs did not cause any additional losses or changes to electrical characteristics. A good review of this work can be found in the references⁸. This section gives a summary of the optimal implantation parameters found in that work, as well as a review of other relevant literature on implantation, and discussion of possible defect identities.

The implantation in both the previous work and for this thesis was performed by collaborators at the University of Western Ontario using a 1.7 MeV Tandemtron accelerator. Most of the research has focused on implantation of P⁺ ions, which, being one of the constituent atoms of InP, does not result in any chemical/doping

changes to the layer structure. Implantation of In⁺ ions has been studied recently⁹, and results indicate that the main effect of the implantation is the creation of crystal damage, which will depends on the ion's atomic mass but not its type (electronic structure).

A study of QWI as a function of implantation energy by Poole et al. gave some insights onto the defects' motion¹⁰. It was found that a substantial amount of intermixing occurred even for low implantation energies (0.5 MeV) which placed the damage about 1 μm above the QWs. Although blueshifts were higher for implants that placed the damage into or deeper than the QWs, this came at a cost of increased PL linewidths and significantly reduced PL intensity. When comparing result with simulations (using SRIM, which will be reviewed shortly), there was a strong correlation between the blueshift and the "total implant damage" (integrated over the entire depth distribution). This seems to indicate that the starting location of these QWI-defects was not important, and that they could diffuse significant distances during annealing. Under this theory, the deeper implants caused more intermixing only because they created more total damage, not because of where the damage was created. In order to keep the end-of-range damage spatially separate from the QWs and thereby minimizing any reduction in their optical efficiency, it is preferable to chose an implantation energy having an end-of-range above the QWs. Thus this study concluded that shallow ion-implantation (above the QW) was viable for the intermixing of InP-based structures. The opposite finding was true for As implanted GaAs, where damage had to be created near the QW in order to be effective at intermixing. Thus the implantation-induced QWI process in GaAs was found to be significantly different than in InP^{11,12,13,14}, and it appeared that either the As implantation process did not create the right kind of defects for GaAs/AlGaAs QWI, or that the defects had much slower diffusion rates.

A rule of thumb that is used by the group is that, using SRIM simulations, the implanted ion concentration should drop by 10^3 from its peak value at a distance of $\sim 0.5 \mu\text{m}$ above the QWs. For a given layer structure (which defines the depth of the

QWs from the surface) the implant energy is adjusted based on this criteria, usually resulting in values in the range of 500 to 1000 keV for structures with a thick cap above the QWs. Good recovery of PL intensity has been observed when following this rule.

During implantation, samples are tilted by 7° and twisted by 20° in order to minimize any channeling effects. In application, simple masking, for example using a thick ($\sim 2\mu\text{m}$) SiO_2 layer, can be employed to implant only in selected regions of the wafer. Other masking materials should be equally useful, provided they are thick/dense enough to completely block the implanted ions (i.e. thicker than the implant range into the mask material) and are stable during implantation, and can be subsequently removed before the anneal. It is also possible to use a thinner mask, which allows some of the ions to penetrate into the semiconductor¹⁵, and then by using a mask with a different thickness in different regions of the wafer, one can shift each region by a different amount while only performing a single implant. For research purposes, our $\sim 6 \times 6$ mm samples are often half masked so that the implantation and thermal effects on QWI can be studied simultaneously. In this case, a thick foil is held in front of half of the sample during implantation, to act as a simple shadow mask.

Implant dose is the main means of adjusting the number of QWI-defects created, and therefore the magnitude of the blueshift. However, the relationship between dose and blueshift is far from linear. There is a minimum threshold dose below which no measurable blueshift occurs due to lack of damage, and a maximum dose, above which the microstructure in the implanted material has become so altered that it inhibits the release of the mobile intermixing-causing defects. These minimum and maximum doses are somewhat dependent on material, implant energy, and anneal conditions, but generally are 10^{11} cm^{-2} and 10^{15} cm^{-2} , respectively^{16,17,18,19,20,21}. For moderate doses of Si into InP, the trend between dose and damage was non-linear¹³. Even if there did exist a linear correlation²² between dose and number of point-defects created for P implants into InP, this will not result

in a linear correlation with blueshift since the relationships of (a) Δ_i to number of defects and (b) ΔE to Δ_i are not necessarily linear. In Paper 3 of Chapter IV, the relationship (a) was approximated by $\Delta_i^2 \propto \int N_d \delta t$, where N_d is the concentration of defects in the QW. The relationship (b) depends significantly on layer structure, and using the QWI modeling program, data sets can be calculated – third order polynomials are required in order to get an equation which satisfactorily fit a data set.

The temperature of the sample during implantation is a critical parameter for the successful application of the P⁺ implantation technique²³. The NRC/UWO group found that room temperature implants result in very little blueshifting, while raising the sample temperature in the 50 to 200°C resulted in increases in the blueshift. This is attributed to a connection between implant temperature and the dynamic annealing that takes place during the implantation²⁴. These affect the defect spatial distribution and possibly even which type of defects are produced. Two possible explanations put forward by the group are (a) the higher temperature allows for dynamic annealing^{12,25}, where the defects diffuse further away from the center of the implant damage track, where they might otherwise be locked up; or (b) the temperature alters the relative concentrations of different defects, with more of the mobile intermixing-causing defect being formed at higher temperatures. Implanting at ~200°C has also been shown to be beneficial for electron mobility²⁶ and percentage activation²⁷ in dopant implantation. Dose rate (the rate at which ions are implanted into the sample, usually expressed as a current) is also interconnected to the type of damage production^{13,28}, and larger QWI blueshifts were found at low dose rates. This may relate to two different implant damage regimes: stage I (at lower dose rates and higher temperatures) which is associated with simple defects within individual collision cascades, and stage II (higher dose rates and lower temperatures) where the accumulation of damage leads to amorphization. Thus the nature of the dependence of QWI on several of these factors, all suggest that the QWI-defects are connected with relatively simple defects. A summary of the typical values for the implantation parameters in QWI is given in table V-2.

Table V-2: Typical parameters used for shallow-ion implantation-induced quantum well intermixing of InP-based structures.

Parameter	Typical selections
Ion species	P ⁺
Implant energy	500 to 1000 keV
Implant dose	10 ¹² to 10 ¹⁵ cm ⁻²
Implant dose rate (flux)	20 to 100 nA/cm ²
Sample Implant Temperature	200°C
Implant non-channeling angles	7° off-axis + 20° azimuthal twist

It is unclear at present whether the distribution of the QWI-defects (or the complexes from which they originate) is the same as the distribution of total damage, as predicted by SRIM, or if these defects originate from a specific regions of the distribution. For example, variations in stoichiometry can result from implantation in compound semiconductors, where lighter atoms, in this case P, are recoiled deeper than the heavier In atoms. There is also an offset between the vacancy and interstitial profiles²⁹. It is possible that this excess of P in the deeper regions is responsible for the production of the QWI-defects. Alternately, a “supertail” relating to diffusion of interstitials has been reported in other material systems³⁰. No thorough study has been undertaken to examine this issue within InP or GaAs. In silicon, some evidence exists that the “+1” model or the “effective +1” model^{29,31,32} can be used to quantify the damage caused by implantation. It is appealing for its simplicity - in essence, the damage left behind after implant is equal to one interstitial per implanted ion – but it may be a bit too simplistic for compound semiconductors.

Simulating Implantation - SRIM

SRIM (formerly TRIM) is a program available from Ziegler³³ which calculate the stopping and range of ions into matter. SRIM simulates the implantation using a

Monte Carlo approach, which follows the motion of an implanted ion through a material, keeping track of inelastic and elastic energy loss mechanisms until the ion comes to rest. By following the history of a large number of ions, sufficient statistics can be obtained. The target material is assumed to be amorphous, with atoms in random positions, and thus the directional properties of the crystal and channeling effects are ignored. SRIM can also follow the motion of any of the atoms which have gained energy due to nuclear collisions. Various results are possible as the result of a collision, including production of a vacancy (both atoms have enough energy to move away from the lattice site), a replacement (the incoming ion stays on the site, but sufficient energy has been transferred to the target atom that it leaves) and an interstitial (neither atom or ion have enough energy to leave the site). Atoms with insufficient energy to move on give off their energy as phonons. Thus SRIM can also output the distribution of vacancies, replacements, and energy lost to phonons. The program's user manual gives an overview of the calculations, while a full description of the science behind the calculations is written by Ziegler and Biersack³⁴.

With regards to the predicted ion distribution, SRIM can produce significant errors for implantation in crystalline materials when channeling occurs^{35,36}. Both the ZBL interatomic potential and the electronic stopping power used by SRIM have inaccuracies of the order of 10-50%³⁷. This being said, the implantation conditions we use are relatively well described by the theory behind SRIM's calculations, and the accuracy of ion distributions for our conditions are reasonable^{11,36}. Different versions of SRIM, in which the stopping power was re-parameterized, have given differences of the order of 10-20% for our implantation conditions³⁸. This accuracy is sufficient for our present purposes. However, SRIM is inherently poor at providing accurate predictions of the lattice damage^{11,36}. First, with each ion calculation, a perfect (undamaged) solid is assumed, and thus any build-up of damage and the effects that this would have on subsequent collisions, as well as the final nature of the residual damage, is not accounted for. Second, SRIM does not account for defect diffusion during the implant or defect interactions, which play

an important role in real materials. Finally, SRIM does not operate using a lattice picture, and for III-V semiconductors, does not differentiate between group-III and V atoms or their lattice sites, therefore the predicted number of vacancies or interstitials are a sum of III and V types. However, SRIM can be used to estimate the shape or *relative* distribution of *total* damage created by implantation³⁹, although the actual concentrations and species distributions are not known. To this extent, the distribution of damage as predicted by SRIM can be used to assess trends in the implantation-created damage in InP⁴⁰ as a function of energy or dose.

Reasonable agreement of the relative damage distribution between SRIM predictions and Rutherford backscattering analysis have been found for 200 keV and 1.6 MeV Ar⁺ implants into InP¹¹.

For a P implant with a dose $1 \times 10^{14} \text{ cm}^{-2}$ and energy of 1000 keV, SRIM will predict a maximum concentration of implanted ions and implantation-created vacancies of $1.6 \times 10^{18} \text{ cm}^{-3}$, and $4.5 \times 10^{21} \text{ cm}^{-3}$ respectively. The latter value implies that one out of every ten atoms is disrupted (InP has a total atom (In and P) concentration of $\sim 4 \times 10^{22} \text{ cm}^{-3}$), and the material would likely be amorphous. But in reality InP is not amorphized by this implant condition², because of the effects of dynamic annealing (especially at elevated implant temperatures) which reduce the residual damage in real material by orders of magnitude. Assuming one order of magnitude decrease in the number of residual “vacancies” (this is an arbitrary choice, although it may be a reasonable estimate of reality^{41,42}) still implies that on average, one out of every one hundred atoms are displaced at the peak of the damage distribution. Since the damage is actually more localized along the cascade tracks, the chance that these point defects have in fact interacted with each other is significant, thus defect complexes would very likely be formed for this magnitude of damage.

QWI-Defect Motion

The mechanism(s) by which these point defects are released from the implant damage are also poorly understood. One means of gaining insight, is to study the dependence of the intermixing on annealing parameters, as will be undertaken latter

in this chapter. Annealing time dependence has been briefly studied by a few groups. The work of Poole et al.¹⁰ indicated that most of the implantation-induced interdiffusion occurs within the first 120 s of annealing at 700°C (500 keV and greater implants), but the work of Paquette et al.⁴³ on a similar layer structure indicated a time of 420 s at 760°C or more was required (360 keV implants). In practical application it will be important to know the dependence on anneal time, since it would generally be desirable to employ one anneal of a long enough length that the interdiffusion has reached a plateau, i.e. no further interdiffusion will occur if the anneal time was further increased. We will refer to this as a saturation of the blueshift. At this point, all the available QWI-defects have been released from the implant damage, and thus the desired effect of the implant (the blueshift) has been maximized while undesired side-effect (the implantation damage) has been diminished. Changes to the anneal temperature will of course affect the time to reach this point. There may also be some trades offs with development of other effects with anneal time, such as loss of group-V from the surface.

The high mobility of these defects, not only in InP, but also in InGaAs(P) and across InGaAs(P)/InP interfaces has been observed. This first evidence that the InGaAs(P)/InP interfaces did not impede defect motion was from an examination the PL from a multi-QW stack. The absence of any increase in the PL linewidth following interdiffusion indicated that all the QWs in the stack interdiffused equally. This was further confirmed using direct physical analysis of the QWs using cross-sectional scanning tunneling microscopy (STM) on a twenty QW stack, in which the uppermost and bottommost intermixed QWs looked identical⁴⁴. This property of InP-based structures is different from GaAs-based structures, where trapping of the defects at interfaces has been found⁴⁵.

Details of the Interdiffusion at the QWs

So far, all these issues have been related to process conditions for the production and diffusion of defects (topic 1 from Chapter I). Some important studies relating to the compositional changes to the QWs (topic 2) have also been undertaken at NRC.

Two different methods have been used to show that for QWI caused by shallow P⁺ implantation, the interdiffusion occurs primarily on the group-V sublattice. From polarization resolved waveguide transmission⁴⁶, the splitting between TE and TM spectra was monitored, and found to decrease to zero for sufficient intermixing, indicating that the hh and lh transitions were degenerate. This was attributed to a development of tensile strain in the QW center, which occurs when $k > 1$ (see Chapter II-D). Implantation-induced intermixing was also studied using cross-sectional STM⁹. In the STM image of the cleaved ($\bar{1}10$) surface of an interdiffused QW, increased tunneling occurred at QW/barrier interfaces but was reduced in the center of the QW. This contrast was attributed to bowing of the surface resulting from biaxial strain in the layers, where compressive biaxial strain causes outward bowing and increased tunneling. The profile exhibited by the sample can only be explained by $k > 1$. Additionally, the exact magnitude of the surface bowing, combined with the known shift of the PL energy for the same sample, were used in combination to determine a value of $k = 1.7$ (with error function interdiffusion assumed). The k ratio from this STM study has been recently revised to be nearer 3.0 using a more precise elastic model⁴⁷.

The shape of the QW following implantation-induced QWI is not yet known. Most published papers still assume error function profiles.

QWI-Defect Identity

The above k ratio is very similar to that found in Chapter IV for QWI due to grown-in defects. Given all the similarities between the two types of intermixing (the starting location of the defects in an upper buffer, similar RTA temperatures and times for saturation, similar k ratios for lattice-matched structures) it seems very likely that it is the same defect mediating the intermixing in both cases. So although the original population of defects in the two systems is likely different, they still seem to produce the same mobile defect. In Chapter IV, we proposed that the QWI-defect in the case of LT growth was a P interstitial, related to excess grown-in P. The QWI-defect is necessarily a native defect in the case of implantation of P into InP, so this

further supports our claims that it is a native defect (and not a growth-incorporated impurity) in the case of grown-in defects. A k ratio larger than one has also been observed from thermal-only processing⁴⁸ and dielectric cap annealing⁴⁹. Some papers claim that the main point defects produced by implantation are interstitials^{7,50,51}. In fact, in silicon, transient enhanced diffusion (transient aspect is governed by a supersaturation of point defects resulting from implantation) has been shown to be due to interstitials created during implantation⁵². For example, implantation of Si into a Si substrate with an already stabilized dopant profile resulted in further diffusion of the dopants, in the case where the diffusion of that dopant species is mediated by interstitials (B, P)^{53,54}. This occurred even when the Si implant was shallower than the location of the dopant distribution, indicating that the interstitials were fast diffusers. In fact, Wendler et al.² argue that the annealing behaviour of implanted InP indicate that the defect production is strongly influenced by the phosphorus interstitials. In a study of Sb (a group-V species) implantation into GaAs/AlGaAs structure induced defects which reached depths 30 times the projected implant range, and that these defects were not Sb, but likely As interstitials. A paper by Glew⁵⁵ showed that intermixing increased with group-V overpressure during annealing, and concludes that the group-V interstitial is the likely identity. Other relevant results pointing to a group-V interstitial mechanism in non-implantation studies were discussed in Chapter IV (Paper 2 in particular).

Arguments have been made that since smaller atoms should be able to more easily fit into interstitial sites, they should have higher interstitial diffusion rates than large atoms⁵⁶. Such a correlation has been found in metals⁵⁷. The zinc blende crystal structure is a relatively open lattice, with significant interstitial sites and large channels. Using estimates of the relevant radii, we have calculated the tetrahedral interstitial sites in InP, with details given in the Appendix A. The results show that neutral group-V atoms (P and As) should fit reasonably easily (P in particular). P_i fit more easily than As_i , which could even be used to develop a model of non-Fickian interdiffusion of the QW consistent with a kick-out mechanism (where P_i diffuse larger distances than As_i before causing a kick-out).

We are not yet at the point of concluding that the QWI-defect is a phosphorous interstitial, but a significant amount of evidence is building that this may be the case. There are also some papers which argue for a vacancy picture of the defect mediating the group-V interdiffusion⁵⁸. For most of this chapter, the defects will simply be referred to as QWI-defects, and only a small additional discussion on their nature will be included at the end of the next section in light of Arrhenius-type analysis. Given the results found for implantation-induced QWI⁹, as well as the relative accuracy of the fits in Chapter IV, assumptions of error function and $k=2$ should be sufficient for modeling blueshift of the implanted samples in this chapter.

C - Growth Comparison Study – Implantation Results

The thermal behaviour of several nominally identical wafers grown in different reactors was studied in Chapter IV, and now we will focus on implantation-induced QWI on these same wafers. However, only the wafers which had exhibited good thermal stability (i.e. had no discernable grown-in defects) will be studied. This includes the three MOCVD p-i-n wafers, one CBE p-i-n wafer, and one CBE Std i-i-i. The first two studies will use the MOCVD wafers to examine the reproducibility of the blueshift under two different implant and anneal conditions. A third study examines the anneal time and temperature dependence of the blueshift, which will also compare the behaviour of the MOCVD p-i-n (1L) wafer with the two CBE wafers. The overall goal of the latter study is to further optimize the annealing parameters for the technique, as well as gain some insights into the dynamics of motion of the QWI-defects.

Reproducibility – Experiment 1

Samples from the three nominally identical MOCVD p-i-n wafers were implanted with 1 MeV P⁺ ions at a dose of $1 \times 10^{14} \text{ cm}^{-2}$ (all other implant parameters were standard, as discussed in Section A). Anneals were performed at 700°C for three 90 s intervals, with 300K PL maps performed between anneals. The three wafers are identified as 1L, 1T, and 2T, as was previously discussed in Chapter IV. The

samples were also divided into two sets, where each set contained at least one sample from each of the 1L, 1T and 2T wafers. The sets were processed (implanted and annealed) in different years, but using nominally identical procedures; within a set, the samples were annealed simultaneously.

Results of the blueshift for total RTA times of 90, 180, and 270 s are shown in figure V-3. Overall all samples behave similarly, irrespective of the wafer # or set #, proving the process has good reproducibility. The averages and standard deviations of the blueshifts of all samples after 90s, 180s, and 270s are 48 ± 4 meV, 68 ± 6 meV, and 73 ± 6 meV; this average and average $\pm$ standard deviation for 270 s are indicated in the figure with dashed lines. For all samples, there is a significant amount blueshifting during the first and second anneals, but only a minor amount of additional shift during the third anneal (compare circles to triangles). Thus the implantation-induced blueshift appears to be approaching saturation after 270 s of annealing at 700°C; further study and discussion of this issue will be done in a later section. The uniformity of the blueshift on a given sample, as assessed by PL mapping (not shown), was very good and on average was ± 2 meV, thus the observed variability is primarily due to sample-to-sample variations. We will discuss this issue in a bit more detail in what follows.

Examining figure V-3 carefully, no correlation can be drawn between blueshift and wafer number, therefore the variability is not wafer dependent. However, there is a small difference on average between the two sets, that may or may not be significant: set A's average is 78 ± 4 and set B's average is 70 ± 4 meV. This difference could be possible due to minor differences in the processing, since the two sets were annealed in different RTA ovens (set A in oven 1, set B in oven 2). Other possible causes for sample-to-sample variations could be differences in the as-grown samples themselves, or sample cleaning. With regards to the first possibility, the sample from set B, wafer 2T which exhibits the largest implantation-induced shift was taken from quite close to the edge of the wafer and exhibited the weakest PL intensity. Non-uniformity of growth near the wafer edge could result

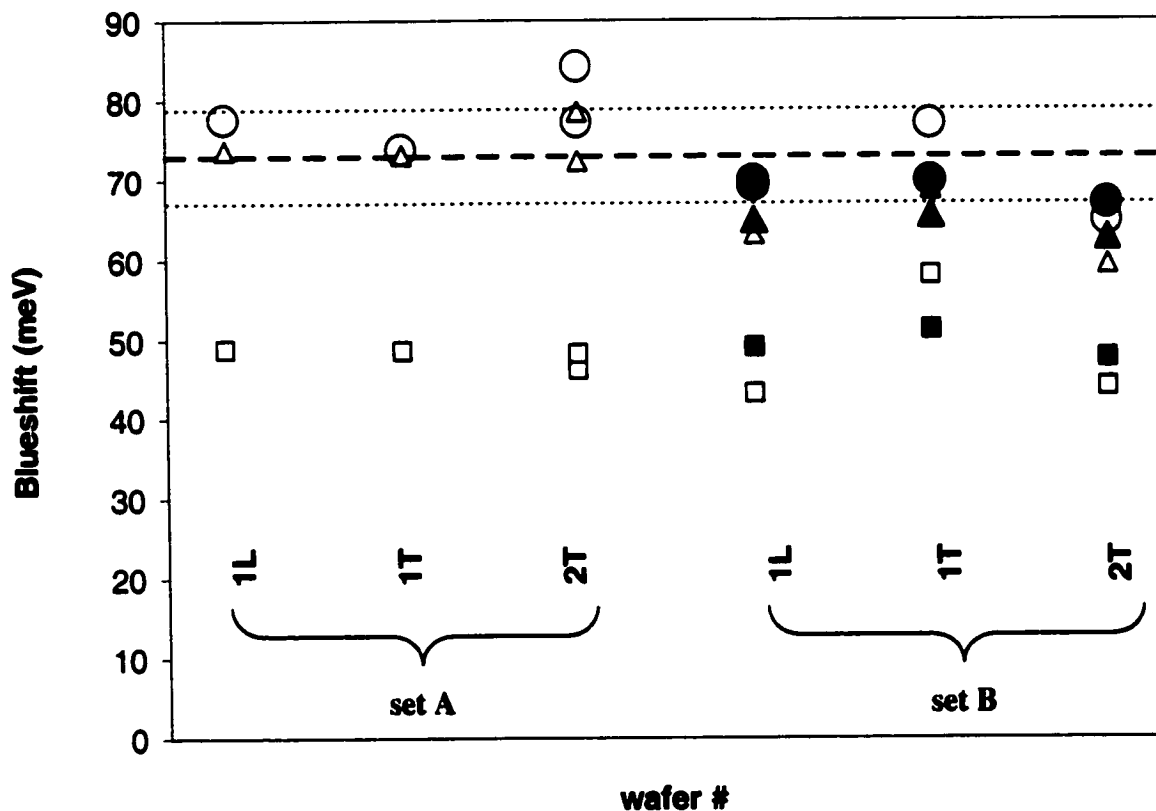


Figure V-3: Reproducibility Experiment 1 - blueshift of several samples from nominally identical MOCVD wafers implanted with 1 MeV P^+ at a dose $1 \times 10^{14} \text{ cm}^{-2}$ and annealed for 90 s (squares), 180 s (triangles) and 270 s (circles). Filled symbols indicate samples which were pre-annealed (see text for more explanation).

in increased incorporation of defects there. With regards to sample cleaning, samples are passed from solvent-to-solvent-to-DI water in batches of 3-4, but the final blow drying of DI water with $N_{2(g)}$ is the one step where a sample is handled individually. Every effort was made to remove the DI water as a sheet from each sample's surface (since allowing a DI water droplet to dry on the sample surface can leave behind residue) and this often required re-rinsing the samples. It is possible that this one sample on this one occasion was not dried properly. It would be surprising if such a seemingly inconsequential effect would cause an additional blueshift, but such a possibility would be in keeping with the result shown in Chapter IV-A, where again an alteration of the cleaning process produced an additional shift.

Within set B there are samples that had an additional anneal of 90 s at 700°C prior to implantation, which we will referred to as a pre-anneal; these samples are represented by filled symbols in figure V-3. No shift was observed following this pre-anneal, as would be expected from the thermal studies of Chapter IV.

Following pre-anneal, the samples were implanted and annealed simultaneously with the other samples of set B. It was speculated that this pre-anneal could reduce the number of defects that might be incorporated during growth, and that such a reduction could affect the defect interactions relating to implantation and standard post-implant annealing. Such an effect was seen during the intermixing of Si-Ge layers²⁵. However, the results on the current material, show that the pre-anneal has no effect on the subsequent implantation-induced shift – filled symbols behave the same as open symbols in figure V-3. This is likely because the material was of very high quality to begin with.

Overall, this study has shown that the reproducibility of the MOCVD wafers and of the implantation is excellent, and within a batch of samples the variability of the blueshift could be as low as ± 4 meV (for samples taken near the center of the wafer). Overall, a variability of ± 6 meV was observed, which was attributed to small variations in annealing, variations in growth near a wafer's edge, and possibly sample cleaning, all of which can be controlled in the future.

Reproducibility – Experiment 2

In this experiment, samples from the MOCVD p-i-n (1L) wafer were implanted with 700 keV P⁺ at a dose of $2.5 \times 10^{13} \text{ cm}^{-2}$ and then annealed for a series of times at various temperatures. The samples were divided into three sets of four, where each set was processed nominally identically, with details given in Table V-3 and discussed below. One sample from each set was annealed at each of the four temperatures of {675, 700, 725, 750} °C.

The difference between set C and sets D and E is the anneal procedure. In what follows we will compare results for total anneal times of 270 s, but the number of anneals performed to reach that time were different, which may introduce a systematic difference if RTA ramp-up and ramp-down have an effect. Set C underwent 5 anneals, for times of {30, 30, 30, 90, 90} s, while sets D and E were annealed three times, for times of {150, 30, 90 s}. Additionally, the first three 30 s anneals of set C were performed in the oven 1, while all remaining anneals for set C and all anneals for sets D and E were performed in oven 2. The only difference between set D and set E is when the implant was done, and since anneals were done simultaneously, this means that there was a delay between implantation and annealing for set D. Effectively, samples of set D were “annealed” for one year at room temperature prior to the normal high temperature RTA. We will examine if this caused any differences in blueshift. Only half on each sample was implanted, so that the thermally-induced shift could also be monitored.

Results of blueshift as a function of RTA temperature for this wafer are shown in figure V-4; the error bars of 2-4 meV correspond to the uniformity of that sample's blueshift. It is obvious that, for all sets, the blueshift increases with anneal temperature (for a fixed anneal time), but we will leave the discussion of this dependence to the next section, and concentrate now on the differences between sets. The curves for sets D and E are within error of each (set E has on average a blueshift of 3 meV more than set D, which may not be significant compared to the

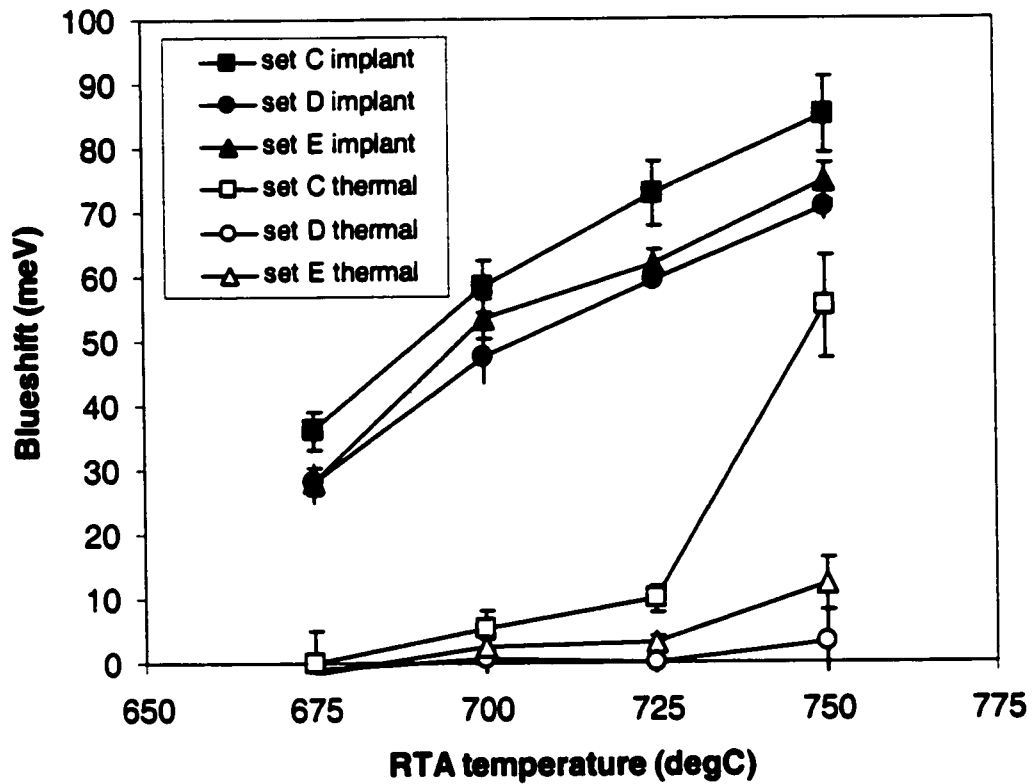


Figure V-4: Reproducibility Experiment 2 - blueshift as a function of RTA temperature for samples from the MOCVD p-i-n wafer 1L, implanted with 700 keV P⁺ ions at a dose $2.5 \times 10^{13} \text{ cm}^{-2}$, and annealed for 270 s. Minor variations in the implant and anneal procedures were applied to each set.

error bars). This result shows (again) that the QWI is very reproducible for samples annealed together. It also shows that there is no effect of room temperature “anneals” experienced by set D. Additionally, the 300 K PL intensity of sets D and E (not shown), after implantation and just before the RTAs were nominally the same. An increase in PL intensity or a difference in blueshift might have occurred if any change to the implantation damage occurred from the 300K anneal. We can conclude that the implantation damage relating to QWI-defects is completely stable at room temperature^{11,59}. This is not an unexpected result since the samples have already been exposed to 200°C for a period of several hours during implantation.

Table V-3: Details of the processing for samples studied in the second reproducibility experiment.

	date of implantation	RTA procedure
set C	Oct. 1998	Nov. 1998, 3x30s, oven 1 + Aug. 2000, 2x90s, oven 2
set D	July 1999	Aug. 2000, 150s + 30s + 90, oven 2
set E	Aug. 2000	Aug. 2000, 150s + 30s + 90s, oven 2

It is clear that set C in figure V-4 has blueshifts that are larger than those of sets D and E. For the four temperatures of {675, 700, 725, 750} °C, the difference between set C and the average from set D and E is {8, 8, 12, 13} meV. This indicates that a systematic difference is present. One possible cause is the use of different ovens and/or the use of a different series of anneals in order to reach the same total RTA time. However, there is also the possibility that the samples themselves had minor differences, since the samples of set C were taken quite close to the edge of the wafer. The thermal blueshift from the non-implanted half of each sample are also included in figure V-4. Samples of set C exhibit more thermal-induced blueshift than set D and E, and this is also more shift than was previously seen for this same wafer in Chapter IV (which was also annealed with

the oven 1). Thus a likely explanation for the larger shift found in set 1 is that the material is less thermally stable since samples were from near the wafer's edge. Such an effect has also been observed by the author in other wafers, including the CBE p-i-n and CBE LT i-i-i wafers. Generally, the last 3-5 mm of the wafer's edge shows non-optimal results. This seems to be the most likely cause for the observed variations – a systematic check, by processing a full wafer, could be done to further confirm this conclusion.

Overall, the result show that for a range of annealing temperatures, the reproducibility of the implantation-induced blueshift is good. The variation found across a given sample (± 3 eV) is the same as the sample-to-sample variation for samples implanted in different years, but which were annealed together. Larger variations of ± 8 meV were either due to minor differences in anneal procedure or in material quality relating to the wafer's edge (first 3-5 mm). Both effects can be avoided (in manufacturing, the first 3-5 mm from a wafer's edge is not normally relied upon for usable devices).

Growth Comparison and Anneal Time Dependence

In this section we will examine the time and temperature dependence of the blueshift for three nearly identical wafers. The conclusions that can be drawn from these studies are complicated by some experimental difficulties, as will be discussed below. However, it is felt that, once all these issues are addressed, the discussions are useful to guide future studies, and the conclusions are valid and relevant to the aims of this thesis.

Four temperatures are studied {675, 700, 725, and 750} °C for total anneal times of {870, 570, 500, and 400} s respectively; longer anneals are performed at lower temperatures to provide the same total thermal energy to the samples, or at least move towards that goal. Samples from MOCVD p-i-n wafer (1L) set C and two CBE wafers – the CBE p-i-n and the CBE Std i-i-i will be compared. Sample processing is the same as was described in the previous section for set C. In Chapter IV, the

thermal behaviour of these three wafers was compared, and conclusions were that the thermal stability of the MOCVD p-i-n wafer and the CBE p-i-n wafer were identical, showing negligible blueshifts for RTA temperatures of 725°C or less, while the CBE Std i-i-i wafer had exhibited negligible shift for temperatures of 700°C or less. In the present study, samples are half-implanted (with 700 keV P⁺ at a dose of $2.5 \times 10^{13} \text{ cm}^{-2}$) with the masked half of each samples serving as a reference which should show the same behaviour as the results in Chapter IV. The goal is to further study anneal behaviour and optimize annealing conditions. It would usually be desirable to anneal long enough that the shift as a function of anneal time has reached a plateau, beyond which further annealing does not provide more shift. This makes use of all the defects created by the implant, and at the same time reduce the amount of residual damage. Operating in this regime will also result in a more repeatable process, where small differences in annealing parameters (time or temperature) will not change the magnitude of the blueshift significantly.

The results of blueshift as a function of anneal time are shown in figure V-5, where all samples that were annealed together (i.e. one sample from each wafer for a chosen temperature) are shown in the same graph. At 675°C it is evident that a saturation of the implantation-induced blueshift has not occurred after 870 s of annealing; this conclusion is derived from the shapes of the curves, which indicate continual increase in blueshift with each anneal step. At 700°C, it appears that we are near saturation for all three wafers after 570 s of annealing. This would be more-or-less in agreement with the results of the reproducibility-experiment 1 results (saturation of the MOCVD p-i-n wafer after 270 s at 700°C). At 725°C and 750°C it is evident that a saturation of the implantation-induced blueshift has occurred after 500 and 400 s, respectively, although a non-zero slope present at those times is due to fact that there is some equilibrium thermal-induced blueshifting. It would have been preferable to continue to anneal the samples for longer times, especially the samples annealed at the lower temperatures, but the surfaces were beginning to degrade due to processing, as will be discussed shortly. As well, the 700 °C MOCVD sample was accidentally miss-processed after 270 s of

annealing, and so data points for 570 s (or longer) were unavailable. Thus with the present data from 700 °C, it is not clear whether the MOCVD p-i-n and the CBE p-i-n would exhibit the same saturated blueshift, although it seems likely that this would be the case. At the upper two temperatures, the curves tend to saturate at a similar blueshift of ~85 meV, indicating that this plateau level is not very temperature dependent. Because saturation is not confirmed at 700 °C, it is not possible to conclude if the plateau level is the same there too, but given the decreasing slope of its curve, it would take significantly longer than 570s (possibly double) to reach a value of 85 meV. If the value of blueshift at saturation was independent of anneal temperature (and thus only dependent on anneal time) it would indicate that a single process was occurring. Otherwise, higher saturation levels at higher temperatures indicate new process are activated at those temperatures. It appears that 700°C might be the optimal temperature to use, since the disadvantage of higher anneals temperatures is the significant thermally-induced blueshift. But the optimal anneal time at 700°C could be much larger than initially anticipated, somewhere in the range of 600 to 1000 s.

The behaviour of each wafer is somewhat different and is deserving of a few comments. Most notably, the CBE i-i-i wafer exhibits the largest thermal-only blueshift, as was previously observed in Chapter IV. The thermal-only blueshift from this wafer is fairly linear with anneal time, indicating that an equilibrium thermally-induced process is in action. This wafer is also the least consistent: in two cases it shifts at the same rate as the p-i-n wafers (at temperatures of 675 °C and 750 °C), but at the two other temperatures (700 °C and 725 °C) it is slower; the reason for this is unknown. Close comparison of the MOCVD p-i-n wafer with the CBE p-i-n wafer reveals that the MOCVD wafer always shifts a bit faster. But in general the differences between MOCVD and CBE p-i-n are quite small, and for the longer times they have shifted (within error) by the same amount. This result is very important, since it indicates that overall, the implantation-induced QWI is the same in nominally identical CBE and MOCVD material. Thus, results from one type of reactor can be transferred to the material grown in another reactor.

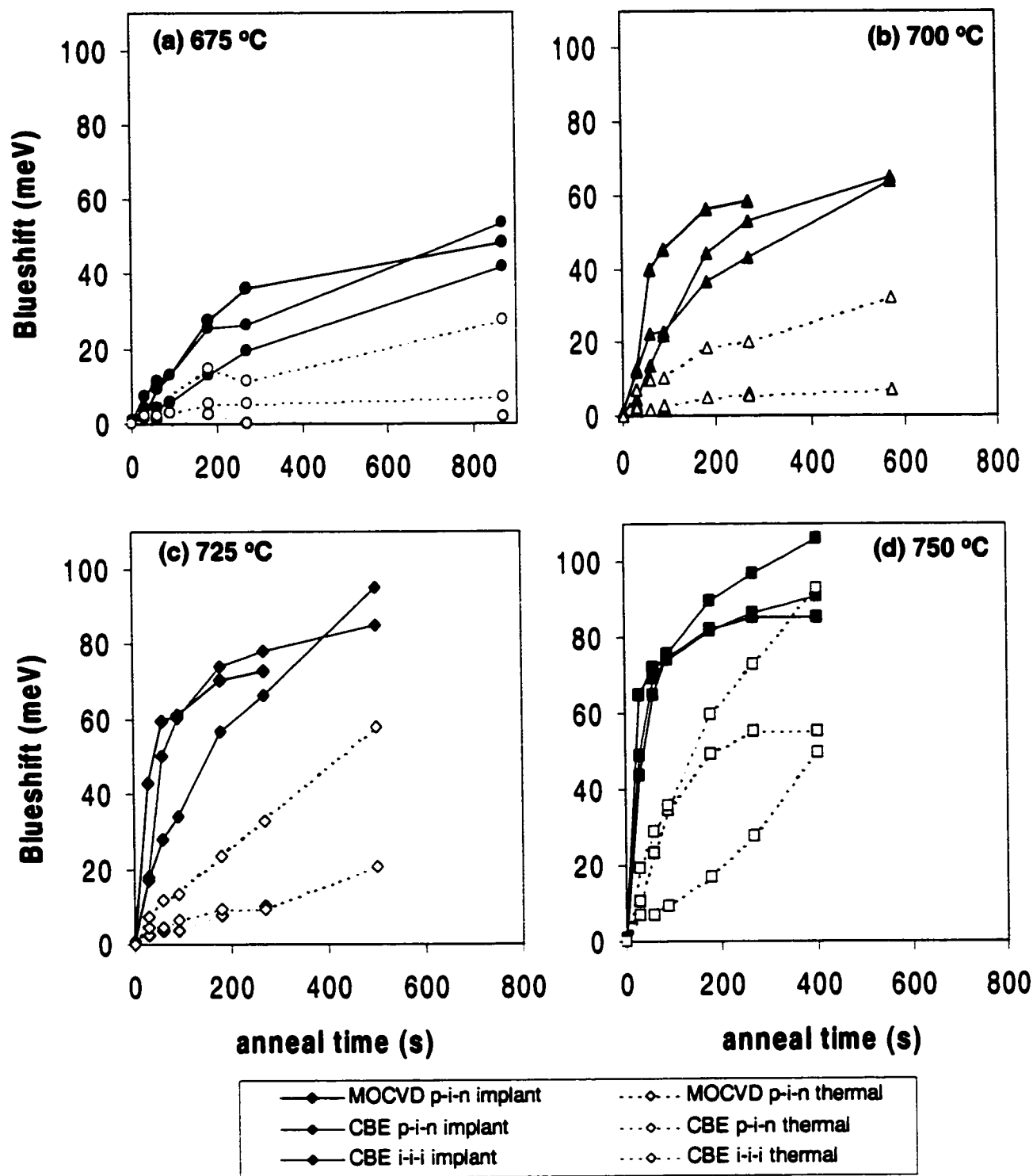


Figure V-5: Blueshift as a function of anneal time for four different anneal temperatures. Samples from three nearly identical wafers are studied - an MOCVD grown p-i-n doped wafer (blue), a CBE p-i-n doped wafer (green), and a CBE i-i-i wafer (red). Results from the implanted half (filled symbols+solid lines) and un-implanted half (open symbols+dashed lines) are shown.

Some of the differences in behaviour between the three wafers may be attributed to minor differences in these three wafers (they were nominally meant to be identical), as discussed below.

Buffer layer thickness: the thickness of the upper InP buffer layers are as follows: 1.227 μm , 1.750 μm , and 1.432 μm for the MOCVD p-i-n, the CBE p-i-n and the CBE i-i-i respectively (nominally all suppose to be 1.3 μm). The implantation energy was identical for all three wafers, thus resulting in differences in the distance between implant damage distribution and the QWs. This might explain the small difference in rate of blueshifting between the two p-i-n wafers, although actually it is surprising how small a difference 0.523 μm makes. This indicates that the QWI-defects are indeed fast diffusers. The buffer layer thickness issue cannot explain the difference between p-i-n and i-i-i wafers, since it's buffer layer thickness is in between the two p-i-n wafer thicknesses.

Doping: P-i-n doping results in an internal electric field, which could affect the motion of the QWI-defects if they carry a charge. The presence of impurity atoms can also bias defect reactions or block defect motion. Either of these possibilities could explain the difference in the thermal-only behaviour between the p-i-n wafers and the i-i-i wafer. Close comparison of the data in figure V-5 reveals that the different doping levels have a stronger effect on the thermal-only blueshift (open symbols) than on the implantation-induced blueshift (filled symbols). Thus the presence of Zn or Be in the upper InP buffer layer does not seem to affect the generation or motion of implantation-created QWI-defects, and likely would not affect the thermally-created QWI-defects. This tends to indicate that the source of the defects causing thermal-only blueshift is from the substrate. Perhaps it is then the presence of Si in the lower InP buffer which blocks thermally-created defects from the substrate from reaching the QWs in the p-i-n wafers. Si has been known to block the movement of other diffusers, such as interstitial Zn⁶⁰. It could also be the presence of the internal electric field in the p-i-n wafers which reduces the

motion of defects from the substrate to the QWs^{61,62}. This should be further investigated by varying the location of p and n doping layers with appropriately placed “marker” QWs. Small differences in the p doping of the two p-i-n wafers (different doping species, and slightly lower doping levels in the CBE wafer - refer to Chapter IV for more details) could also have caused the small differences in rate of blueshifting, although the layer thickness effect explained above is more likely.

Group-V Overpressure: The thickness of the substrate of the MOCVD wafer was 500 μm , while both CBE wafers were grown on 350 μm thick substrates. Since samples from the three wafers were annealed simultaneously (for each temperature) with a common 600 μm thick border material, this means that the distances between sample surface and proximity cap were greater for both CBE wafers in comparison to the MOCVD wafer (see Chapter IV figure IV-5). This increased distance may have the effect of reducing the group-V overpressure over the CBE wafers. Additionally, the two p-i-n wafers were InGaAs terminated, while the CBE i-i-i wafer had an additional an 0.1 μm InP overcap above the usual InGaAs layer. Both of these parameters (border thickness and surface termination) were previously found to have no effect on QWI blueshifts for thermal-only results, but must be considered again here because the blueshifts here are larger and the anneal times longer, and thus this experiment will better test any effect. Optical analysis reveals that some degradation of the sample surfaces did occur. Optical micrographs of the surfaces of samples annealed at 750°C are shown in figure V-6. Pits in the surfaces, relating to loss of group-V atoms⁶³, are visible on all samples. The density of pits is much lower for the MOCVD sample than for both CBE wafers, which could be explained by a lower group-V overpressure over CBE wafers. Higher magnification images of the pits (d)-(f), reveal similar looking defects for the MOCVD and CBE p-i-n samples (both InGaAs terminated), while the pits on the CBE i-i-i sample (InP terminated) were generally deeper and on occasion contained what looked like a ball of In metal. The pits for all samples, and for the i-i-i wafer in particular, tended to be oriented along [110] crystallographic directions, although they were not as square as seen by Pearton⁵. Similar trends in the surface

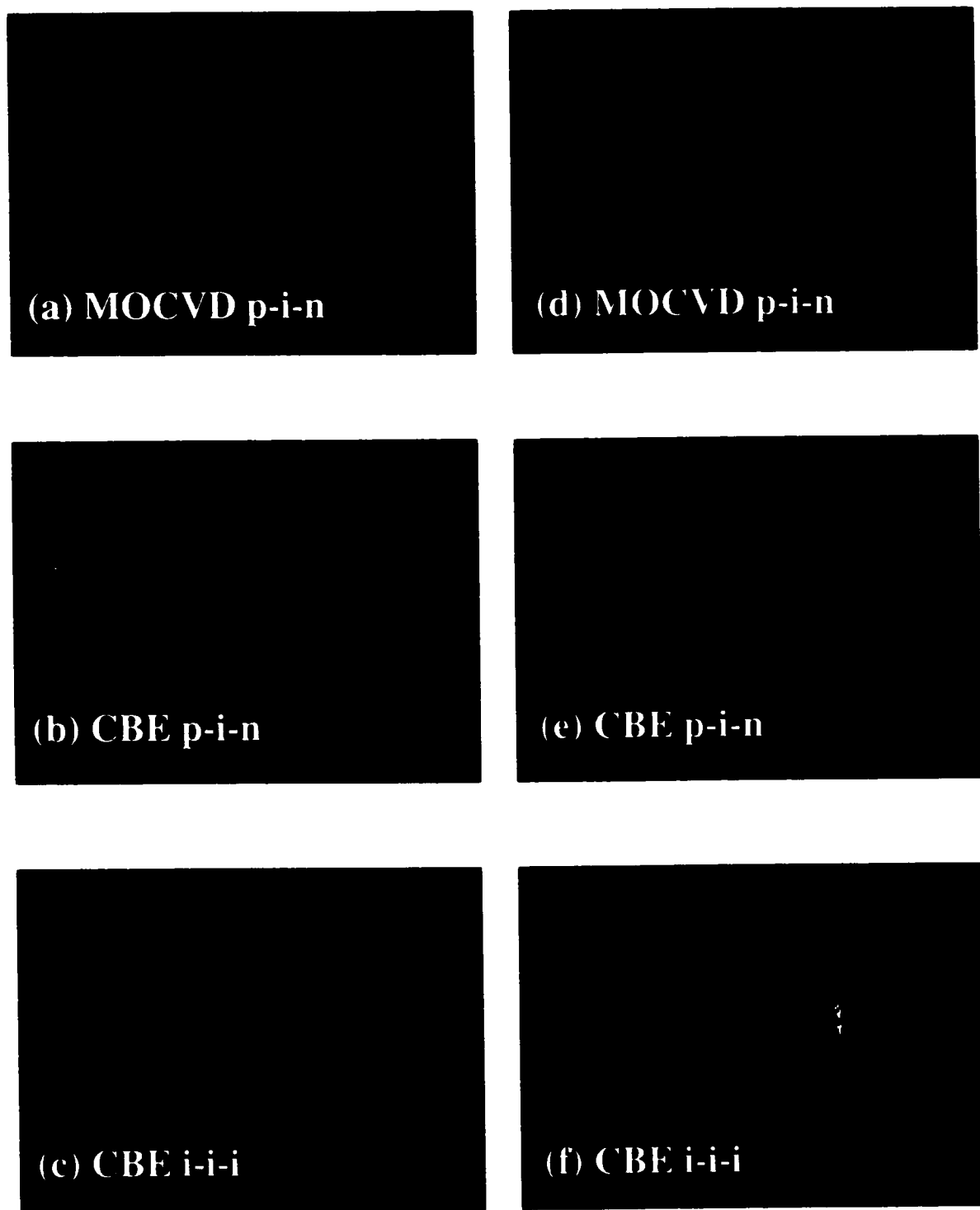


Figure V-6: Optical micrographs of sample surfaces for samples of the three different wafers annealed at 750°C for 400 s. (a)-(c) are low-magnification micrographs, while (d)-(f) show high-magnification micrographs of one of the typical surface pits found on the sample (length bars are accurate to $\pm 10\%$).

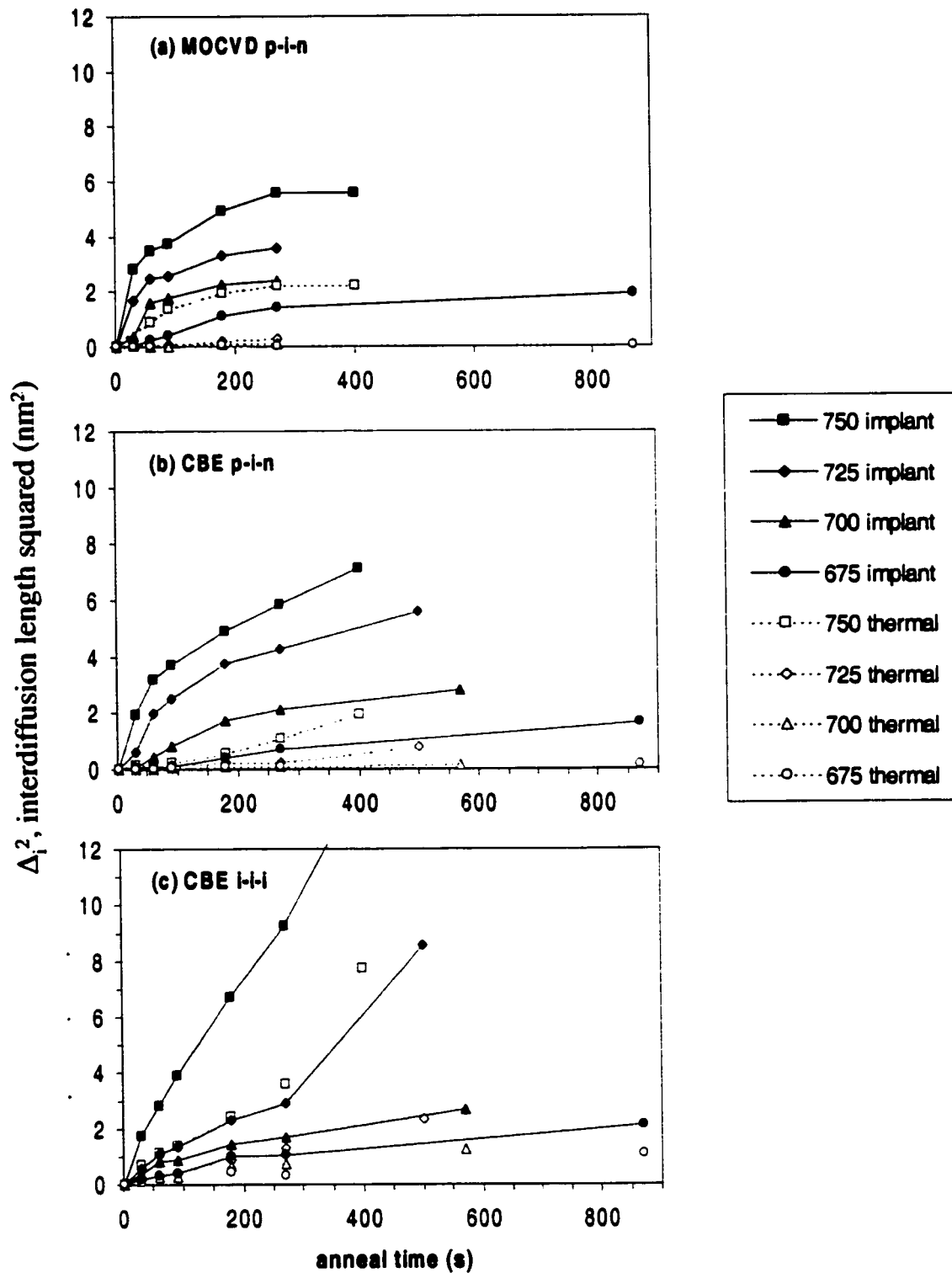


Figure V-7: Interdiffusion length as a function of anneal time for the three different wafers. Each graph includes data for four anneal temperatures - 675°C (circles), 700°C (triangles), 725°C (diamonds), and 750°C (squares) - and both implanted (filled symbols+solid lines) and thermal-only (open symbols+dashed lines). Note that for a given sample, the same symbol, colour, and line types are used in this figure as in figure V-5.

defects were seen on the samples annealed at other temperatures, although somewhat lower defect densities occurred at the lower temperatures. It would have been better to anneal samples from the different wafers separately, using a border of similar thickness to the wafer for each anneal, and/or the proximity cap should have been replaced more frequently in order to maximize its ability to provide group-V overpressure. Alternately, the same substrates should be used in any future studies. The role of this degradation on the blueshifts is not completely obvious. It does not seem to have caused a difference for the CBE p-i-n in comparison to the MOCVD p-i-n wafer. But the increased blueshifts (implantation and thermally-induced) in the CBE i-i-i wafer could also be connected with its InP surface termination (instead of the doping dependence proposed above).

The three differences between the three wafers have obviously complicated the results of this study. Their potential effects are clearly discussed and outlined so that they can be avoided in future experiments. Nevertheless, the results provide useful data on the anneal time dependence of implantation-induced QWI. The results also allow for further study of the kinetics of the QWI process, as discussed in the next section.

Activation Energy

From a material science perspective, it is more useful to discuss interdiffusion length than blueshift. We will convert the ΔE results from the previous section into Δ_i , and briefly review the data plotted in this form. Then, the interdiffusion length values will be used to determine an activation energy for the implantation-induced QWI process.

We can determine the relationship between blueshift and Δ_i using the intermixing modeling program with error function and $k=2$ assumptions. The exact Δ_i for each ΔE datum can be calculated from a (third order) polynomial fit to the (Δ_i , ΔE) data set output by the program. Figure V-7 (a)-(c) show the results of Δ_i^2 plotted as a function of anneal time, for both thermal only (dotted lines) and implanted (solid

lines) halves of the samples for each wafer. Results for all four RTA temperatures for the same wafer are included on the same graph (note that the same symbol and line combination for each sample is the same as from figure V-5). Data points for $\Delta_i=0$ at a time of zero have been included in each of the data sets.

For equilibrium processes $\Delta_i^2=D_i t$, and thus the thermal results in these Δ_i^2 vs t plots should exhibit linear relationships – this is the case for a majority of the thermal data (dotted lines), with a few exceptions:

- For an unknown reason, the 750°C curve for the the MOCVD p-i-n wafer exhibits fast diffusion at short anneal times, which then slows down for longer anneal times. It could be that this sample, and its masked half in particular, is from the edge of the wafer.
- Curves for the CBE p-i-n and i-i-i wafers at the two highest temperatures exhibit an increase in slope after 180 to 270 s of annealing. This could be explained by development of a new defect generation mechanism due to loss of group-V from the samples' surfaces as was discussed in the previous section.

Curves for the implants exhibit a very non-linear dependence on time, as expected since the material had an excess of defects at $t=0$, which then decrease in number as annealing proceeded. Thus we assume that D_i is changing with time because the number of defects present at the QW is changing⁶⁴. For long enough anneals, the surplus defects will disappear, after which any further interdiffusion will be caused by equilibrium defect generation. At this point, the curves should flatten out to the point at which they exhibit the same linear dependence with time as the thermal-only data curves. This is more or less what happens for 750°C curves of all three wafers. The exception may be for the MOCVD wafer, whose blueshifting has ended by 270 s for the 700 and 725°C curves. For the lower temperatures, it appears that intermixing due to excess defects is still occurring, as was also concluded from the analysis of blueshifts.

The time dependence of Δ_i will be related to how far the defects have diffused, as characterized by the defect diffusion length, Δ_d . The relationship can be quantified^{65,66} although for our particular case here all that must be known is that they are uniquely related one to the other (see Appendix B for a further discussion):

$$\Delta_d \Leftrightarrow \Delta_i \quad [1]$$

Assuming the defects follow Fickian diffusion and ignoring any defect loss mechanisms, then Δ_d will be related to the anneal time:

$$\Delta_d^2 = D_d t \quad [2]$$

where the defect diffusion rate will depend on anneal temperature following an Arrhenius relation:

$$D_d = D_o \exp\left(\frac{-E_a}{kT}\right) \quad [3]$$

If we consider a fixed Δ_i^2 (i.e. Δ_i^2 and Δ_d^2 are constant) then equation [2] can be written as $D_d \propto 1/t$. Combining this with equation [3] we get

$$\frac{1}{t_{(fixed \Delta_i^2)}} \propto \exp\left(\frac{-E_a}{kT}\right) \quad [4]$$

where E_a is an effective activation energy, which may encompass several steps in the defect's history, including:

- defect reactions leading to the production of the QWI-defect from the implant damage, and
- motion of the QWI-defect, and
- interaction with the lattice and mediation of interdiffusion at the QW (zero for vacancies, possibly non-zero for an interstitial, which requires a kick-out process to occur).

By extracting from our data the time required to obtain a chosen Δ_i^2 at several temperatures, and plotting the results as $\ln(1/t)$ versus $1/T$, we are able to determine the activation energy for the process from the slope of a linear fit. Results are shown in figure V-8 (a) for a Δ_i^2 value of 2 nm^2 for several different sets of samples, which include the three different growth comparison wafers. This value of Δ_i corresponds to a blueshift of 51 meV. Set C and D refer to the batch in which the samples were processed, as was previously described in the Reproducibility – Experiment 2 section (this is the first time data points from CBE p-i-n set D has been shown, but it behaved similarly to set C, which was discussed in the previous section). Either three or four data points are collected for each set, depending on the quality of the data near $\Delta_i^2=2 \text{ nm}^2$ (too much interpolation between data points at small times and high RTA temperatures, as well as extrapolation beyond maximum measured times, was avoided). A linear fit to each data set is shown by the coloured lines in the figure, while the average of the data sets is shown in heavy black line. The slope of this line gives $E_a=3.5 \text{ eV}$ with standard deviation of 0.6 eV. The same process is repeated for a Δ_i^2 value of 3 nm^2 (67 meV) in figure V-8 (b). The values of E_a are on average larger for this second Δ_i^2 value, giving an average of 4.2 eV with standard deviation of 0.3 eV. The true error on these values could be even larger than these quoted standard deviations, since the temperature range employed here is quite small⁶⁷ and it has been assumed that only one implantation-induced process occurs, and that this process is identical in all wafers. Recall that some differences in behaviour were previously observed, most importantly that thermally-induced QWI was different and this plays a role for the blueshifts at anneal temperatures of 725 °C and 750°C.

These two values of E_a are (only just) within error of each other, and have a average value of 3.85 eV. If the E_a for different interdiffusion lengths were truly different, it could imply that more than one defect process is occurring, where a lower activation energy process will dominate at short times (small Δ_i^2) while larger energy processes will dominate at larger times (large Δ_i^2). This could happen if, for example, the QWI-defects are released from two different types of defect

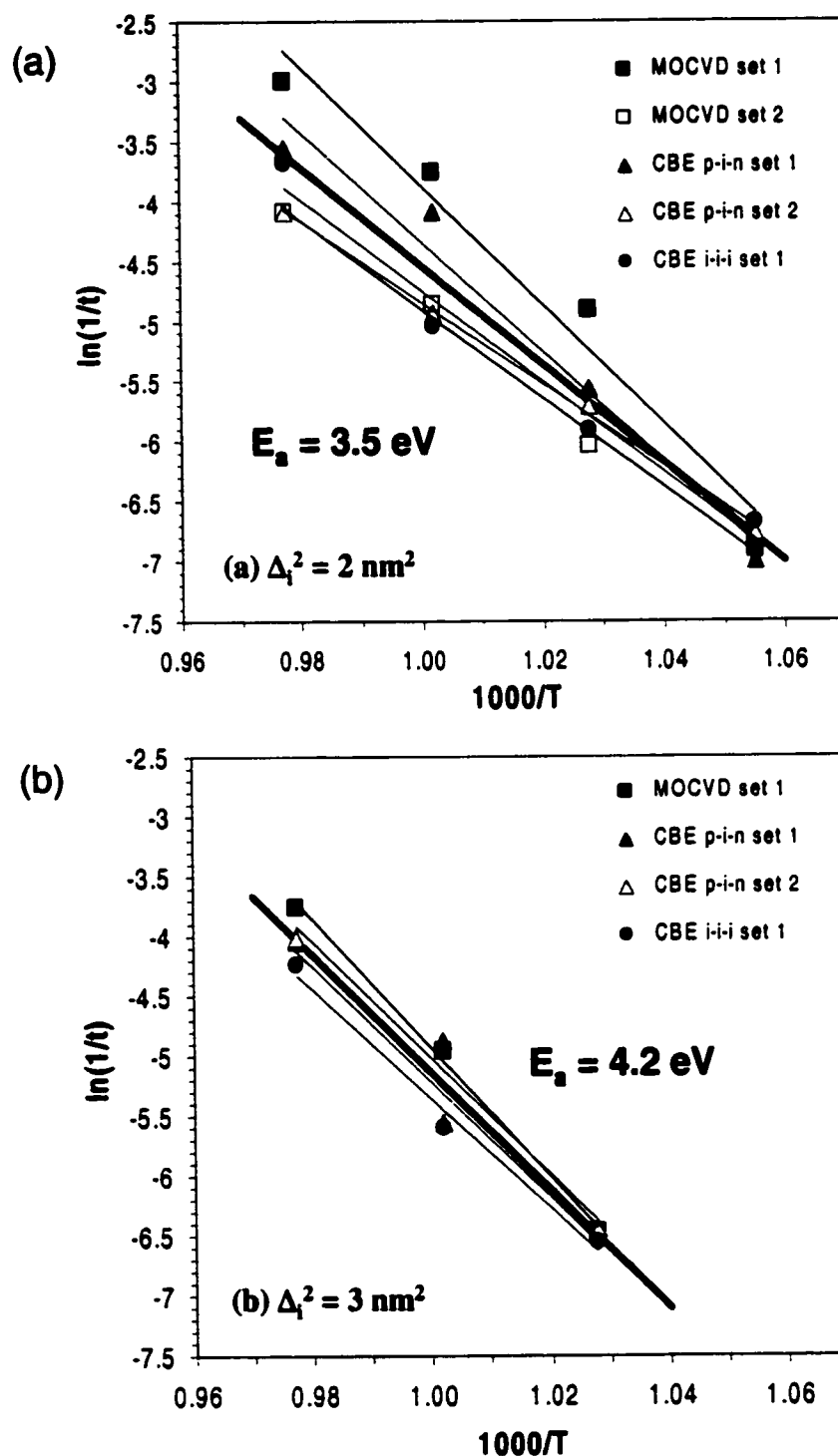


Fig. V-8 Determination of activation energy, E_a , from the time required to reach a Δ_i^2 value of 2 nm^2 (a) and 3 nm^2 (b). Thick bold lines and text within each plot give the average of the linear fits for all the data sets of the plot.

complexes, and the release mechanisms have different E_a , or alternately if two different types of QWI-defects exist, which have different E_a for their motion. The difference in the two E_a values could also be accounted for with a defect loss mechanism, similar to what was done when modeling defect diffusion from grown-in defects in Paper 3 (the loss mechanism was required to obtain good fits to experimental data). It would be beneficial to repeat the process for other Δ_i^2 to further elucidate these issues. Unfortunately, with this type of experiment, one will always be limited to a small temperature range since anneal temperatures below 650 °C will not result in significant blueshifts, and at temperatures greater than 750 °C there will very likely be surface degradation. Finally, because the activation energies derived here have a large error we cannot make any conclusions about any differences between the three wafers with regard to E_a . But we can conclude that the intermixing caused by implantation on all wafers is generally characterized by an activation energy in the range of 3-4 eV.

Further Discussion on QWI-Defect Identity

It has been argued that interstitial diffusion has a very low activation energy, the order of 0.2 eV, while vacancy mediated diffusion has activation energies in the range of 2 or more eV⁶⁸, although the majority of the proof for this is in metals³⁰. In InP, Wendler et al. measure an E_a of 0.33 to 0.35 eV for the motion of an InP defect they believe is P_i , while Schultz et al.³⁶ believe the P_i are mobile at room temperature.

Values for the activation energy of QWI reported in the literature are 3.2 eV for dielectric-cap QWI in GaAs/AlGaAs⁶⁹, 1 to 3 eV^{70,71} for thermal-only QWI in InP, and 3.7 eV for implantation-induced QWI (implant depth was such that the ions stopped in the vicinity of the QWs) into the InGaAs/GaAs and InGaAs/InGaAsP structure⁶⁷, where diffusion is on the group-III and group-V sublattice, respectfully. In the latter reference, Gillin argues that because there is evidence that the group-III sublattice in GaAs is controlled by Ga vacancies, and that he measures the same activation energy in both his structures, this proves that diffusion on the group-V

sublattice in InP is controlled by vacancies. However, to our knowledge, only one other paper⁵⁸ supports this conclusion. The defect proposals given in this thesis may be in disagreement with these arguments, since we claim an interstitial model for the QWI-defect with an activation energy $E_a \approx 3.85$ eV.

However, arguments where the value of the activation energy directly allows for determination of the defect identity may be too simplistic. In fact, in silicon, an activation energy of 3.8 eV has been measured for interstitial-mediated transient enhanced diffusion (TED) of boron, which is primarily due to the release of interstitials from more complex {311} defects⁴². In analogy with the models for silicon TED, it is proposed that the 3-4 eV activation energy measured in this thesis, as well as the similar values measured by others for InGaAs(P) based structures, is an effective activation energy which includes a defect reaction that releases interstitials (e.g. conversion of P_{In} into $V_{In} + P_i$), the migration energy for the interstitial, and any energy associated with the interdiffusion (kick-out) mechanism. In fact, the experiments within this section may point to a low energy of migration for the QWI-defects: a differences of 0.523 μm in the distance between implant damage and QWs (which occurred between the MOCVD p-i-n wafer with the CBE p-i-n wafer due to different upper InP layer thicknesses) resulted in very little difference in time required to achieve an equal amount of QWI. If so, the majority of the 3.85 eV effective activation energy measured here is due to defect reactions.

Summary of Growth Comparison

With proper care, the reproducibility of the implantation-induced QWI technique was found to be very good, with errors of 3-4 meV on blueshifts of 36-70 meV (~6%). The largest cause for variations (which were still quite small) was the use of different RTA ovens and/or the non-uniformity of the wafers themselves (samples from near the edges of the wafers always shifted more). The implantation procedure was very repeatable over a period of three years. It was also found that the implantation damage is stable at room temperature, and thus time between implant and anneal steps is inconsequential for these implant conditions.

The criteria for the best anneal temperature are usually maximal shift without causing surface degradation or blueshifting in non-implanted regions, and thus ~ 700°C is the best choice of anneal temperature (at least for the RTA annealing procedure studied in this thesis), which is in keeping with previous studies. However, the present data suggests that longer anneal times than were initially anticipated may be required to saturate the blueshift. It was unclear whether times of 570 s at 700°C used in this experiment were sufficient, and given the shape of the curve and results at higher temperatures, times as long as 600 to 1000 s at 700°C would ensure saturation. It should be possible to reduce the anneal temperature, but this must be compensated in terms of longer anneal times. However, at any temperature, degradation of the surface may become an issue. It would be important to equal, if not improve upon, the methods of group-V overpressure used in this thesis when annealing such times are undertaken. In general the CBE and MOCVD p-i-n wafers exhibited similar behaviour. It was unclear whether the differences in layer thickness, doping or overpressure influenced the minor behavioral differences between the two p-i-n wafers, while it certainly was evident that one or both of the two latter variables did influence the thermal-only behaviour of the i-i-i wafer. It was unfortunate that these variables existed, they certainly could be avoided in future experiments. Finally, the activation energy for the entire implantation-induced process (QWI-defect release, motion and interdiffusion) was found to be in the range of 3-4 eV. It is expected that this is an effective activation energy, encompassing defect reactions as well as defect motion, and that this is not inconsistent with an interstitial picture of the QWI-defect or findings by many others on the subject of defects in semiconductors.

D - Lateral Selectivity

Introduction

One of the key parameters that must be understood when using QWI as a tool for opto-electronics integration is the spatial resolution, or lateral selectivity of the

technique. In other words, one needs to know what is the width of the transition region between intermixed and non-intermixed regions. This will control how small of an area can be successfully processed, and for blueshifting larger areas, it will give the length of the transition region from shifted to unshifted areas. The selectivity will depend very much on the processing conditions and on the nature of the defects. For most applications, involving the integration of intermixed with non-intermixed devices, the footprint of each device is of the order $50 \times 100 \mu\text{m}$ or more. Lateral selectivity of the order of a few microns will thus be sufficient for definition of the bandgap of each device. We have determined that implantation-induced QWI achieves these specifications. All of the details of this work has been published, and the paper is included herein to form a portion of this thesis.

Paper 4 - JVSA

J. E. Haysom, P. J. Poole, Y. Feng, Emil S. Koteles, J. J. He, S. Charbonneau, R. D. Goldberg, I. V. Mitchell; Spatial Resolution of Ion-induced Quantum Well Intermixing; J. Vac. Sci. Technol. A, 16(2), 817-820, Mar/Apr 1998.

In this paper, the lateral selectivity is studied for 1 MeV P⁺ implantation into a MQW structure where the QWs are located 1.77 μm below the surface. This is done by monitoring the blueshift of QWs under mask stripes as a function of stripe width. A specially designed mask is employed so that standard PL set-up (with a spot size of $\sim 50 \mu\text{m}$) can be used to extract information on lateral variations of the order of a few microns. The result is a selectivity of $\sim 2.5 \mu\text{m}$, which is attributed to both implantation straggle and lateral defect diffusion. The initial design of these samples and much of the processing was performed by co-authors. The author of this thesis performed all the characterization, analysis, and writing of the paper.

Lateral selectivity of ion-induced quantum well intermixing

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Quantum well (QW) intermixing using high-energy ion implantation is a promising technique for laterally selective, post-growth modification of a quantum well structure. In this work, we investigate the lateral selectivity of the technique, which is a function of the ion straggling during implantation and of the lateral diffusion of defects during post-implantation annealing. We have used photoluminescence and a specially designed mask to monitor the intermixing of QWs under masked regions. A significant amount of intermixing, resulting in a blueshift of the QW band-gap energy, was observed when the mask stripe width was less than 5 μm , thus giving a lateral selectivity of 2.5 μm . © 1998 American Vacuum Society. [S0734-2101(98)03502-7]

I. INTRODUCTION

Over the past decade, there has been a significant amount of research on techniques which will enable the monolithic integration of opto-electronic devices such as lasers, modulators, and waveguides. Integration requires the ability to vary the band-gap energy across the wafer, which can be accomplished through specialized growth procedures, etching and re-growth of epitaxial layers,¹ or through post-growth modification of completed epitaxial structures. Quantum well intermixing (QWI) is a powerful post-growth technique which has been successfully applied to SiGe,² GaAs³ and InP^{4,5} structures. Recently, research in InP-based QWI has intensified due to commercial interest in opto-electronic systems for communications in the 1.3 and 1.55 μm wavelengths.

The interdiffusion of atoms between a QW and its barriers is often modeled using Fickian diffusion,⁶ such that the atomic concentration and energy band profiles are altered from an initially square shape to a more rounded shape which can be described by a double error function. This causes a shift of the quantum states of the well and results in an increase in the well's band-gap energy. This intermixing can occur when the material is annealed at sufficiently high temperatures, but it can also be enhanced at lower anneal temperatures using dielectric caps, ion implantation, or diffusion of impurities where vacancies, defects, or impurity species are introduced into the material.⁷ Localized annealing using a directed laser beam has also been used to perform QWI.⁸

Implantation induced QWI is a method which meets many of the criteria required of successful implementation by industry, such as a minimal number of additional process steps, applicability to standard epitaxial multiple-quantum well

structures, reproducibility, minimal degradation of device performance, and lateral selectivity.

The process steps involved are first, implantation of ions (either impurity or non-impurity species) at energies varying from a few tens of keV up to 8 MeV, followed by an annealing step which mobilizes the defects and initiates intermixing. The optimum implantation energy depends on the material⁹ and depth of the QW (it is possible to intermix QWs located several microns below the surface). We have observed high defect diffusivities in InP-based materials, making it possible and often preferable to implant above the QW in order to keep implant damage away from the active region.

In relation to device performance, ion implantation using non-impurity species has been used to shift the band-gap energy of many InP-based optical devices, including low loss waveguides which are transparent at the as-grown band-gap energy,¹⁰ polarization insensitive optical amplifiers,¹¹ wavelength shifted lasers with unchanged threshold current densities and excellent predicted device lifetimes.^{12,13} Implants using impurity species tend to alter other material and device properties, and are thus only useful for specific applications where the change is advantageous.

In this article, we examine the degree of lateral selectivity which can be obtained with high-energy implantation of non-impurity ions into an InP-based structure where QWs are located nearly 2 μm below the surface. To the authors' knowledge, the only other published studies on lateral selectivity of QWI have been on GaAs-based materials,^{14,15} where the structure and implantation conditions were not as relevant for typical commercial devices.

II. EXPERIMENT

The structure used in this study was a metalorganic chemical vapor deposition (MOCVD) grown InGaAs/

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InGaAsP unstrained laser structure designed to emit at 1.5 μm . There are five 6 nm InGaAs quantum wells situated 1.77 μm below the surface. The detailed layer structure is as follows: a S-doped InP substrate, 350 μm of S-doped InP, 1.0 μm of Si-doped InP, 50 nm of index-doped $\text{In}_{0.74}\text{Ga}_{0.26}\text{As}_{0.57}\text{P}_{0.43}$, five 6 nm $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ QWs with six 20 nm $\text{In}_{0.74}\text{Ga}_{0.26}\text{As}_{0.57}\text{P}_{0.43}$ barriers (all undoped), 50 nm of index-doped $\text{In}_{0.74}\text{Ga}_{0.26}\text{As}_{0.57}\text{P}_{0.43}$, 1.5 μm of Zn-doped InP, and 0.2 μm of Zn-doped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

Implantation was performed in a 1.7 MV Tandemron accelerator located at the University of Western Ontario. Phosphorus ions were implanted at an energy of 1.0 MeV, to a dose of $1.0 \times 10^{14} \text{ cm}^{-2}$ (phosphorus was chosen since it is not an impurity in the InP-based structure). Samples were held at 200 $^{\circ}\text{C}$ during the implantation and flux was kept low (7 nA/cm^2) to prevent additional heating. Samples were also tilted 7° off axis to avoid channeling effects. The implant range was calculated to be $1.0 \mu\text{m} \pm 0.28 \mu\text{m}$ using SRIM97,¹⁶ thus no phosphorus ions should reach the active region of the structure. Prior to implantation, a 2.0 μm silicon dioxide layer was deposited on the surface and patterned to act as a selective area mask (the mask pattern is described in more detail below). Where it did cover the surface, the thick oxide completely blocked any ions from reaching the sample.

After implantation, the silicon dioxide was removed and the samples were annealed in a Heatpulse 410 rapid thermal annealer (RTA) with flowing nitrogen. GaAs pieces were used to surround and cover the sample in order to reduce desorption of As from the surfaces. An anneal was performed at a nominal temperature and time of 675 $^{\circ}\text{C}$ for 180 seconds. These conditions were previously found to give a near-zero shift in the photoluminescence (PL) peak of as-grown material, and energy shifts of implanted material are saturated.

The implantation mask had 13 distinct arrays, each containing parallel stripes of oxide of the same width and spacing (X_1 and X_2 respectively, as shown on Figure 1a and listed in Table I). From one array to the next, the mask stripe width, X_1 , varied from 1.5 μm to 23.5 μm , while the spacing between masked stripes, X_2 , also increased proportionately from 6.5 μm to 32.5 μm (the regions between masked stripes will be referred to as implanted stripes). Each array was approximately 1.2 mm square, and thus contained 20 or more masked stripes. During low temperature (5 K) PL, the excitation laser was directed at the center of an array, with a spot size of approximately 100 μm . Due to this spot size, PL spectra from an array show luminescence peaks from both the implanted and the masked stripes. The excitation laser was a Ti:sapphire tuned to 880 nm with an excitation power of a few milliwatts.

In Figure 2, low temperature PL spectra are shown. Spectra A and B are reference spectra taken from relatively large regions of the same material which were completely masked and implanted, respectively, while spectra C–G were taken from arrays with masked stripes of varying widths (X_1). Spectra from arrays which are not shown (those from arrays

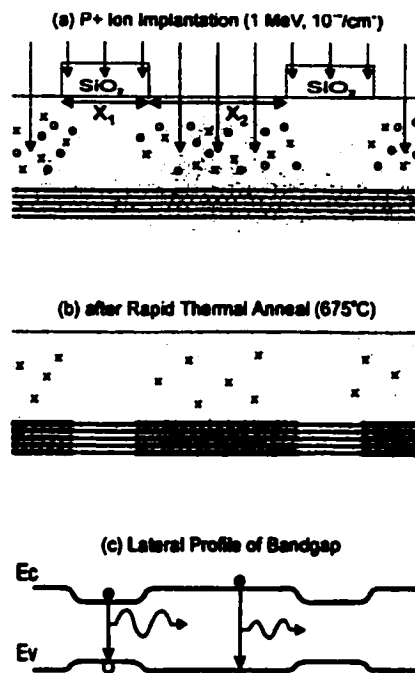


FIG. 1. Schematic cross section through a sample illustrating selective area intermixing of five quantum wells located 1.77 μm below the surface: (a) ion implantation of P^+ ions using a patterned 2.0 μm thick silicon dioxide mask; (b) after rapid thermal annealing, QWs underneath implanted regions and near the edges of masked regions have been intermixed; (c) the resultant change in the band-gap energy of the QWs along the lateral direction.

with X_1 between 6.0 μm and 23.5 μm) were nominally identical to spectra C and D. For spectra C–G, the longer wavelength peak at 1.39 μm is taken to be from the QWs of masked stripes, while the shorter wavelength peak at 1.33 μm originates from intermixed QWs of implanted stripes. For masked stripes with $X_1 \geq 6.0 \mu\text{m}$, the PL peak from masked stripes is in the same position as peaks from the reference spectrum A, but as masked stripes become narrower (spectra E and F) these peaks are partially shifted due

TABLE I. Measured stripe widths of each array in the implantation mask, where X_1 is the width of the silicon dioxide mask stripes, and X_2 is the distance between adjacent stripes. Columns 3 and 4 give the positions of the photoluminescence peaks of implanted and masked stripes.

X_1 (μm)	X_2 (μm)	Implanted (μm)	Masked (μm)
1.5	6.5	1.330	1.330
3.0	9.0	1.333	1.361
4.5	11.5	1.334	1.384
6.0	14.0	1.334	1.390
7.5	16.5	1.328	1.388
9.5	18.5	1.331	1.391
11.5	20.5	1.332	1.391
13.5	22.5	1.333	1.391
15.5	24.5	1.333	1.391
17.5	26.5	1.324	1.387
19.5	28.5	1.324	1.389
21.5	30.5	1.329	1.390
23.5	32.5	1.331	1.390

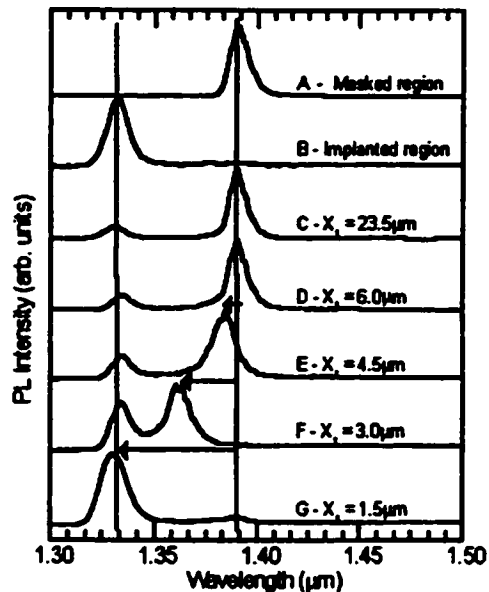


FIG. 2. Normalized low temperature (5 K) PL spectra from a large masked region (spectrum A), a large uniformly implanted region (spectrum B), and from arrays with varying mask stripe widths, as noted by the value of X_1 (spectra C–G).

to partial intermixing of the QWs. The degree of intermixing increases until this peak merges with the $1.33 \mu\text{m}$ peak of neighbouring implanted stripes (spectrum G). In contrast, implanted stripes from all arrays were shifted by approximately the same amount, 57 nm (40 meV), equal to the shift of uniformly implanted material (spectrum B). The PL linewidths of the masked stripes were $8 \pm 1 \text{ nm}$ ($6 \pm 1 \text{ meV}$), and those of the implanted stripes were slightly larger, $10 \pm 1 \text{ nm}$ ($8 \pm 1 \text{ meV}$). The linewidths of partially intermixed “masked” stripes (spectra F and G) were comparable to those of the implanted stripes.

III. DISCUSSION

The position of the PL peaks from both implanted and masked stripes are compared with the peak position of masked regions from surrounding material, and an energy shift is calculated. The mask stripe width, X_1 , is divided by 2 to give a value for the lateral distance from a mask edge. In Figure 3, a plot showing the energy shift as a function of $X_1/2$ clearly indicates that QWs within the first $2.5 \mu\text{m}$ of a mask edge undergo some degree of intermixing. From these observations, the lateral selectivity of QWI when using this implantation energy is determined to be $2.5 \mu\text{m}$.

The intermixing of quantum wells under masked regions will be due to two effects: (1) during implantation, the lateral spread of ions, and thus the lateral distribution of created defects to regions under the mask edge, and (2) the lateral diffusion of defects during annealing. Here we do some very rough calculations to demonstrate the approximate magnitudes of these two effects. Using SRIM97 to simulate the implantation, we obtain a plot of the lateral straggle of ions as a function of depth, as shown in Figure 4 (this gives the

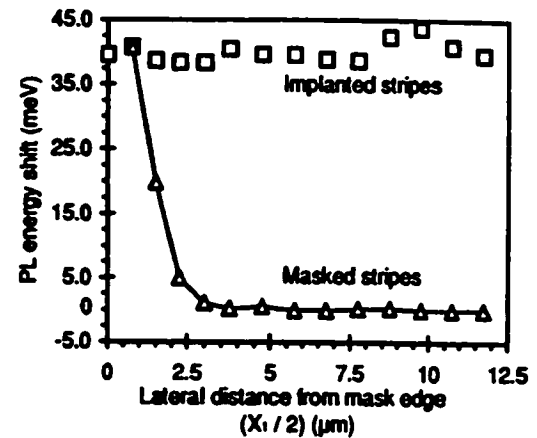


FIG. 3. Energy shifts of PL peaks from QWs in implanted stripes (squares) and masked stripes (triangles). The shift is obtained by comparison to PL peaks in fully masked regions surrounding each array.

distance at which the ion concentration drops to approximately 30% of its uniform implantation value). From other work performed on this same material,⁸ diffusion lengths of defects can be taken to be at least $1.8 \mu\text{m}$, since it was found that all defects, including those created near the surface, were able to diffuse to QWs and cause intermixing. A wave front with a radius of $1.8 \mu\text{m}$ is added to the plot of Figure 4, illustrating a path (with the largest lateral reach) for the diffusing defects created by straggling ions. This wave front of diffusing defects is able to reach the regions of the QWs that are at a lateral distance of $2.0 \mu\text{m}$ from the mask edge. Thus we expect that QWs at this position will exhibit a small amount of intermixing, while regions slightly further under the mask will not be intermixed at all. This rough prediction

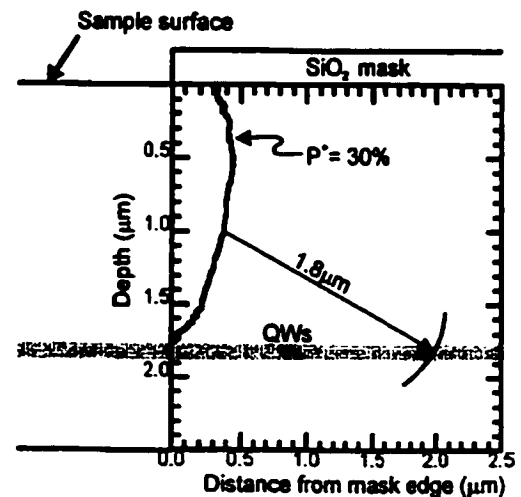


FIG. 4. The lateral straggle of implanted ions to regions under the mask edge, shown as a function of depth into the sample. The plot shows an isoconcentration contour where the P^+ ion concentration drops to 30% of its uniform implantation concentration. Superimposed on the plot is a wave front with a radius of $1.8 \mu\text{m}$, depicting a possible path for the diffusion of defects created by the straggling ions.

agrees very well with the experimental results of Figure 3. In reality, the effects of ion straggle and lateral diffusion cannot simply be summed; a more accurate prediction would require numerical modeling taking into account the damage distribution¹⁷ caused by straggling ions and proper diffusion equations. It may be possible to experimentally determine with more precision the roles of the two processes (ion straggle and lateral diffusion) through repetition of this experiment with other implant energies. Conversely, the lateral resolution should exhibit some dependence on implantation energies.

IV. CONCLUSION

We have used low temperature photoluminescence to study implantation induced intermixing in an InGaAs/InGaAsP system, where the QWs were situated 1.77 μm below the surface, and 1 MeV P^+ ions were implanted into regions above the QWs. We have shown that the lateral selectivity which can be obtained for ion-induced quantum well intermixing under these conditions is approximately 2.5 μm , a value which is small in comparison to many device dimensions. Since it has also been proven elsewhere that these conditions provide band-gap shifted devices with commendable performance, we believe that this technique shows excellent promise for use in monolithic integration.

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Additional Comments on Lateral Motion of Defects

In section C of this chapter, it was observed that complete saturation of the implantation-induced blueshift did not happen as quickly as was previously expected – for 675°C anneals, times of more than 1000 s may be required.

Although the anneal for the current lateral selectivity study (180 s at 675°C) caused a significant amount of intermixing, it may not have been sufficient to completely saturate the defect motion. The lateral selectivity measured on the samples in Paper 4 might degrade somewhat from the value of 2.5 μm if longer anneal times are used. If QWI-defect diffusion is isotropic, then, as a function of anneal time, the degradation of lateral selectivity should change at the same rate as the blueshift saturates. Both parameters could be studied simultaneously by repeating the above study over a range of anneal times. Furthermore, by expanding the study to include different implantation energies, results might yield further information relating to the QWI-defect location following implantation. For example, modeling of the defect motion in a parallel manner to what was done for the LT growth in Paper 3, with different assumptions as to the starting distribution of the implant damage, either following standard LSS theory^{34,72}, the interstitial “effective +1” model²⁹, or the excess vacancy model⁷³.

E – Buried Waveguides

Introduction

For any material, the absorption and the refractive index are interconnected via the Kramers-Kronig relations⁷⁴. Thus the blueshift of the QW bandedge caused by QWI will also result in changes to the refractive index of the material. Although the Kramers-Kronig dependence between absorption and refractive index involve integration over all energies, the strongest contributions come from resonances at the bandedge energy. We will study the refractive index change, Δn , caused by implantation-induced QWI and confirm that the main effect is the change to the bandedge energy (and not due to any other effect, such as crystal damage).

Secondly, we take advantage of the lateral selectivity found in the previous study, and in combination with the refractive index changes, create a narrow waveguide device. Since the Δn is created without changing the topography of the surface (i.e. without etching a ridge in the top surface of the semiconductor, as was illustrated in figure I-2) the device is called a buried waveguide. There have not been many studies on Δn changes caused by QWI, and none on implantation-induced QWI. Thus this work was of much interest to the research community and was published in 1998. The paper is included herein to directly form part of this thesis.

Paper 5 - JQE

J. E. Haysom, A. Delage, J.-J. He, Emil S. Koteles, P.J. Poole, Y. Feng, R.D. Goldberg, I.V. Mitchell and S. Charbonneau; Experimental Analysis and Modeling of Buried Waveguides Fabricated by Quantum Well Intermixing; J. Quantum Electron., vol. 35(9), 1354-1363, Sept. 1999.

This paper includes some repeat of the lateral selectivity study, combined with a study of the Δn changes. The Δn are measured as a function of wavelength on slab waveguides in uniformly intermixed, and non-intermixed material. The group Δn is derived from the frequency of the fabry-perot fringes of the waveguide, and then using an oscillator model, it is converted to phase Δn . Experimentally measured values of the hh and lh transition energies are input parameters to the oscillator model. Buried waveguides (BWGs) are fabricated by using narrow (4.5 and 6.0 μm) mask stripes during implantation, such that the refractive index is increased in the implanted regions, but unchanged in the center of the stripe. The refractive index profile is diffuse, as estimated using the ΔE profile found in the lateral selectivity study. Both the spectra and the mode profiles of these BWGs are analyzed. Detailed modal analysis and beam propagation modeling are employed to confirm the assumed Δn profile. In all the measurements, both TE and TM polarizations are recorded separately, and changes in splitting between the two polarizations during intermixing is attributed to $k > 1$. The initial sample design and much of the processing was performed by co-authors. Final annealing and all device characterization was performed by the author of this thesis. The modeling aspects of this paper were done by A. Delage based on joint discussions.

Experimental Analysis and Modeling of Buried Waveguides Fabricated by Quantum-Well Intermixing

Joan E. Haysom, André Delâge, Jian-Jun He, Emil S. Koteles, Philip J. Poole, Yan Feng, Richard D. Goldberg, Ian V. Mitchell, and Sylvain Charbonneau

Abstract—The fabrication of buried waveguides in InP-based quantum-well (QW) material through the use of implantation-enhanced QW band edge blue-shifting is reported. First, the lateral selectivity of implantation-induced QW intermixing is investigated using a specially designed implantation mask and photoluminescence. The refractive index change of the intermixed material is measured near the band edge. In combination, the lateral resolution and the index difference have allowed for the fabrication of narrow buried waveguides in an InP-based laser structure. Detailed modeling of the mode excitation and beam propagation of these devices is performed, and results are compared with experimental near-field profiles. We demonstrate that the waveguides are single-mode for both TE and TM polarizations at wavelengths near the band edge. The potential applications of this waveguide structure include post-growth fabrication of buried waveguide lasers and other integrated components.

Index Terms—Buried waveguide, InGaAs(P), InP, lateral selectivity, quantum-well intermixing, refractive index, semiconductor devices.

I. INTRODUCTION

THE integration of photonic components, such as lasers with modulators and waveguides, is motivated by the desire for increased coupling efficiency between devices, lower packaging costs, smaller size, and highly reliable complex photonics circuits. Presently available hybrid integration techniques are expected to give way to monolithic integration on semiconductor heterostructures, with quantum-well intermixing (QWI) being contemplated as a potential technology for this task. This postgrowth modification technique is a powerful tool for shifting the absorption band edges and altering the refractive indices of quantum wells (QW's) in a spatially selective manner. The technique relies on the enhanced interdiffusion (intermixing) of atoms of the quantum well and barrier layers, leading to a modification of the QW shape (for recent overviews on quantum-well intermixing,

see, for example, [1]). The resultant shape can be described by a double error function if Fickian diffusion is assumed. Thus, the energy potential profile of the QW is changed from its initially square shape, resulting in shifts of the quantized energy levels. Typically, the energy of the lowest bandgap transition increases, producing a blueshift of the band edge and an associated reduction in absorption losses and refractive indices at the band edge wavelength of the original structure.

QWI using shallow ion implantation is a promising technique for InP-based structures, where nonimpurity species such as phosphorus can be implanted above the QW's, thus keeping implantation damage away from the QW's. Lattice defects created during the implantation have been shown to diffuse during a high-temperature anneal, causing enhanced intermixing of atoms at the well-barrier interface when compared with nonimplanted regions [2]. The anneal temperature is chosen so that there are no changes to the nonimplanted regions, while the peak wavelengths of implanted regions can exhibit blueshifts of the order of 50–100 nm for anneal times of the order of 100 s [2]. Shallow implantation-induced QWI meets many of the criteria required for successful commercial exploitation, such as simple processing steps, applicability to standard epitaxial multi-QW structures, reproducibility, ability to shift the bandgap in several regions by different amounts without additional steps, very low absorption losses, and minimal degradation of device performance [3]–[5].

The purpose of this study was to investigate the use of QWI as a simple method for fabricating buried waveguides. Buried waveguides have the interesting and potentially valuable property of confining not only the optical modes but also the charge carriers. However, typical buried waveguides are fabricated in a complicated procedure requiring several growth and etch steps. A simplified procedure for their fabrication would be a valuable addition to the device designer's tool chest—the technique of QWI offers such simplifications. Furthermore, the planar nature of buried waveguides fabricated by QWI simplifies the fabrication of additional complex structures such as waveguide Bragg gratings and ohmic contacts. Thus, there are potential applications for such buried waveguides within buried lasers, distributed feedback (DFB) lasers, distributed Bragg reflector (DBR) lasers, and other complex or integrated components.

In this paper, we report on experimental analysis of fabricated buried waveguide devices, as well as experimental

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studies of the two parameters that control the optical properties of waveguide modes—the lateral selectivity and the refractive index change of QWI. Direct knowledge of these parameters was important for the device modeling. A short review of relevant literature in the field is presented below.

There have been several studies on lateral selectivity using other QWI methods, including direct implantation into QW's or superlattices which are within a few hundred nanometers of the surface in GaAs [6]–[10] and InP [11], [12]. This method can achieve a selectivity as low as 30 nm—a very impressive value—but it comes at the expense of damage to the QW's, and often requires regrowth of an upper cladding layer [13], [14]. For many applications involving the integration of intermixed with nonintermixed devices and even the creation of narrow optical structures, lateral selectivity of the order of a few microns is acceptable. As will be shown, this value is achievable by shallow implantation-induced QWI. Dielectric cap disordering [15] and impurity-induced QWI have also shown selectivity in this range, but each technique has certain disadvantages, such as reproducibility problems for the former, and undesirable effects associated with impurities in the QW's for the latter. Studies of laser annealing-induced QWI report a lateral selectivity of the order of 25 μm [16], which is likely a consequence of thermal gradients. The present technique is free from these drawbacks.

Reported values for QWI-induced Δn changes at the band edge are in the range of 0.01–0.04 [14], [17], but these values will of course depend on the layer structure and degree of intermixing. There have been several demonstrations of buried heterostructures fabricated by QWI in GaAs systems, including waveguides [18]–[21], index-guided lasers [22], modulators [23], and, more recently, vertical-cavity index-guided lasers [24], [25]. In the InP systems, QWI-induced refractive index changes have been modeled theoretically by Li [26] and Meney [27] but, thus far, the only experimental results have been on waveguides [14], [28]. In all of these examples, the QWI was accomplished by either dielectric cap disordering or the introduction of impurities into the QW's (via implantation or diffusion from the surface).

All results reported in this paper were obtained from experiments on an InGaAs–InGaAsP QW structure, as will be described in detail in Section II. Section III will focus on the quantification of the lateral selectivity, while section IV contains an analysis of the optical properties of broad area intermixed material and the buried waveguides. Section V contains an examination of the near-field profiles of the buried waveguides and their modal behavior, including both experimental analysis and modeling. Conclusions will be drawn in Section VI.

II. MATERIAL AND PROCESSING

The structure used in this study was a lattice-matched QW p-i-n laser structure, which produced laser emission at 1.52 μm . It was grown by metal–organic chemical vapor deposition (MOCVD). The active region consisted of five 6.0-nm InGaAs well layers surrounded by InGaAsP barrier layers, with the uppermost QW located 1.77 μm below the surface. From the bottom up, the layers were:

n-doped InP substrate ($3 \times 10^{18} \text{ cm}^{-3} \text{ S}$), 1.0- μm epitaxial InP ($1 \times 10^{18} \text{ cm}^{-3} \text{ S}$), 70-nm $\text{In}_{0.74}\text{Ga}_{0.26}\text{As}_{0.57}\text{P}_{0.43}$ (undoped), five 6.0-nm $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ QW's separated by 20.0-nm $\text{In}_{0.74}\text{Ga}_{0.26}\text{As}_{0.57}\text{P}_{0.43}$ barriers (all undoped), 70-nm $\text{In}_{0.74}\text{Ga}_{0.26}\text{As}_{0.57}\text{P}_{0.43}$ (undoped), 1.5- μm InP ($5 \times 10^{17} \text{ cm}^{-3} \text{ Zn}$), and 0.2- μm $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ ($1 \times 10^{19} \text{ cm}^{-3} \text{ Zn}$). Implantation of 1.0 MeV phosphorus ions at a dose of $1.0 \times 10^{14} \text{ cm}^{-2}$ was performed at an angle of 7° off normal in order to minimize channeling effects. The expected implantation range, as calculated using TRIM'97, was $1.0 \pm 0.3 \mu\text{m}$ and, thus, no phosphorus ions were expected to reach the active region. In order to produce mobile point defects and avoid amorphization, it is important that the sample is held at elevated temperatures during the implantation; we have found 200 $^\circ\text{C}$ to be the optimal temperature [29].

For both the lateral selectivity and the buried waveguide studies, a 2.2- μm -thick SiO_2 layer was patterned and used to mask selected areas during implantation, then removed before annealing. Annealing (675 $^\circ\text{C}$ for 180 s) was performed in a rapid thermal annealer in an N_2 ambient, with GaAs material surrounding and covering the sample.

III. LATERAL SELECTIVITY STUDY

For the lateral selectivity study, a special implantation mask was designed. It had thirteen distinct arrays, each containing parallel stripes of oxide. From one array to the next, the mask stripe width varied from 1.5 to 23.5 μm , in increments of 1.5 μm , while the spacing between mask stripes also increased proportionately from 6.5 to 32.5 μm in increments of 2.5 μm (these regions will be referred to as implanted stripes). Each array was approximately 1.2 mm square, and thus contained 20 or more mask stripes. After implantation, the mask was removed and the sample was annealed. To obtain low-temperature (5 K) photoluminescence (PL) spectra, a weak (0.5 mW) 880-nm laser with a spot size of approximately 100 μm was directed at the center of an array. Since this spot size is much larger than the stripe and spacing widths, each PL spectrum exhibited emission peaks from both the implanted and masked stripes.

Several typical PL spectra are shown in Fig. 1. Spectra A and B are reference spectra taken from relatively large regions that were completely masked or implanted, respectively. Spectrum A is nominally identical to spectra from as-grown material, while spectrum B exhibits the maximum PL blueshift of 60 nm. Spectra C–G were taken from arrays with mask stripes of varying widths. Spectra that are not shown (arrays with stripe widths between 6.0 and 23.5 μm) were nominally identical to spectra C and D. In these spectra, the PL peak from the masked stripes (at 1.39 μm) is at the same wavelength as the peak of spectra A. However, as the mask stripes become narrower (spectra E and F), these peaks are partially shifted due to partial intermixing of the QW's under the mask stripes. The degree of intermixing increases until this peak merges with the 1.33- μm peak of neighboring implanted stripes (spectra G).

The wavelengths of the PL peaks from masked stripes are compared with the peak positions of surrounding large masked regions, and a blueshift is calculated as a function

would be for the fabrication of buried heterostructure lasers or other active devices in which gain would offset the losses. But, alternatively, a waveguide that is transparent at the lasing wavelength can also be fabricated by purposefully causing a small amount of intermixing at the waveguide center and further intermixing in the surrounding regions (as was discussed above). Careful analysis is required for choosing the degree of intermixing for the two regions, as well as the stripe width, since there will be tradeoffs between a reduction in the losses, the achieved index difference, the modal behavior, and the polarization dependence. For example, the current 6.0- μm buried waveguide may be suitable for a TE-only laser at $\lambda = 1.52 \mu\text{m}$. Alternately, to fabricate a single-mode polarization-insensitive device that has low losses at $\lambda = 1.52 \mu\text{m}$, one might work with a 4–5- μm -wide buried waveguide that has a small amount of intermixing in the center of the guide. We will soon be testing buried waveguides that have been designed following these ideas, and will thus examine these tradeoffs.

V. MODAL BEHAVIOR OF THE BURIED WAVEGUIDES

A. Modal Analysis

Using a trapezoidal approximation to the lateral profile of the refractive index as depicted in Fig. 6, simple mode calculations indicated that the 6.0- μm buried waveguide would be single mode for Δn values below 0.007. This value occurs at a wavelength of $\lambda \approx 1.52 \mu\text{m}$, as indicated in Fig. 5. The threshold for multimode behavior in the 4.5- μm buried waveguide was 0.0164, which is higher than all measured values of Δn , and thus simple mode calculations predicted that it should be single mode over the entire wavelength range in which it guides light.

In order to experimentally evaluate their modal behavior, and to confirm the index difference derived in Section IV, near-field profiles of the buried waveguides have been measured. The profiles were obtained by horizontally scanning a lensed fiber at the output facet for several different injection positions (the position of the lensed fiber at the input facet with respect to the center of the buried waveguide). Fig. 7 shows four such scans from the 6.0- μm buried waveguide at $\lambda = 1.56 \mu\text{m}$, for injection positions at the center of the buried guide (curve A), and for injection positions 1.0, 2.0, and 3.0 μm to the right of center for curves B–D. As expected, the relative intensity of the signals decreased as the injection position was moved further away from the center of the buried guide since less power was coupled into the guide. However, there were measurable horizontal shifts in the position of the maxima, which was unexpected since such behavior usually indicates the presence of more than one mode. Near-field profiles of the 4.5- μm buried waveguide exhibited similar characteristics, but the horizontal shifts were very small. The additional modes required to account for the horizontal shifts could be guided modes if the buried waveguide were multimode, or could be radiation modes (which were not completely damped out after propagating the length of the waveguide) in combination with a single mode guide. Analysis under the assumption that the buried

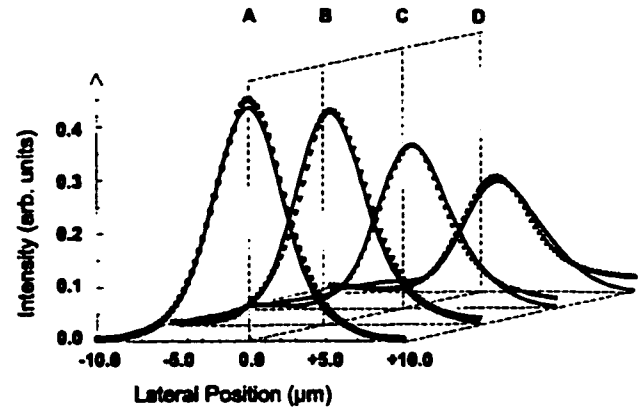


Fig. 7. Near-field profiles for the 6.0- μm buried waveguide at $\lambda = 1.56 \mu\text{m}$, including experimental data (symbols) and theoretical fits (—). The injection positions for profiles A to D are 0.0 μm (centered), +1.0 μm (right of center), +2.0 and +3.0 μm , respectively.

waveguide was multimode was performed on the 6.0- μm buried waveguide by applying the following steps.

- 1) The incoming light provided by the injection fiber was assumed to be Gaussian and was characterized by an amplitude A_0 , a width w , and a maximum position at x_c .
- 2) For a given lateral index profile, the guided mode profiles M_i were computed. Here, a simplified trapezoidal shape for the 6.0- μm buried waveguide index profile was again assumed; we have confirmed that this shape approximation has a negligible effect on results. Then, the coupling coefficient c_i for each mode was evaluated using an overlap integral of the injection and mode profiles

$$c_i = \int_{-\infty}^{+\infty} A_0 \cdot e^{-\ln(16) \cdot [x-x_c/w]^2} \cdot M_i(x) dx. \quad (4)$$

- 3) The field at the end of the waveguide was calculated as a sum of excited modes, each with a phase given by the product of the propagation constant β_i and the waveguide length L .
- 4) The detected intensity $I(x)$ was evaluated using an overlap integral of the above calculated field and the fiber mode profile for each x position of the collection fiber

$$I(x) = \int_{-\infty}^{+\infty} e^{-\ln(16) \cdot [x-x'/w]^2} \cdot \sum_i c_i M_i(x') \cdot e^{j\beta_i L} dx'. \quad (5)$$

The fiber mode was described by the same Gaussian as in 1)

- 5) The final output shape is compared to experimental data through a standard least mean square fitting procedure that minimizes the quadratic differences. Adjustable parameters were A_0 , w , and Δn (the latter of which is contained within the calculation of the M_i 's).

Results indicated that a Δn value as high as 0.034 was required in order to provide for enough guided modes to fit the experimental profiles at $\lambda = 1.56 \mu\text{m}$. This index difference was 15 times larger than the experimentally determined index

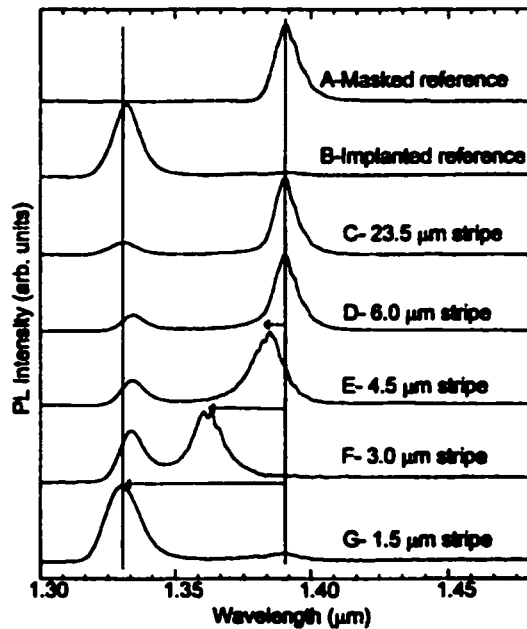


Fig. 1. PL spectra from different arrays of stripes, illustrating the shift of the PL peak from the masked QW's when the stripe width is decreased below $5.0 \mu\text{m}$.

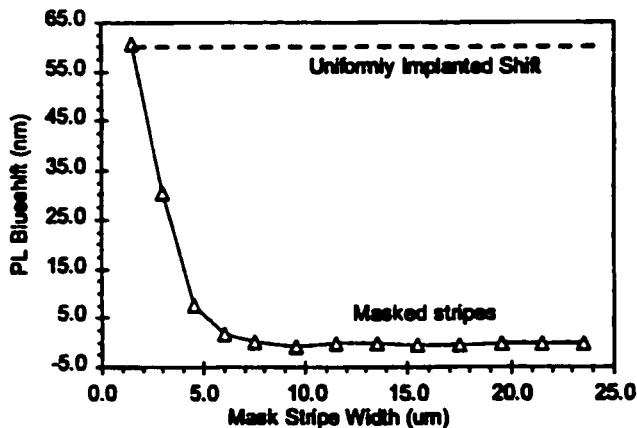


Fig. 2. Blueshift of the QW PL peak under masked stripes as a function of stripe width.

of mask stripe width, as shown in Fig. 2. The data indicate that mask stripes of $5.0 \mu\text{m}$ or larger sufficiently shield the underlying QW's, so that no intermixing occurs in at least a central portion of the underlying region. Of course, for all stripe widths, there will still be some intermixing at the stripe edges. From these observations, we conclude that the lateral selectivity of QWI is $2.5 \mu\text{m}$ when using these implantation and annealing conditions on this structure. The intermixing of QW's under masked regions is due to two effects: 1) the lateral straggle of ions during implantation and 2) the lateral diffusion of defects during annealing. A rough estimate of these two effects was shown to be in good agreement with our experimental result [30]. Further studies are underway to determine the effects of implantation energy and annealing time on the lateral selectivity.

IV. WAVEGUIDE MEASUREMENTS

SiO_2 mask stripes of various widths as well as large masked and unmasked areas were placed in parallel on one

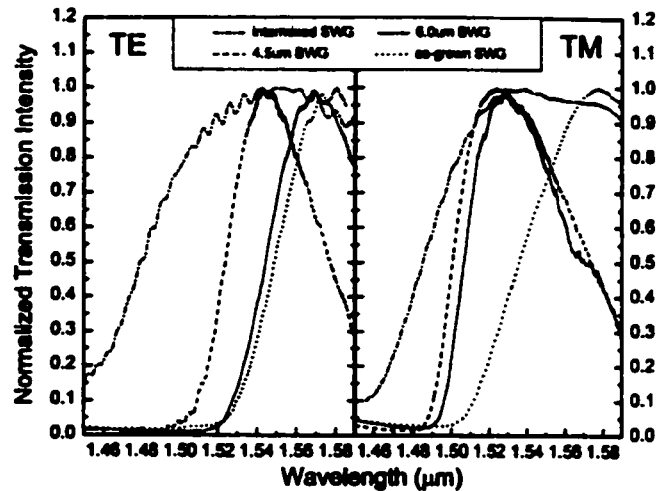


Fig. 3. Smoothed and normalized transmission spectra from slab waveguides on large as-grown ($\cdots$) and intermixed ($-\cdot-\cdot-$) regions, and from buried waveguides fabricated using $4.5\text{-}\mu\text{m}$ ($---$) and $6.0\text{-}\mu\text{m}$ ($----$) mask stripes.

sample, processed as described in Section II, and then cleaved to form 1.0-mm -long Fabry–Perot cavities. Measurements were performed using a tunable ($1.45\text{--}1.59 \mu\text{m}$) diode laser, modulated at 10 kHz , and detected using a Ge detector and lock-in amplifier. Two polarization-preserving fibers were used to couple light into one facet of the waveguide and then collect the transmitted light at the opposite facet; lenses at the fiber ends focused to a spot size of approximately $2 \mu\text{m}$.

A. QWI-Induced Band Edge Shifts and Refractive Index Changes

By measuring the optical transmission spectra of slab waveguides in the large masked and unmasked areas of the sample, QWI-induced changes in the waveguide refractive index were derived. Fig. 3 shows the transmission spectra of these slab waveguides, which have been mathematically smoothed (to minimize Fabry–Perot fringes) and normalized for clarity. The band edge of the intermixed material was blueshifted by 60 nm for TE polarization and 55 nm for TM polarization. The smaller shift of the TM band edge resulted in an overlap of the TE and TM band edges in the intermixed material, thus producing a polarization-insensitive QW heterostructure. This had been predicted theoretically [31] and demonstrated experimentally [32] to occur if the diffusion rate of group V atoms is greater than the diffusion rate of group III atoms. Under these conditions, although there is no net change in the strain, there is a complicated variation of strain across the QW, with tensile strain in the center of the QW and compressive strain at the well–barrier interfaces [33]. The tensile strain in the QW center produces a light-hole/heavy-hole splitting of an opposite sign to that caused by quantum confinement. If the strain is large enough, the two effects cancel each other, resulting in a net splitting equal to zero, and thus equivalent band edges for TE and TM polarizations.

From the raw transmission spectra (i.e., without smoothing, not shown), we analyzed the spacing of the Fabry–Perot fringes and obtained the group (or “average”) refractive index

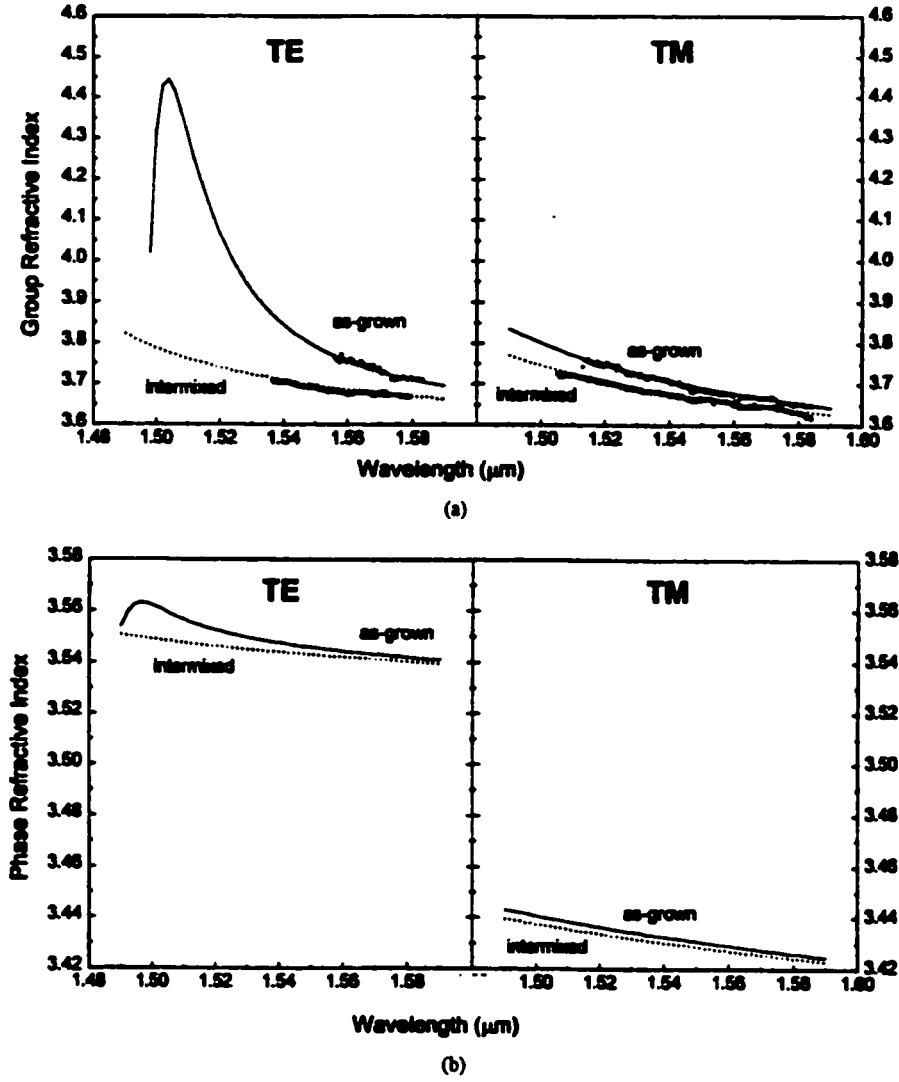


Fig. 4. (a) Experimental group refractive index data (for TE and TM polarizations) and theoretical fits. (b) Phase refractive index theoretical fits; as-grown data (+) and fit (—), and intermixed data (o) and fit (---).

as a function of wavelength. Results are shown in Fig. 4(a), including a fit to the data using an oscillator model (measurements are limited at short wavelengths because of band edge absorption). The oscillator model was used to describe the dielectric constant of the material $\epsilon(\lambda)$ as a function of wavelength, which is approximately equal to the square of the refractive index for values below the band edge [34] [see (1)]. The phase and group indices are then related through

$$(n_{\text{phase}})^2 \approx \epsilon(\lambda) = a \cdot \epsilon(\text{InGaAsP}, \lambda) + b + \sum_{i=\text{lh, hh}} \frac{A_i}{E_i^2 - (hc/\lambda)^2 - j(hc/\lambda)\Gamma_i} \quad (1)$$

and

$$n_{\text{group}} = n_{\text{phase}} - \lambda \frac{\partial n_{\text{phase}}}{\partial \lambda} \quad (2)$$

The first two terms of (1) represent the effective background dielectric constant of the bulk heterostructure [35]. The sum term represents the supplementary contributions of the light- and heavy-hole QW excitons, which are characterized by

a resonance energy (E_i), a resonance width (Γ_i), and an oscillator strength (A_i). The photon energy is given by the usual hc/λ . Identical values of all parameters are used for the as-grown and intermixed material, except that the excitonic resonances of the intermixed material are blueshifted by an amount ΔE_i . Of the several free parameters, the fit is most sensitive to the resonance energies, and thus the accuracy of the model is attested by the close agreement between the values of E_{hh} and ΔE_{hh} obtained in the best fit of the TE data (1.488 μm and 60 nm) with values obtained by 300 K PL (1.490 μm and 60 nm).

Curves for the phase refractive index, which is more useful than the group index for waveguide modeling, are derived using (1) and (2) and are shown in Fig. 4(b). Using these fitted curves, the phase index difference (Δn) caused by QWI can be calculated using

$$\Delta n = n_{\text{As-grown}} - n_{\text{Intermixed}} \quad (3)$$

and are presented in Fig. 5 for both TE and TM polarizations

It is obvious from Fig. 5 that Δn varied strongly with wavelength (especially for the TE modes). This had a signifi-

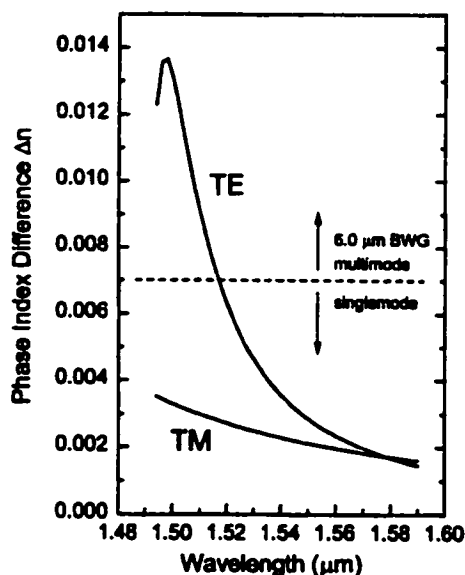


Fig. 5. Phase refractive index difference caused by QWI (Δn) for TE and TM polarizations, derived from the curves in Fig. 4(b). A dashed line depicts the Δn value where a crossover between single-mode and multimode behavior is expected for the 6.0- μm buried waveguide.

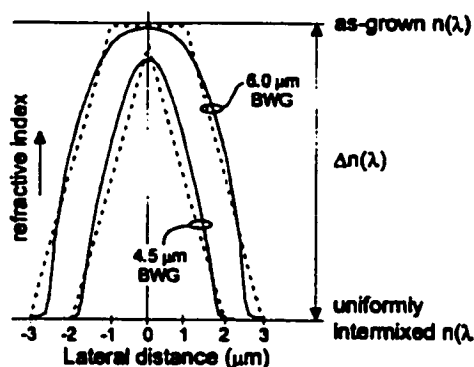


Fig. 6. Schematic of the assumed lateral profile (—) of the refractive index of the 6.0- and 4.5- μm buried waveguides, as derived from the curve of Fig. 2, and trapezoidal approximation used in modeling (---).

cant effect on the guiding behavior of the buried waveguides, as will be discussed the next section. A Δn value of 0.006 (0.15%) was obtained at $\lambda = 1.52 \mu\text{m}$ (the band edge) for TE.

B. Buried Waveguide Characterization

Buried waveguides were fabricated by using SiO_2 implantation mask stripes with widths of 6.0, 4.5, and 3.75 μm and even narrower stripes, which were surrounded by implanted regions. The difference in refractive index between the masked (nominally identical to as-grown material) and implanted material results in a narrow region of large n surrounded by material with smaller n , and thus there is lateral optical confinement along the stripe. Due to partial intermixing under mask stripes, the lateral profile of the refractive index will be graded, similar to the lateral profile of the bandgap found in Section III. We have used the curve of Fig. 2 to predict refractive index profiles of the 6.0- and 4.5- μm stripes, as shown in Fig. 6.

The transmission spectra for buried waveguides formed using 6.0- and 4.5- μm stripes are included in Fig. 3 (again smoothed and normalized for clarity). Three important characteristics of the transmission spectra are worth discussing. First, before normalization, the buried waveguide transmission spectra were an order of magnitude more intense than the slab waveguides, proving their effectiveness at guiding light. However, what is striking is that there is a maximum in their intensity (e.g., at $\lambda \approx 1.54 \mu\text{m}$ for the 4.5- μm buried waveguide), with an appreciable decrease in intensity at longer and shorter wavelengths. Transmission decreases at shorter wavelengths due to band edge absorption. At the longer wavelengths, the buried waveguides are less effective at guiding light due to the decreasing values of Δn , as is evident in Fig. 4(b). Nevertheless, since Δn is positive, the raw transmission intensity is still more intense than that for the slab waveguides at all wavelengths.

Second, the partial intermixing under mask stripes results in a blueshift of the buried waveguide band edges as compared with the as-grown slab waveguide band edge. This shift is very small for the 6.0- μm stripe and more significant for the 4.5- μm stripe. For mask stripes of 3.75 μm and narrower, intermixing under the stripes was so complete that the resultant lateral width and the net Δn were both too small to be effective at confining light. Thus, transmission spectra for these buried waveguides are essentially similar to implanted slab waveguides and are not shown here.

Third, the 4.5- and 6.0- μm buried waveguides guide both TE and TM polarizations, with a reduced birefringence in comparison with the as-grown slab waveguide. This is again due to the development of strain in the QW's during the intermixing process, as was discussed in Section IV-A. With careful control of the degree of intermixing, it should be possible to fabricate a polarization-insensitive buried waveguide structure. This could be accomplished by using an implantation mask which does not act as a complete block to the ions (by reducing the SiO_2 mask thickness), such that there is some amount of intermixing even under the center of the stripe [4]. The implant would still accomplish an additional degree of intermixing on either side of the stripe, in order to achieve a sufficient Δn for guiding.

Although not shown here, the effective refractive index curves of buried waveguides exhibit the same shape as the as-grown and intermixed slab waveguides and lie between the slab waveguide curves, as expected.

From the raw transmission spectra, the contrast of the Fabry-Perot intensity fringes was used to calculate absorption losses [5]. Since the center of the buried waveguide is not intermixed and thus not blueshifted, the absorption losses at the band edge are expected to be high. For the 6.0- μm buried waveguide, the losses were found to be 180 dB/cm at $\lambda = 1.52 \mu\text{m}$ for TE polarization. At longer wavelengths, the values were lower (40 dB/cm at $\lambda = 1.56 \mu\text{m}$). For the 4.5- μm buried waveguide, the losses were lower (75 dB/cm at $\lambda = 1.52 \mu\text{m}$ and 30 dB/cm at $\lambda = 1.55 \mu\text{m}$), as was predicted given the partial intermixing and thus blueshifting of the band edge in the waveguide center. Since these loss values are high, the most obvious applications for these buried waveguides

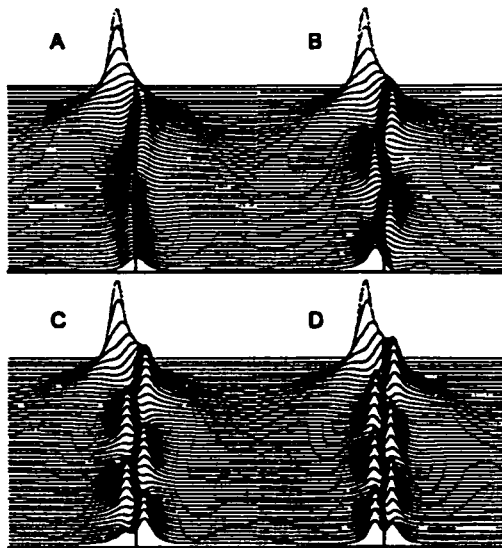


Fig. 8. BPM analysis (including radiation modes) of the field intensities along the 6.0- μm buried waveguide for $\lambda = 1.56 \mu\text{m}$ and injection at $+3.0 \mu\text{m}$. A and B illustrate different cases of single-mode guides, while C and D illustrate two cases of multimode guides. The Δn values used for A–D are 0.0003, 0.0005, 0.0007, and 0.0009, respectively. Propagation is from the back to the front.

difference of 0.0022 given in Fig. 5. This result suggested that we must consider the second possibility—that the presence of radiation modes caused a horizontal shift of the maxima. As a first step toward using this description of the buried waveguides, the above algorithm was applied to find a best fit for the central curve only [in which the effects of radiation modes can be neglected—see Fig. 7(a)]. A value of $\Delta n = 0.0022$ was obtained, which agreed exactly with the results in Fig. 5. This exercise also confirmed our choices for several parameters, including the spot size of the injected light (2.0 μm) and the buried waveguide index profiles of Fig. 6, which were also used in the analysis below.

B. Beam Propagation Method

We postulated that the horizontal shifts of the near-field profile maximum at the end of the buried waveguides, which occurred during off-center injection, were due to the presence of radiation modes in conjunction with a single-mode buried waveguide. The simplest way to model these radiation modes was to use the beam propagation method (BPM). In this approach, the BPM replaced steps 1) and 2) of the analysis in the previous section. In step 4), the summation within (5) was replaced by the field computed using the BPM. In addition, instead of the automatic optimization procedure of step 5), a systematic study of the effect of different Δn values was carried out (since it was difficult to implement an automatic optimization within the BPM).

In Fig. 8, we show propagation along the 6.0- μm buried waveguide for several different assumed values of Δn . In all cases, the injection position was 3.0 μm to the right of center, the waveguides were 1.0 mm long, and radiation modes have been included. C and D of Fig. 8 are typical of multimode propagation where at least two guided modes are present. The incoming beam excites two modes whose

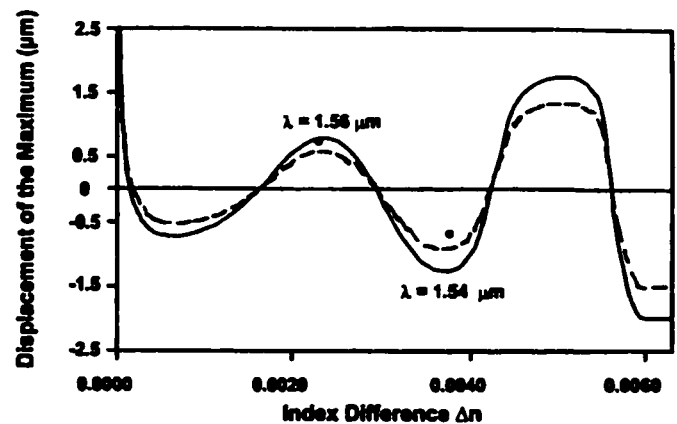


Fig. 9. Displacement of the mode maximum as a function of the index difference (Δn) for the 6.0- μm buried waveguide with injection 3.0 μm right of center, as determined using the BPM and including slab modes. Two experimental data points are included where displacement values are taken from the measured near-field profiles, and the Δn values are taken from Fig. 5.

coherent contributions to the signal are manifested by the reflection of the light beam from one wall of the waveguide to the other. The frequency of this “bouncing” is proportional to the inverse of the difference in the propagation constants of each mode. For multimode waveguides, this bouncing is repeated without loss of energy (after an initial radiative adjustment between the Gaussian shape and the mode profile at the beginning of the waveguide). A and B of Fig. 8 were calculated for Δn values lower than the multimode threshold condition. Again, an oscillatory behavior was observed, except that now the intensity gradually diminished with propagation distance. For A, the propagation constant was such that the oscillatory movement was reduced to nearly one cycle. For both of these single-mode waveguides, this radiation mode behavior resulted in a small horizontal shift of the mode maximum at the output facet. If the guide were infinitely long, propagation cases of A and B of Fig. 8 would converge into a unique central mode profile with no horizontal shift. Our simulations indicate that this situation occurs for waveguide lengths between 6 and 7 mm for these Δn values.

Fig. 9 summarizes the results of several BPM iterations, where Δn has been taken as a free parameter and the injection position was fixed at 3.0 μm to the right of center. The dashed curve represents the horizontal displacement of the intensity maximum at the output facet, while the solid curve models experimental data by including the effect of coupling into the output fiber following step 3). Two experimental data points are also indicated on the graph, with Δn values taken from Fig. 5 ($\Delta n = 0.0022$ at $\lambda = 1.56 \mu\text{m}$ and $\Delta n = 0.0036$ at $\lambda = 1.54 \mu\text{m}$), and the displacements of the maxima taken from the measured near-field profiles. We cannot experimentally determine the number of bounces which occur; however, by comparison with the experimental data points on the figure, we believe that the field is at its second (third) bounce for $\lambda = 1.56 \mu\text{m}$ ($\lambda = 1.54 \mu\text{m}$). As a final test of the modeling, we have again used these Δn values and BPM analysis to fit the experimental near-field profiles for the 6.0- μm buried waveguide. A good agreement between

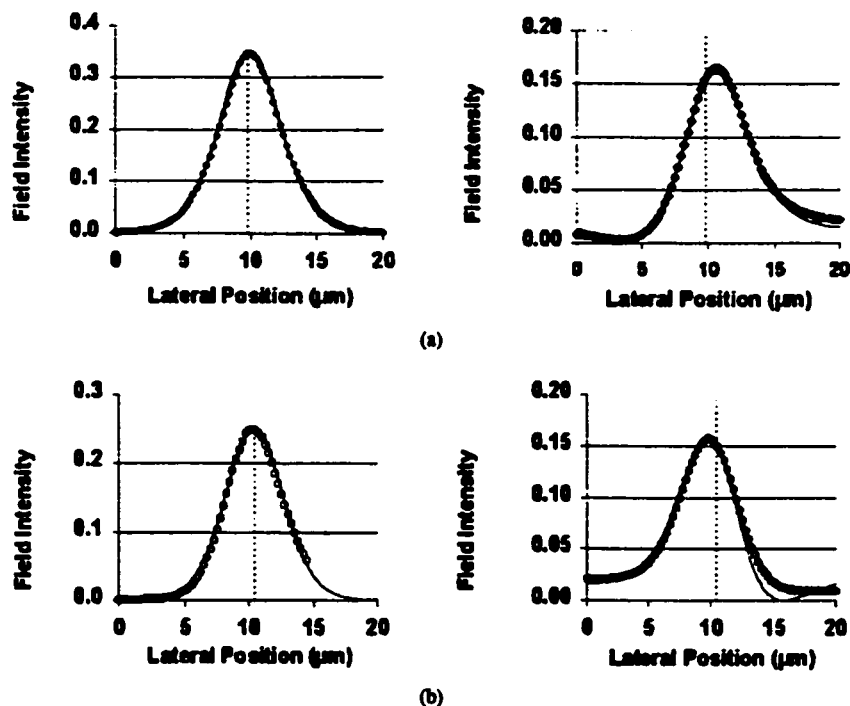


Fig. 10. Experimental and BPM calculated near-field profiles for the 6.0- μm buried waveguide. For A and B, $\lambda = 1.56 \mu\text{m}$, while for C and D, $\lambda = 1.54 \mu\text{m}$; A and C are for centered injection, while B and D are for injection at $+3.0 \mu\text{m}$ (right of center).

model and experiment is achieved (here the field amplitude A_0 is the only adjustable parameter) as shown in Fig. 10, where near-field profiles for $\lambda = 1.56 \mu\text{m}$ (A, B) and $\lambda = 1.54 \mu\text{m}$ (C, D) are presented. Profiles for a central injection position (A, C) reproduce experimental scans exactly, while profiles for an injection position $3 \mu\text{m}$ off-center (B, D) give the right displacement, intensity and width, with only a minor mismatch in the low-intensity tails.

VI. CONCLUSIONS

The high spatial selectivity of bandgap modification using QWI provides a simple procedure for fabricating narrow index-guided buried waveguides. The lateral selectivity of implantation-induced QWI was determined to be $\sim 2.5 \mu\text{m}$ in our structure, and the degree of intermixing under a mask was used to describe the graded profile of the refractive index change (Δn). The net phase refractive index change was determined to be of the order of 0.006 (0.15%) for a band edge shift of 60 nm and was found to be dependent on wavelength and polarization. Buried waveguides fabricated using 4.5- and 6.0- μm mask stripes were effective single-mode guides. Theoretical fits of experimental near-field profiles of these waveguides confirmed the above derived lateral index profile and net Δn . Since these buried waveguide samples were too short to damp out the radiation modes, the BPM was used instead of modal analysis to explain the displacement and the asymmetry of the near-field profiles. These computations clearly illustrate that the oscillatory movement, normally understood as a characteristic of multimode waveguides, may also be present in single-mode waveguides even after a significant distance, if radiation modes are present.

For most applications, single-mode transmission is desirable, and this behavior has been demonstrated for the 4.5-

and 6.0- μm -wide buried waveguides. Multimode transmission could also be achieved by either increasing the amount of intermixing and thus increasing the Δn , or by making the guides wider. It was also shown that the birefringence of the material is altered by QWI and that this could be used advantageously to produce polarization-insensitive waveguides. These buried waveguides laterally confine the light for a small range of wavelengths, limited at shorter wavelengths by absorption losses at the band edge, and at longer wavelengths by a decrease in the index difference. The wavelength range over which they are effective guides is automatically tuned to the band edge of the as-grown material. These characteristics make buried waveguides significantly different from ridge waveguides, which could limit their potential use. Two possible applications are buried heterostructure lasers and polarization-insensitive waveguides integrated with active devices.

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Additional Comments on Refractive Index Changes

The refractive index changes achieved in the previous paper could be made smaller or larger depending on layer structure and/or processing conditions. Firstly, the measured Δn is in fact the change in the guided mode index, so if the optical mode were to have a different mode shape (by altering cladding layers in the structure) this would affect the mode overlap with the QWs and thus change the Δn for the same amount of intermixing. Similarly, adding more QWs to the structure would also alter (increase) the Δn . If a significantly larger Δn was desired, one could use a different QW structure that was more “susceptible” to intermixing⁷⁵. For example, a structure with narrower QWs, or larger difference in composition between wells and barriers (such as InGaAs QWs with InP barriers), will exhibit more ΔE and more Δn for the same Δi . With regards to processing, the implantation conditions (1 MeV, $1 \times 10^{14} \text{ cm}^{-2} \text{ P}^+$) are the same as for Reproducibility - Experiment 1, but the anneal temperature and time are both lower (675 °C for 180 s here, versus 700 °C for 270 s for the reproducibility study) resulting in half the expected blueshift. Thus, optimization of the processing conditions should allow for an increase in Δn , also by a factor of around two.

F – Conclusions

This chapter has covered several aspects relating to implantation induced QWI. The introductory chapter reviewed what is currently understood in terms of damage created during implantation, the defect motion, and the way in which interdiffusion take place. Building on arguments presented in Chapter IV, further support of the interstitial picture of the QWI-defect has been discussed. One new piece of experimental information provided in this chapter is the measurement of an activation energy for QWI. The value was in the range of 3-4 eV, which was similar to values measured by others using different QWI techniques. It is unclear if this value can be used to argue one defect identity over another of the QWI-defect. We think it is consistent with a three step process, which first involves a defect reaction

to create the QWI-defect, plus its motion, and finally a mechanism by which it mediates interdiffusion at the QW (such as a kick-out mechanism).

One of the important focuses of this chapter was to optimize the annealing process specific to implantation, and to measure the reproducibility of the technique, including studying some of the variants which might influence the reproducibility. It was found that with proper care, the reproducibility of the implantation-induced QWI technique can be good, giving a variability of the blueshift of $\pm 3\text{--}4$ meV on shifts of 70 meV ($\pm 6\text{--}8$ nm on 135 nm blueshift for a layer structure originally emitting at 1550 nm). Slightly larger variations of $\pm 6\text{--}8$ meV were observed when comparing samples that were annealed in different RTA ovens which had slightly different time/temperature profiles, but most importantly, when comparing samples which had differences in the material itself. One of the influencing factors was distance from the wafer edge: samples taken within the first 5-10 mm of the edge tended to show more shift than the center of the wafer. It was also shown that, following implantation at 200°C, the damage is very stable at room temperature, implying that the time between implant and subsequent processing is not important.

Differences in the thermal behaviour of i-i-i wafers versus p-i-n doped wafers were observed, with undoped wafers exhibiting more blueshift. This effect complicated the implantation-induced blueshift, making it hard to say if the implantation-induced blueshift specifically had any dependence on doping. More work on wafers with various doping profiles should be investigated in the future.

It was found that longer anneals than was originally anticipated are required for achieving complete saturation of the blueshift: the recommended recipe for saturating the blueshift after implantation is ~ 1000 s at $\sim 700^\circ\text{C}$. Some surface degradation may occur under these conditions. Measures to reduce this effect while still using the anneal procedure of this thesis would be: minimize the distance between the sample surface and the proximity cap, use a fresh proximity cap for every anneal, and use a GaAs cap and an InGaAs terminated sample.

The other main focus of this chapter was to demonstrate ways in which implantation-induced QWI could be used in the fabrication of devices. It was shown that the shallow implantation-induced QWI process studied here has a lateral selectivity of $\sim 2.5 \mu\text{m}$. This is sufficient for many monolithic integration applications of QWI, and is even sufficient to create narrow stripe structures leading to novel devices. The bandedge blueshift also results in a change to the refractive index. Here a phase index change of 0.006 at $1.55 \mu\text{m}$ was obtained. These last two properties were used in combination to create a buried waveguide structure with stripe widths of 4.5 and $6.0 \mu\text{m}$. The lateral profile of the refractive index is diffuse, and was estimated following the results for the lateral selectivity of the blueshift. The refractive index change, and thus the waveguide behaviour was found to vary significantly with wavelength, because the change is based on small shifts in the excitonic band edges. The waveguides were found to be single mode at most wavelengths studied. Because the intermixing affects the strain in the QWs, the splitting between the heavy hole and light hole transitions, and thus between the TE and TM bandedge changed with amount of blueshift. Thus the polarization sensitivity could be tuned.

Appendix A – Interstitial Sites

The InP lattice can be considered as two interpenetrating FCC lattices, one with In atoms and one with P atoms, as illustrated in figure II-2. Alternately, we consider the structure as an In FCC lattice, with four P atoms located at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})a$, $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})a$, and $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})a$ positions. The P atoms thus fill four of the eight “tetrahedral interstitial” sites of the In FCC lattice, where each of the eight sites are surrounded by four In atoms. The other four sites remain open, where an extra atom, or interstitial of the zinc blende structure may be located. By substituting In for P and vice versa in the above analysis results in four other interstitial sites of the zinc blende structure, and these sites are surrounded by four P atoms. Thus there are two types of interstitial sites: In tetrahedral sites and P tetrahedral sites.

The distance between the interstitial sites and the neighbouring atoms (center to center) will be the same as the bond length between the normal In and P atoms, which is $a\sqrt{3}/4$. By subtracting the covalent radius for surrounding atoms (either In or P atoms) from this length, we get the radius of largest sphere which can be fit into the empty space, or the size of the interstitial site. Using the values listed in table V-4 results in the following:

In tetrahedral interstitial site radius = 1.14 Å

P tetrahedral interstitial site radius = 1.41 Å

Since In is the larger atom, the In interstitial space is smaller. These values for the covalent radii of the In, Ga, As, and P atoms, are expected to be sufficiently accurate, as per the following arguments. Note that the sum of In + P radii (or of the sum of the Ga + As radii) equals 2.533 which translates into a lattice constant of 5.850, which is quite comparable to the actual lattice constant of 5.8694. In the third column of table V-4, the radii for a neutral (unbonded) atom are listed; we assume that these values provide a good estimation of size of a neutral interstitial in the InP lattice. Comparing the values to the above calculated site radii, we conclude that the P atom can easily fit in the P tetrahedral site, and is very close to fitting into the In tetrahedral site (with a small amount of lattice distortion it could). An As interstitial is a bit larger than the P interstitial, but also fits into the P tetrahedral site.

Table V-4: Approximate radii for atoms in a covalently bonded and unbonded neutral states.

	covalent radius ⁷⁶ (Å)	atomic radius ⁷⁷ (Å)
In	1.405	2.00
Ga	1.225	1.81
As	1.225	1.33
P	1.128	1.23

Appendix B – Defect Diffusion

In this analysis we will assume that the QWI is caused by a single defect process, and assume that there are no defect loss mechanisms (at least in the regions above and in the vicinity of the QWs). For a given starting distribution of defects, the profiles after an anneal of time t will depend on the diffusion rate of the defects, D_d . A schematic is shown in figure V-9 of the concentration of defects (N_d) at $t=0$, and for three different lengths of anneals, t_1 , t_2 , and t_3 , all for the same anneal temperature.

Following Cibert and Petroff⁶⁶, the amount of interdiffusion at the QW will be related to the time integrated concentration of defects at the QW, as expressed by:

$$\Delta_i^2 \propto \int_0^t \partial t' N_d(D_d, t') \quad [5]$$

which is related to the total number of defects that have passed through the QW, or proportional to the shaded area under the profile beyond the QW. This relation can then be converted into Δ_i^2 versus time, as illustrated in figure V-9 (b). The Δ_i is small at low t , before the defects have reached the QW, then increases quickly as the peak in the defect profile moves through the QW (t_2 and t_3), and eventually saturates when all the defects have disappeared. Higher temperature anneals give faster diffusion, thus requiring less time to reach the same diffuse defect profiles (same Δ_d).

For the analysis performed in this chapter, the exact shape of the defect distribution at $t=0$ is not important, nor is the exact nature of the relationship between Δ_i and N_d important, only that there are several $D_d t$ combinations that will result in the same defect distributions, which will be true as long as only one diffusion process is occurring and that defect trapping is not a significant factor.

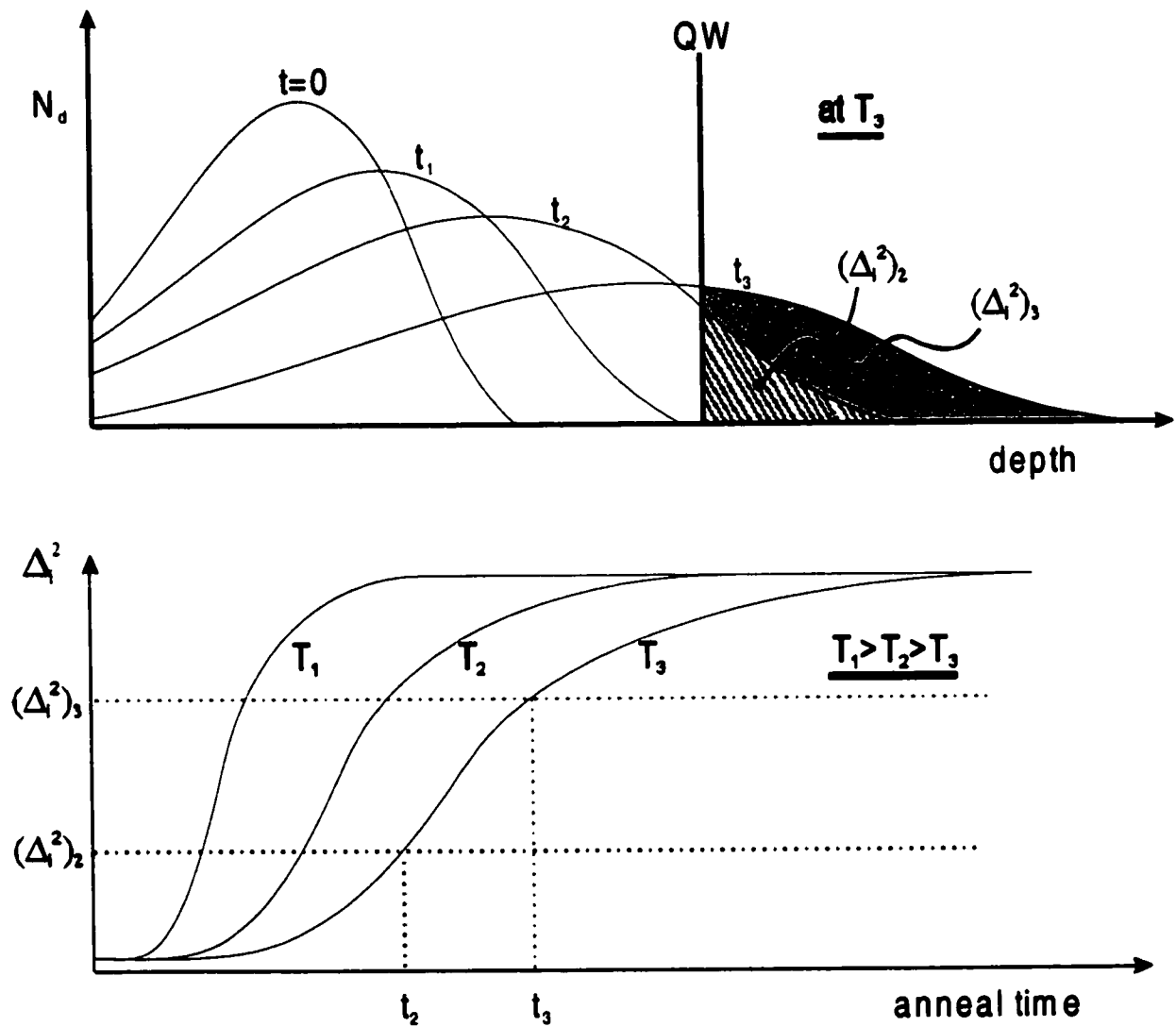


Figure V-9: (a) Schematic of the defect concentration profile (N_d) as a function of annealing time, where interdiffusion length (Δ_l) of the QW is proportional to the total number of defects which have passed through the QW; and (b) schematic of the interdiffusion length as a function of both anneal temperature (T) and anneal time (t).

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Chapter VI - Conclusions

This thesis has attempted to cover the interdiffusion of InGaAs(P)/InP QW structures from the fundamental defect mechanisms, through optimization of processing parameters, to analysis of optical properties including a foray into device applications. Conclusions from each of these areas have been made which further the scientific understanding and the manufacturability of the technique. A brief summary of these conclusions is given, subdivided into processing issues, scientific aspects, and device applications, followed by suggestions for further work.

A – Processing Issues

QWI relies on having good control of point defects in the semiconductor, and it should be recognized that each growth and processing step has the potential to affect the distribution and movement of the defects. The final processing step for QWI, the annealing, raises the material to very high temperatures (higher than growth temperatures, and $\sim 3/4$ of InP's melting point) and thus subtle changes in previous processing steps can have important effects. This thesis attempts to delineate which parameters are important, and has shown that the QWI technique can be made reproducible. This is a very important result if the technique is to be adopted by industry. The timing is appropriate, since, as was outlined in the introduction, the need for devices with advanced functionality and integration is now present.

Growth

Results in chapter IV have shown that subtle changes in epitaxial growth can influence QWI. The thermal behaviour of several layer structures grown by three different epitaxial growth reactors have been compared. Multiple anneals were used to determine that a poor thermal stability exhibited by some wafers was caused by excess grown-in defects. It was found that small reductions ($\sim 25^\circ\text{C}$) in growth temperature for CBE growth could introduce these excess defects. The one

MBE wafer that was included in the work also had excess grown-in defects, and it was speculated that MBE growth, with its lower growth temperature, may be more susceptible to grown-in defects. For the many wafers studied here, “good” material exhibited no blueshift for anneals at 675°C. For several wafers, even those which exhibited excellent thermal stability, it was observed that material near the edge of the wafer blueshifted more than that from the center of the wafer, and thus material from the first 5 mm from the edge could produce erroneous results. A high quality CBE wafer was found behave similarly to several MOCVD wafers, indicating that transfer of process details between different growths can be done.

It is proposed that thermally-induced QWI can be used as a new metric for measuring the quality of epitaxial growth. Certainly, the thermal stability of any structure which is to be used in QWI studies should be known. Alternately, one can purposely make use of grown-in defects as a new technique for QWI. By introducing excess defects into only an upper buffer layer, and removing this layer in selected regions of a wafer using lithography and etching, selective intermixing can be accomplished. Such an approach may offer cost savings over the implantation-induced QWI technique, which requires an implanter.

Finally, although a thorough study was not conducted, trends in the data revealed that strain and dopants may alter the thermally-induced blueshift. For the strain effect, it was unclear whether increased blueshifts were related to difficulties in the growth of strained layers, or if the strain simply enhanced the interdiffusion processes. In view of the observed build-up of local strain in intermixed samples, the latter seems unlikely. For the dopants, all that can be said is that the i-i-i wafers shifted slightly more than p-i-n wafers, and several mechanisms for the difference were speculated. More study of both of these dependencies are warranted.

Implantation

Many parameters must be properly selected during implantation of P⁺ ions for QWI, and a detailed study of most of these parameters was previously performed by

other colleagues. In this thesis, the reproducibility of the technique was studied. It was found that the reproducibility of the implantation-induced QWI technique can be very good, giving a variability of the blueshift in some cases as good as ± 3 -4 meV on shifts of 70 meV (equal to ± 6 -8 nm on 135 nm blueshift for a layer structure originally emitting at 1550 nm). Slightly larger variations of ± 6 -8 meV were observed when comparing sample sets where either one set of samples was from the edge of the wafer (which always tended to blueshift more) or anneals were done slightly differently. The samples used in the studies either came from the same wafer, or from sequentially grown wafers. It was also shown that, following implantation at 200°C, the lattice damage is very stable at room temperature, implying that the time between implant and subsequent processing is not important.

Annealing

Reproducible annealing is a key requirement for all diffusion studies, whether material is implanted or not, and this demands good control of the semiconductor surface. Processing prior to annealing has the potential to influence the blueshift - an example of the presence of solvents was given. For all compound semiconductors, and InP in particular, control of the group-V overpressure during the anneal must be carefully considered. The proximity cap method used in this thesis was the best of the available options, but was still imperfect. An inverse relationship between PL intensity and anneal temperature might have been connected with increased surface degradation at higher anneal temperatures. Following long anneals in the higher temperatures range (400 s at 750°C), significant surface defects relating to the loss of group-V atoms were observable on the surface. Such defects were also observed, but to a lesser extent in anneals of 500 s at 725 °C and even lesser extent for anneals of 570 s at 700°C. Several options were employed to optimize the proximity cap method. Use of GaAs proximity caps for InGaAs terminated wafers, and InP proximity caps for InP terminated samples showed the best results in terms of preventing a reduction in PL intensity, although the effect on blueshift was minimal. Using a sacrificial border material to surround small samples improved the uniformity of the blueshift, but

these pieces should be slightly thicker than the sample – if they are thinner, then the proximity cap is balanced on the sample and uniformity decreases, but if they are too thick then the group-V overpressure is reduced. It is possible that more frequent replacement of the proximity caps would have reduced the observed surface degradation. Since most of the studies in this thesis relate to relative differences between samples, the imperfections of the annealing technique do not strongly affect the general conclusions. However, one may question whether the loss of group-V after long anneals has influenced the intermixing mechanisms. Ultimately, it would be preferable to improve the control of group-V overpressure, for example by using a direct flow of arsine or phosphine gases, although this would require significant equipment upgrades or use of a growth chamber. All this being said, the reproducibility of the anneal was shown to be good, even when using different ovens, two different methods of temperature measurement (pyrometer or thermocouple) and whether or not a susceptor was employed.

Finally, it was found that longer anneals than were originally anticipated are required for achieving complete saturation of the implantation-induced blueshift: the recommended recipe in terms of saturating the implantation-induced blueshift while causing negligible blueshifts in non-implanted material is 600 to 1000 s at $\sim 700^{\circ}\text{C}$. If the proximity cap method is used to provide group-V overpressure during the anneal, some trade-offs may exist between maximizing saturation at the expense of surface deterioration.

B – Scientific Aspects of QWI

Obtaining a complete picture of the diffusion mechanisms in a material requires an enormous amount of research, and can easily take thirty or more years of research¹. GaAs has been studied for a period of around twenty five years, while InP has only been studied seriously for the past twelve years. The current understanding of defects and diffusion in InP has certainly benefited from the earlier work in elemental and other III-V semiconductors, although some differences are expected theoretically, and observed experimentally, between the different systems.

Most books that make a serious attempt to cover defects in III-V semiconductors and their properties still cover very little detail with regard to InP properties - in the background research for this thesis sentences such as “such calculations have not yet been carried out for InP”² were regularly encountered in texts and review papers. More recently, texts specific to InP have appeared^{3,4} but with a primary focus on the technology and devices. Work on the subject seems to be driven by problems in device manufacturing rather than by the desire to build an understanding of the defect properties, and since the optical properties and band structure are key to the devices, these properties have been relatively well studied⁵. But no authoritative work exists which captures the past ten years of research on defects and diffusion in InP (a decent review text was published in 1990 by Academic Press⁶). One has to rely on published papers and conference proceedings, which are at least summarized on a regular basis in “Defect and Diffusion Forum”⁷.

Defects

A study of implantation-induced QWI concluded that the process has an activation energy in the range of 3-4 eV. This is believed to be an effective activation energy which likely encompasses three steps: a defect reaction which releases the QWI-defects, the diffusion of these defects, and finally a mechanism by which these QWI-defects mediate interdiffusion at the QWs (such as a kick-out mechanism).

Detailed analysis of CBE grown at reduced temperatures (low temperature - LT) allowed for some new insights to be drawn on the mechanisms of the QWI - it is was proposed that the grown-in defects in this LT grown InP are related to excess P (possibly P antisites), and the QWI-defect which is released is a P interstitials. A related study of grown-in defects, which did not assume a particular identity of the QWI-defect, did determine that the defects' diffusion coefficient was in the range of 4×10^{-10} to 4×10^{-11} cm²/s, with the exact value depending on what assumptions are used with regards to the role that the semiconductor's surface has on defect annihilation. Since the RTA conditions and resultant changes to the QW are similar

to those observed for implantation-induced QWI (shallow P⁺ implantation), it is suspected that the QWI-defect is the same in both LT growth and implantation-induced QWI.

The above proposals, are simply that – proposals, which have been based on some indirect experimental evidence and on review of a significant number of other literature. Nothing here has proved an interstitial nature to the QWI-defect, nor has it disproved a vacancy nature, and it is always possible that both interstitials and vacancies can play a role, dependent on experimental conditions. What this thesis has attempted is to create a set of arguments as to why the interstitial picture must be seriously considered. More research is obviously required in this area.

Compositional Changes

It was determined, using both low temperature normal incidence optical transmission and using X-ray diffraction (XRD), that intermixing caused by LT growth occurs predominately on the group-V sublattice, with a k ratio (the ratio of group-V interdiffusion length over group-III interdiffusion length) between 2 and 4 being an appropriate description. Waveguide transmission analysis of implantation-induced intermixing similarly confirmed a k ratio greater than 1. These results are in agreement with what has been previously reported for implantation-induced and dielectric-cap induced QWI, indicating that high diffusion rate of the group-V sublattice may be a common feature in InP-based heterostructures.

Finally, it was shown that although analysis of the relative energy shifts between the heavy hole (hh) and light hole (lh) states was useful for determining the k ratio, it was not useful for determining whether or not the intermixing is Fickian. Instead, direct characterization of the compositions, although challenging, will be beneficial. A brief look at using XRD indicated that it may be possible to differentiate between different shapes of QWs if more rigorous modeling of the XRD spectra is undertaken.

C – Devices

It was shown that the shallow implantation-induced QWI process studied here has a lateral selectivity of $\sim 2.5 \mu\text{m}$. This is sufficient for many monolithic integration applications of QWI, and is even sufficient to create narrow stripe structures leading to novel devices. The bandedge blueshift also results in a change to the refractive index - a modal phase index change of 0.006 at $1.55 \mu\text{m}$ was obtained in this thesis. These two properties were used in combination to create a buried waveguide structure with stripe widths of 4.5 and $6.0 \mu\text{m}$. The refractive index change, and thus the behaviour of the waveguide device, was found to vary significantly with wavelength, which makes the waveguide devices significantly different, and less universally applicable, than standard ridge waveguide devices. However, their planar nature may offer certain advantages for manufacturing. Finally, because the splitting between the heavy hole and light hole transitions changed with intermixing, the TE/TM polarization dependence of the devices also changed with the amount of QWI, offering polarization dispersion tunability.

D – Suggestions for Further Research

While this thesis has included a number of fruitful experiments, as well as exploring some theoretical aspects of QWI, the sheer breadth of this topic combined with the comparatively small number of man-years of research in this field dictates that many further avenues of research remain either under- or even un-explored. Some possibly useful areas that remain to be fully investigated include:

- The reproducibility of grown-in defects by LT CBE growth, as well as the dependence on growth temperature or other growth parameters needs to be further understood. It could also be interesting to explore whether growth by other epitaxial methods can be used for purposeful QWI by grown-in defects.

- The role that the surface plays in defect diffusion and defect annihilation was unknown in our analysis. Some simple structures with LT layers in specific locations could be used to further elucidate its effect.
- For both grown-in and implantation-induced defects, characterization of defects using capacitance and magneto-optical techniques could help ascertain their identity(ies). Detailed theoretical analysis of InP and its defects could help in the evaluation of various proposals for the defect identities.
- The effect of doping and strain on the whole intermixing process needs to be further studied using specifically designed sets of wafers. Such a study should include measurements of k ratios for these layer structures, since it is possible that the intermixing mechanism, and thus the k ratio, will vary with either of these structure parameters.
- A detailed study of QWI using high-resolution XRD with advanced fitting algorithms could be very fruitful for determination of the k ratio and the shape of the interdiffused QW.

Parting Thoughts

Because QWI encompasses such a wide range of topics, the research for this thesis was both exciting and fulfilling, and has also served as an excellent springboard to a career in compound semiconductors. Given the choice, I would do it all again.

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