Photomodulated Reflectance Spectroscopy
of Novel Semiconductor Materials

Gareth Llywelyn Rowland
June 1999

A thesis submitted to the University of Surrey for the degree of
Doctor of Philosophy

Department of Physics, University of Surrey, Guildford, Surrey, GU2 5XH
Abstract

Room temperature photomodulated reflectance (PR), Photoluminescence (PL) and double crystal x-ray diffraction (DCXRD) measurements have been performed on a series of tensilely strained In$_x$Ga$_{1-x}$As (0.316 ≤ x ≤ 0.533) multiple quantum well (QW) structures, with In$_{0.80}$Ga$_{0.20}$As$_{0.43}$P$_{0.57}$ barriers. The DCXRD measurements provided accurate information on composition, strain and layer thickness, while PR was used to determine the energies of the full manifold of allowed and forbidden critical point interband QW transitions. A three-band effective mass formalism was used to model the QW transitions to derive structural information on each sample. The energies of the ground-state QW transitions, $H_{11}$ and $L_{11}$, were found to increase with tensile strain, becoming degenerate near 0.36% tensile strain.

Room temperature PR and conventional reflectance (R) measurement have been performed on two I.R. emitting InGaAs/GaAs/AlAs vertical cavity surface emitting laser (VCSEL) structures. The R measurements were modelled using a transfer matrix formalism to determine errors in the growth fluxes. A new PR lineshape model has been developed based on energy dependent Séraphin coefficients, to describe the cavity mode interaction with a confined-state QW transition. The model is demonstrated on a set of PR spectra, and used in a novel way to derive the Δe$_2$ spectrum of the QW layers directly. The results are compared with those taken of the QW layers directly after removing the top Bragg stack reflector. Whilst the QW layers in one sample were found to be close to nominal, the In composition of QW in the other sample was found to depart significantly from the nominal 23%, and was found to be 28%.

Room temperature and ~ 80K PR measurements were performed on three InAs/GaAs self-assembled quantum dot (QD) structures: a sample with a single layer of QDs, and two with two layers. The PR revealed five equally spaced confined-state QD
transitions, at both 80K and room temperature, with ~ 54 meV separation. The behaviour of the QD1 transition as a function of temperature was investigated and an anomalous increase in linewidth was observed on cooling. Annealing of one of the samples produced a strong blue shift (~ 250 meV) and narrowing of the QD transitions.
Acknowledgements

In completing this thesis, I have learnt a great deal not only about the physics involved, but also about myself. Many colleagues have assisted me, both directly and indirectly, and I would like to take this opportunity to thank them all.

First and foremost, I would like to extend my gratitude to my Supervisor Dr. T. J. C. Hosea without whom this thesis would not have existed. I thank him not only for his knowledge, expertise and for the reading of this manuscript, but also for the fact that his perseverance and pragmatic approach to work has instilled in me a greater sense of confidence in the depth of my own abilities.

I am indebted to Dr. P. J. Klar for the time spent working on vertical cavity surface emitting lasers (VCSEL), for his guidance, skills and good sense of humour. I am also grateful to Dr. T. Sale for his expertise on VCSELs and for the loan of samples. I would like to thank Dr. M. Silver for his advice on $k \cdot p$ and QCSE calculations, and Dr. I. Morris for his advice on the numerical solution of Poisson's equation. I also thank Prof. E. P. O'Reilly for the many discussions on theoretical aspects of the whole thesis, to Dr. R. Murray for his expertise and loan of QD samples, and to Dr. P. Kidd for the assistance on the double crystal x-ray diffraction measurements. Furthermore, I extend my thanks to the mechanical and electrical workshop staff, W. Scherrer, R. Warren, and E. Worpe. I would also like to thank E. Griffiths for her patience, and for the loan of equipment from the undergraduate lab.

In thanking people outside the academic sphere, I am deeply grateful for the support of both my parents and extended families. I thank my father for his intellectual and financial support during my academic career, and for the invaluable proof reading of this manuscript; and my mother for her constant kindness and friendship. I would also like to thank all those I have lived and worked with during my time at Guildford:
Mark, Omar, Felix, Dwaine, Danny, Marco, Carl, Mark, Vicky, those at Hazel Farm, and the Chancellor’s Friday lunch time crew. I also thank EPSRC for the funding of this Ph.D.

* I would also like to thank Dr. A Onischenko for his assistance with theoretical aspects of the VCSEL studies.
Publications


Contents

Abstract i
Acknowledgements iii
Publications v

1 Review of III-V Semiconductor Physics 1

1.1 Introduction 1
1.2 III-V Semiconductors 3
  1.2.1 Crystal Structure and Band Structure 3
  1.2.2 Material Constants for III-V Binary, Ternary and
       Quaternary Compounds 6
1.3 Heterostructures 8
  1.3.1 Heterojunctions and Quantum Wells 9
  1.3.2 Strain 12
  1.3.3 Modelling of Heterostructures 14
1.4 Optical Confinement 17
1.5 Lower Dimensional Systems 21
1.6 References 24

2 Experimental Techniques 27

2.1 Introduction 27
2.2 Photomodulated Reflectance 28
  2.2.1 Modulated Spectroscopy and Photomodulated Reflectance 28
  2.2.2 Historical Development of ER Theory 29
  2.2.3 Theory of Photomodulated Reflectance 30
  2.2.4 Lineshape Models 45
  2.2.5 Experimental Apparatus for PR Experiments 47
3 PR, PL, and DCXRD Studies of Tensilely Strained InGaAs/InGaAsP Quantum Well Structures

3.1 Introduction

3.1.1 Strain in QW Systems

3.1.2 InGaAs/InGaAsP Material Systems in Optical Devices

3.1.3 Samples

3.2 PR and PL Measurements

3.2.1 Experimental Details

3.2.2 PR Measurements

3.2.3 PL Measurements

3.3 DCXRD Measurements

3.3.1 Experimental Details

3.3.2 Modelling of DCXRD Spectra

3.3.3 Results

3.4 Modelling the Full Manifold of QW Transitions Observed in the PR spectra

3.4.1 Theoretical Model

3.4.2 Identification of All Confined-State QW Transitions Observed in the PR Spectra
3.5 The Effect of Strain on the Ground-State QW Interband Transitions $H_{11}$ and $L_{11}$

3.5.1 Energies of Ground-State QW Interband Transitions $H_{11}$ and $L_{11}$

3.5.2 Linewidths of Ground-State QW Interband Transitions $H_{11}$ and $L_{11}$

3.6 Summary

3.7 References

4 Photomodulated Reflectance and Conventional Reflectance Studies of Vertical Cavity Surface Emitting Lasers

4.1 Introduction

4.1.1 Review of VCSELs

4.1.2 I. R. VCSEL Samples

4.2 Photomodulated Reflectance of a VCSEL

4.2.1 Experimental Details

4.2.2 Identification of Confined-state QW Transitions and Cavity Mode Features in the PR Spectrum of a VCSEL

4.3 Reflectance Studies of VCSELs

4.3.1 Transfer Matrix Theory

4.3.2 Polarisation Effects on the R and PR Spectra of VCSELs

4.3.3 Modelling and Fitting of VCSEL Reflectance Spectra

4.4 Summary

4.5 References

5 Lineshape Model for the PR Spectrum of a VCSEL

5.1 Introduction

5.2 Lineshape Model for a Confined-State QW Transition in
5.2.1 Calculating the Séraphin Coefficients of a VCSEL Structure

5.2.2 Lineshape for the Modulated Change in the Complex Dielectric Function of the QW Layers

5.3 Application of the Model for Resonance Between the CM and Ground-state QW Transition

5.3.1 Experimental Details

5.3.2 Results

5.4 A Novel Application of the Lineshape Model to Calculate $\Delta \varepsilon_2$

5.4.1 Deriving $\Delta \varepsilon_2$

5.4.2 Experimental Details

5.4.3 The Derived $\Delta \varepsilon_2$ Spectrum

5.4.4 Modelling of CM Interaction with Higher-Order QW Transitions

5.5 Investigation the QW Layer of RMB1048 by Removing the Top DBR Stack

5.5.1 Experimental Details

5.5.2 Results

5.6 Theoretical Modelling of QW Layers in RMB627 and RMB1048

5.6.1 Theoretical Model

5.6.2 Results of Modelling

5.7 Summary

5.8 References

6 Photomodulated Reflectance Studies of Self-Assembled InAs/GaAs Quantum Dot Structures

6.1 Introduction

6.1.1 Self-Assembled Quantum Dots and the Stranski-Krstanow Growth Mode

191
CHAPTER 1

Review of III-V Semiconductor Physics

1.1 Introduction

This work is a study of a number of different material systems based on so called III-V semiconductor compounds. All of the material systems investigated here play some role in the design of opto-electronic components, generally semiconductor lasers. The work uses a number of spectroscopic techniques to determine the electronic, optical, and structural properties of a variety of novel material systems. However, the focus of the study is on the application and development of a particular type of modulation spectroscopy known as photomodulated reflectance (PR).

The material systems studied are multi-layered structures fabricated using modern epitaxial growth techniques such as MBE and MOCVD. With such technology it is possible to grow high quality layers of different semiconductor compounds pseudomorphically on one another with almost atomically abrupt interfaces. This allows the effects of quantum confinement and strain in individual layers to be used to engineer the optical properties of the structure. With the continued growth of the telecommunications industry, there is an ever-increasing demand on the performance of all related technology. One of the key components of optical fibre communication systems is the semiconductor laser. Laser technology began in the 1960’s with the first lasers, such as the He-Ne laser, relying on dilute active media with discrete energy levels such as gases or dopant ions scattered in a solid. In 1962, the
A semiconductor laser was developed simultaneously at the MIT laboratory, General Electric and IBM. The active region of the laser uses a semiconductor p-n junction, and is pumped by using the current flowing through the junction to create electron and hole pairs. The resonator mirrors are formed using cleaved surfaces of the material. These have a sufficiently high reflectivity due to the large refractive index of the semiconductor material.

PR is a member of a family of spectroscopic techniques generically known as modulation spectroscopy. PR uses the periodic application of a high intensity light source to generate electron and hole pairs within a sample. These modulate the surface electric field which results in small but detectable changes in the reflectance response of the system. PR is used to give a range of information on the semiconductor system under study including the energies of critical point interband, and intersubband transitions, and the size of built-in electric fields within the structure. PR is non-destructive and can be used at room temperature making it a particularly powerful technique for the analysis of semiconductors.

The work in this thesis examines the application of PR to three separate semiconductor material systems. Although the systems are quite different, and are treated as such, there is some degree of overlap between the different sections of work, and the thesis should be read as a natural progression of ideas. The different systems under study are tensilely strained multiple quantum wells, vertical cavity surface emitting lasers, and self-assembled quantum dot structures.

Chapter 3 examines a series of InGaAs/InGaAsP tensilely strained multiple quantum well (QW) samples, and uses the results to determine the effects of tensile strain on the band structure of this material system. PR and photoluminescence are used to determine the energies of confined-state interband transitions within the QW layers. Double crystal x-ray diffraction spectra are modelled to derive the compositions, strains, and widths of individual layers within each structure. The structures are then modelled by comparing the experimentally determined confined-state QW transition energies with those predicted by a theoretical model.
Chapters 3 and 4 are a combined study on vertical cavity surface emitting lasers (VCSEL), and use PR and conventional reflectance (R) to investigate two I.R. emitting VCSEL structures. Chapter 3 examines the basic features of PR and R spectra of VCSELs and demonstrates how experimental R spectra can be modelled using a transfer matrix method. Chapter 4 develops a model for the PR lineshape of a VCSEL where there is an interaction between the optical mode of the cavity and a confined-state QW transition. Further features of this model are then demonstrated using a novel experiment to derive the imaginary part of the complex dielectric function.

Chapter 6 examines a number of InAs/GaAs self-assembled quantum dot (QD) structures. PR measurements are performed at both room temperature and ~ 80K. PR spectra of such structures display confined-state CP interband transitions both within the QDs as well as in the surrounding confining layer material. The results of these studies are used to speculate on the nature and properties of the dots.

The remainder of this chapter gives an overview of the semiconductor physics relevant to this work. Chapter 2 describes the experimental techniques used throughout the work: photomodulated reflectance, conventional reflectance, photoluminescence, and double crystal x-ray diffraction.

1.2 III-V Semiconductors

1.2.1 Crystal Structure and Band Structure

The various material systems examined in this thesis are based on the so-called III-V semiconductor materials. As the name suggests, these compounds are formed from elements of group III (Al, Ga, In) and group V (P, As, Sb) of the periodic table. This section gives a brief overview of bulk III-V semiconductor physics. For further information on solid state theory, and bulk III-V physics, the reader is referred to (Kittel, 1986), and (Kelly, 1995), respectively.
Most group III-V compounds crystallise into the zinc blende structure. Fig. 1.1 demonstrates the zinc-blende structure using GaAs as an example. The large dark spheres represent the Ga atoms, and the smaller light spheres, the As atoms. The zinc blende structure can be interpreted as two interpenetrating face centred cubic lattices. The group III elements possess two valence $s$ electrons and one valence $p$ electron, whereas the group V elements have two valence $s$ electrons and three valence $p$ electrons. The result is an average of four valence electrons per atom and consequently the $s$ and $p$ electron orbitals of each atom hybridise to form four $sp^3$ orbitals. Within the crystal lattice, each atom of one species (group III, or group V) is tetrahedrally bonded to four atoms of the other species. The unit cell of the lattice contains two atoms, one group III atom and one group V atom.

An important aspect of any particular semiconductor is its band structure. The band structure defines the allowed energy and momentum states an electron can possess within the crystal. The band structures of semiconductors are conventionally represented using a plot of energy, $E$, against wavevector, $k$, for an electron within the crystal lattice. Such a plot displays a number of curves, with each curve representing a single band of allowed energy and momentum states that an electron can occupy. It is useful to consider an electron in terms of its de Broglie wavelength, which is defined as Planck's constant divided by the electron's momentum. The momentum of the
electron can increase until its associated wavelength becomes of comparable length to the crystal lattice spacing, upon which the electron will undergo diffraction. By representing the momentum of an electron in reciprocal lattice space by its wavevector, it is possible to map out the limiting range of electron momenta below which electron does not undergo diffraction. This is known as the first Brillouin zone. Fig. 1.2 depicts the first Brillouin zone for the zinc blende structure, which takes the form of a truncated octahedron. Also shown in this figure are the points of high symmetry in the band structure along with their respective designations. These are namely the $\Gamma$ point at the zone centre, the $X$ point at the zone boundary in the (001) direction and the $L$ point at the zone boundary in the (111) direction. Band structure diagrams are conventionally drawn along one of these crystallographic directions.

Fig. 1.3 shows the band structure calculated for GaAs, neglecting the spin-orbit interaction. An enlarged section of the band structure around the Brillouin zone centre is depicted in Fig. 1.7(a). In this figure, the most significant bands can be seen, which are namely the conduction band (CB), and the three valence bands; heavy hole (HH), light hole (LH), and spin-orbit split-off (SO) bands. The potential energy of the bands is conventionally taken to be zero at the top of the valence band maximum, at the zone centre.

One of the fundamentally important parameters intrinsic to any particular semiconductor material is its bandgap. This is defined as the forbidden energy gap between the minimum of the conduction band and the maximum of the highest lying
valence band, and is labelled $E_0$ in Fig. 1.7(a). In GaAs, both of these band extrema exist at the same value of electron wavevector, $k = 0$, that is to say at the Brillouin zone centre. This type of semiconductor is consequently described as being a direct gap semiconductor. The bandgap is important when considering the optical process of emission or absorption in a semiconductor as it defines the characteristic wavelength of the photon involved. An indirect gap III-V semiconductor has the minimum of the conduction band occurring at a position in k-space away from the zone centre. Optical processes in such materials require phonon interaction to conserve momentum.

The two upper lying valence bands are designated as the heavy hole (HH) and light hole (LH) valence bands according to their dispersion relations. The third valence band, known as the spin-orbit split-off band is split from the other two valence bands by a spin-orbit interaction energy, shown as $\Delta$ in Fig. 1.7(a). All four bands are spin degenerate. Near the zone centre the bands are near parabolic and can be approximated by using an effective mass constant where the effective mass, $m^*$, is defined as:

$$m^* = \frac{\hbar^2}{\left( \frac{d^2 E}{dk^2} \right)}$$

1.2.2 Material Constants for III-V Binary, Ternary and Quaternary Compounds

The majority of the samples studied in this work are multi-layered structures, fabricated using epitaxial growth techniques such as metal organic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE). For further information on growth technologies see (Kelly, 1995). Individual layers in each structure are either binary, ternary and quaternary compounds formed from group III and group V elements. The structures typically consist of a number of layers, with each layer being of a different compound in order to achieve the desired optical and electronic properties for the whole structure. Using only the group III elements; aluminium,
gallium, and indium, and the group V elements; phosphorus and arsenic, it is possible to form a total of six binary compounds: AlP, AlAs, GaP, GaAs, InP, and InAs. Table 1.1 lists the room temperature values of the lattice constant and fundamental bandgap of each of these compounds.

<table>
<thead>
<tr>
<th>Binary</th>
<th>Lattice Constant (Å)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlP</td>
<td>5.451</td>
<td>3.58*</td>
</tr>
<tr>
<td>AlAs</td>
<td>5.660</td>
<td>2.95*</td>
</tr>
<tr>
<td>GaP</td>
<td>5.451</td>
<td>2.74*</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.653</td>
<td>1.42</td>
</tr>
<tr>
<td>InP</td>
<td>5.869</td>
<td>1.35</td>
</tr>
<tr>
<td>InAs</td>
<td>6.058</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 1.1 Room temperature values of lattice constant and bandgap for various III-V binary compounds. Values marked with an * indicate that the bandgap is indirect.

It is possible to form ternary, and even quaternary, alloys from the above binary compounds. Vergard's law allows the material parameters of a particular ternary, with the exception of the bandgap, to be calculated by simple linear interpolation of the material parameters of the two constituent binary alloys. The bandgap of a ternary compound, however, undergoes a certain amount of deviation from the linear interpolation. This deviation, or 'bowing' as it is known, can be accounted for by a bowing constant intrinsic to each particular ternary alloy. A full description of the correct interpolation scheme is given by Krijn (Krijn, 1991) along with the respective bowing constants for most III-V ternary alloys. The extent of the bowing can be seen in the Fig. 1.4. This figure shows the bandgaps and lattice constants for the above listed binary compounds, along with a number of other semiconductor binaries. Binaries with a similar lattice constant, for example GaAs and AlAs, can be grown
pseudomorphically with each other, enabling the bandgap of such a ternary compound to be tailored to the desired energy.

Fig. 1.4 Graph of semiconductor binaries plotted as a function of lattice constant and bandgap. Group IV, group III-V and group II-VI binaries are represented by squares, filled circles and open circles respectively. Full lines represent direct gap ternary alloys and broken lines represent indirect gap ternary alloys.

The temperature dependence of the bandgap of a semiconductor can be expressed by a universal function, after Varshni (Varshni, 1967),

\[
E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T}
\]

Values for the coefficients \(E_g(0), \alpha, \) and \(\beta\) for GaAs, are 1.517 (eV), \(5.5 \times 10^{-4}\) (eV/K), and 225 (K) respectively for GaAs (Lautenschlager, 1987).

1.3 Heterostructures
1.3.1 Heterojunctions and Quantum Wells

A heterojunction is the name given to the interface formed when two different semiconductor materials are brought into contact with one another. With the advent of modern epitaxial growth techniques, such as MBE and MOCVD, it is possible to create atomically abrupt interfaces between different semiconductor materials. At a heterojunction interface, the conduction and valence bands of the structure experience a discontinuity. The nature of this discontinuity has important effects in terms of device application, and consequently has received a great deal of attention. If two semiconductor materials A and B are brought together to form a heterojunction such that the band gap of material B is greater than that of A, the ensuing bandgap discontinuities at the interface are described as $\Delta E_c$ and $\Delta E_v$ for the conduction band and the valence band respectively. This leads to the definitions for the so called conduction band and valence band offsets, $Q_c$ and $Q_v$:

$$Q_c = \frac{\Delta E_c}{(\Delta E_c + \Delta E_v)}$$

$$Q_v = \frac{\Delta E_v}{(\Delta E_c + \Delta E_v)}$$

The conduction and valence band offsets at a heterojunction interface can be determined by the bulk properties of the two materials involved. It has been shown that $Q_c$ and $Q_v$ can be calculated by comparing the materials in terms of their absolute chemical valence band potentials (Van de Walle, 1989).

The real importance of band alignment becomes evident when two heterojunctions are formed adjacent to one another to create a quantum well (QW) (Dingle, 1975). A QW consists of a thin layer of one type of material, sandwiched between two layers of a differing material. The types of QWs that can be formed are shown in Fig. 1.5. The most important type QW in terms of useful application is designated type I. This type of QW has a sandwiched layer (A) of a material with a smaller bandgap than the
bandgap of the two encompassing layers (B) which are described as the barrier layers. In a type I QW, the alignment of the bands at the heterojunction interfaces are such that both the conduction band and valence band of material A form a potential well, effectively confining carriers to this layer of material. In the other two types of QW, this type of confinement is no longer experienced for both the electrons and holes. The remaining two types of QW, shown in Fig. 1.5, are called type IIA (staggered), and type IIB (misaligned). For further descriptions of these types of QW see (Kelly, 1995).

A system can be regarded as a QW when the sandwiched layer is of a thickness typically <30 nm. Below this thickness, carriers in this layer begin to experience quantum confinement effects. This leads to quantisation of the bands in the growth direction. This situation is analogous to a finite square potential well problem. In a type (I) QW, the conduction and valence bands now exist as a number of discrete states within the QW layer, as shown in Fig. 1.6. The levels depicted within the QW represent conduction and valence band states at the zone centre. The energy levels of the confined states within a QW are a function of the effective masses of the carriers involved, and consequently the energy levels of the LH and HH valence bands are no longer degenerate. The arrows in Fig. 1.6 indicate critical point interband transitions that can occur within the QW. Transitions between the $n^{th}$ confined conduction subband to the $n^{th}$ confined heavy hole valence subband are designated as $H_{mn}$, and
similarly transitions to the \( n^{th} \) confined light hole valence subband are described as \( L_{mn} \). For the ideal case of an infinitely deep well, selection rules are such that only transitions occurring between levels with equal sub-band indices are possible i.e. where \( m - n = 0 \). However in real QWs, where the well has a finite depth, this selection rule is relaxed allowing all transitions, where the difference between subband indices is even, \( m - n = 0, 2, 4, \text{ etc.} \) Such transitions are known as 'allowed' transitions. Often these selection rules can be violated, and optical transitions can be observed between confined levels where \( m - n \) is odd. This situation can be a result of a number of factors, such as non-abrupt interfaces of the QW or electric fields in the well polarising the electron and hole wavefunctions. Transitions where \( m - n = \text{ odd} \) are known as 'forbidden' transitions.

![Fig. 1.6 Schematic diagram of a quantum well. Dashed lines represent bound states for electrons in the conduction band and for heavy and light holes in the valence bands. Critical point inter sub-band transitions \( H_{11} \) and \( L_{31} \) are shown by the arrows.](image)

Multiple QWs can be grown in a single structure. If the barrier layers between adjacent QWs are sufficiently thin, the wavefunctions of confined states in the well can penetrate through the barrier region and overlap. Carriers are no longer confined to a single well and are again free to move throughout the structure. The discrete
confined states now broaden into mini-bands. Such a system is called a superlattice (SL).

1.3.2 Strain

The existence of strain in epitaxially grown layers plays an important role in the design and realisation of many semiconductor systems. For example, the presence of strain within the active region of semiconductor laser diodes was originally assumed to have a detrimental effect on device performance. However, Adams (Adams, 1986) demonstrated that by using a strained layer superlattice for the active region of a QW laser, the amount of unwanted Auger recombination and intervalence band absorption, occurring within the device, could be greatly reduced. More recently, O'Reilly has shown that strain can indeed be used to tailor the valence band properties of a particular system (O'Reilly, 1994). The use of strain in such a manner is often referred to as band structure engineering.

Strain is introduced into an epitaxially grown layer when it is grown pseudomorphically on an underlying layer of a differing lattice constant. The epitaxial layer grows dislocation-free under bi-axial stress such that the in-plane lattice constant is now the same as the underlying layer's lattice constant $a$. If growth is assumed to be in the (001) direction, the strain in the layer plane, $\varepsilon_n$, is given as:

$$\varepsilon_n = \varepsilon = \frac{(a_s - a_e)}{a_e}$$  \hspace{1cm} (1.5)

where $a_e$ is the unstressed bulk lattice constant of the epitaxially grown material.

The lattice constant of the epi-layer in the growth direction relaxes in response to the deformation of the in-plane lattice constant. The strain in the growth direction $\varepsilon_z$ is given as:

$$\varepsilon_z = 2 \frac{C_{12}}{C_{11}} \left( 1 - \frac{a_s}{a_e} \right)$$  \hspace{1cm} (1.6)
where $C_{11}$ and $C_{12}$ are the elastic constants for the stressed layer. Values of $C_{11}$ and $C_{12}$ for most III-V binaries can be found in (Krijn, 1991).

The total strain can be resolved into a hydrostatic component, $\varepsilon_{vol}$, and an axial or shear component, $\varepsilon_{ax}$, as:

$$\varepsilon_{vol} = \varepsilon_x + \varepsilon_y + \varepsilon_z$$ (1.7)

$$\varepsilon_{ax} = \varepsilon_z - \varepsilon_x$$ (1.8)

It is possible to grow a strained epitaxial layer until it reaches such a thickness that it becomes energetically favourable to relieve the strain via a dislocation. In such a situation, the critical thickness of the layer is said to have been reached (O’Reilly, 1989). The stability of such systems was first considered by Frank and van der Merwe (Frank, 1949). As a general approximation, the critical thickness of an epitaxial grown layer is reached when the product of its strain and thickness exceeds 200 Å. % (O’Reilly, 1989).

When considering the effects of strain on the band structure of III-V semiconductors, it is convenient to examine the effect of the hydrostatic and axial components separately. The hydrostatic component, which depends on the overall change in the volume of the unit cell, leads to a shift in the average valence and conduction band energies, resulting in a net change in the bulk bandgap. The axial component of the strain causes a splitting of the heavy-hole and light-hole valence bands at the zone centre and leads to an anisotropic band structure.

These two effects can be seen in Fig. 1.7 which gives a schematic representation of the band structure of a direct-gap tetrahedral semiconductor, both unstrained and under bi-axial tensile strain.
An overall reduction in the mean band gap can be seen in the system under tensile strain due to the hydrostatic component of strain, along with a lifting of the valence band degeneracy at the Γ-point due to the axial component of the strain. In the system under tensile strain, the highest lying valence band is now light along the growth direction (z), and heavy in the in-plane direction (x, y).

1.3.3 Modelling of Heterostructures

Much of the work in this thesis involves the examination of optical transitions between confined states in QWs. It is often necessary to qualify and validate the
experimental observations by comparison with a theoretical model. For the type of optical experiments performed in this work, only critical point (CP) transitions in the vicinity of the direct $E_0$ bandgap are observed. Details of the actual model used to calculate confined-states within QWs are given in the relevant chapters. However, additional considerations such as exciton binding energies and the quantum confined Stark effect are discussed here.

**Exciton Binding Energies**

After the absorption of a photon within a semiconductor crystal, instead of a free electron and hole pair being formed, the situation can occur where the electron and hole are bound together via a Coulomb attraction. The bound electron and hole pair is known as an exciton (Wannier, 1937), and displays a number of bound states, analogous to a simple hydrogen atom. In bulk semiconductor, at room temperature, excitons are quickly destroyed as the thermal energy of the particle overcomes the Coulomb force. However, in 2-D systems, excitons can still exist even at room temperature, or in the presence of large electric fields (Glembocki, 1989; Shanabrook, 1987). Hence, for quantum confined systems, exciton binding energies need to be accounted for when comparing theoretically calculated transition energies with those determined experimentally.

In the simplest approximation, the binding energy of an exciton, $E_b$, can be calculated by treating the bound pair of particles as a simple hydrogen atom and substituting both the dielectric constant of the material, and the respective effective masses of the electron and hole (Shinada, 1966). Thus

$$E_b = -R_e \frac{\mu^*}{m_0} \frac{1}{\varepsilon^2 n^2}$$

(1.9)

where $R_e$ is the Rydberg energy of a hydrogen atom (13.6 eV), $\varepsilon$ is the dielectric constant of the semiconductor, $n$ an integer and $\mu^*$ is the reduced mass of the electron and hole pair in the semiconductor, given as:
where $m_e^*$ is the effective mass of an electron, and $m_h^*$ is the effective mass of an HH or LH in the material. The dependence of the reduced mass on the type of hole leads to different binding energies for HH and LH excitons.

Typical values for the reduced mass of an electron and HH pair, and for the dielectric constant of a semiconductor, are $0.06m_o$ and 12.25 respectively. This gives a 3D exciton binding energy of approximately 5meV. For the lowest bound state ($n = 1$) this binding energy has been shown to increase by a factor of four in moving from three dimensions to two (Shinada, 1966). In a realistic quasi-2D system such as a quantum well, we would expect the actual binding energy to be of some value between these two limits. Where it has been necessary to calculate values for the binding energies in QW structures, such as those examined in this work, a fractional dimensionality approach has been used as described by Mathieu (Mathieu, 1992a; Mathieu, 1992b). This analytical approach allows for a realistic approximation to be made, giving a value for the binding energy somewhere between the limits of two and three dimensions.

Quantum Confined Stark Effect.

When an electric field is applied to a bulk semiconductor, absorption can occur below the band edge. This is as a consequence of the conduction and valence band wave functions having evanescent tails that extend into the forbidden gap. Owing to the tilted bands, the wave functions now have a finite amount of overlap, resulting in a broadening of the band edge absorption. This is known as the Franz-Keldysh effect (Franz, 1958; Keldysh, 1958). The shift of the absorption edge in bulk semiconductors is quite limited, as with increasing fields the spatial overlap of the wave functions diminishes. However in quantum confined systems such as QWs, the effect of an electric field along the growth direction can be dramatic.
Fig. 1.8 shows a QW system with an electric field along its growth axis. The applied field leads to a polarisation of the electron and hole wave functions, resulting in a Stark shift of the transition energies. This is known as the quantum confined Stark effect (QCSE) (Miller, 1984). Even with large electric fields, the electron and hole wave functions still retain a finite amount of overlap due to their confinement, and thus a large reduction in the absorption energy can be seen without excessive broadening.

### 1.4 Optical Confinement
The main drive for development of III-V semiconductors over the past few decades has been their use in the production of semiconductor lasers and other related photonic components. Although none of this work is concerned with actual laser devices, all of the samples investigated bear some relevance to the design process of future laser diodes.

Shortly after the advent of the laser in 1958 (Schawlow, 1958), the use of semiconductors as the gain medium of a laser was reported simultaneously by a number of groups in 1962 (Nathan, 1962; Quist, 1962; Holonyak, 1962; Schawlow, 1962). In a semiconductor laser, the active region is formed from the depletion region of a conventional \( p-n \) diode. The optical gain is provided by electron and hole recombination in this depletion region. A Fabry-Pérot (FP) cavity is fabricated from the active region using either cleaved facets or distributed Bragg reflector (DBR) stacks as mirrors, depending on the alignment of the cavity with respect to the growth direction. Fig. 1.9 gives simplified schematic diagrams of both (a) a conventional semiconductor laser, and (b) a vertical cavity surface emitting laser (VCSEL).

![Schematic Diagrams](image)

Fig. 1.9 A schematic diagram of (a) a conventional semiconductor laser diode, and (b) a vertical cavity surface emitting laser (VCSEL).

A conventional edge-emitting semiconductor laser is designed such that the light propagates along the layer situated in the depletion region of the \( p-n \) junction. Two opposite ends of the device are cleaved to create surfaces with sufficiently high
reflectivities to act as mirrors for the FP cavity. The original semiconductor laser, which was fabricated from one material only, was later superseded by the double heterostructure laser (Kroemer, 1963; Alferov, 1963). This design uses a material with a relatively wider bandgap for cladding layers either side of the active region layer. The advantages of such a device are two-fold. Firstly, the wider bandgap cladding layers help confine electrons and holes to the active region where it is desirable for them to recombine. Secondly, the refractive index difference helps confine the optical mode to the active layer thus reducing internal losses. Modern semiconductor laser diodes use QWs embedded in the active region to provide the optical gain.

As the name suggests, a vertical-cavity surface-emitting laser (VCSEL) is constructed, with the FP cavity aligned vertically along the growth direction. Such a device has a number of obvious advantages over conventional edge-emitting devices in terms of the manufacturing process. A large number of such devices can be produced closely packed on a single wafer. In addition, many of the costly processes involved in the fabrication of a conventional laser diode can now be avoided. These include the cleaving of the laser, facet coating, and diode bonding. Furthermore, testing of individual VCSELs can be performed non-intrusively on a wafer scale.

The first VCSEL to be constructed in 1979 (Soda, 1982) used Au, and Au/Zn mirrors to enclose the FP cavity. These had relatively poor reflectivities and consequently a large cavity thickness was required to enable a high enough single pass gain for lasing. Modern VCSELs use distributed Bragg reflector (DBR) stacks to form highly reflective mirrors. The idea for this type of VCSEL design was first described in a patent of different VCSEL designs filed in 1982 (Burnham, 1982), with the first epitaxially grown mirrors being demonstrated in 1983 (Chailertvanitkul, 1983). However, it was not until 1989, when epitaxial technologies had progressed sufficiently to allow Bragg reflectors of high uniformity and reflectivity to be grown, that the first room-temperature operated, low threshold current VCSELs were developed, first pulsed operated (Jewell, 1989) and then continuous wave (Lee, 1989). For comprehensive account of early research the reader is referred to Jewell (Jewell, 1990).
When considering the design of a VCSEL, the structure can be divided into two components, the top and bottom DBRs, and the cavity region. The DBRs are typically highly doped, with the top DBR conventionally being p-doped, and the bottom n-doped. The cavity is usually very short, often being half the intended lasing wavelength, $\lambda_{\text{cav}}$, in length (or a few multiples of it). Consequently, the spacing between the optical modes of the cavity is far greater than one would find in a conventional semiconductor laser. This is very desirable if one wants to produce a laser with only a single mode of operation. As in a conventional QW semiconductor laser, QWs are used to provide the gain in the active region. To increase their effectiveness, the QWs are situated at the anti-nodes of the standing wave in the cavity. The short round-trip gain-path of the cavity requires that the DBRs have extremely high reflectivities, greater than 99% over the required lasing wavelength region.

The DBRs themselves consist of multiple pairs of quarter-wave thick layers with differing refractive indices. A DBR typically has a very high reflectance stop-band over a broad spectral region. Indeed, reflectivities over 99.9% can be anticipated for AlAs/GaAs DBRs with more than 45 pairs of layers (Sale, 1995a). Fig. 1.10 shows the calculated reflectance spectrum for a DBR formed from 20 pairs of layers of AlAs.
and GaAs. Often more complex DBRs are constructed using stepped indices over four layers instead of the usual pair (Sale, 1995b). This is done to reduce the resistance of the DBR. For the correct operation of a VCSEL it is essential that the central wavelength of the DBRs, $\lambda_{DBR}$, and the cavity wavelength, $\lambda_{cav}$, coincide with the lasing wavelength of the QWs at the operating temperature of the VCSEL. For a detailed examination of VCSEL design, see (Geels, 1991; Jewell, 1991; Geels, 1993; Sale, 1995a).

### 1.5 Lower Dimensional Systems

It has long been recognised that there are advantages to be gained by reducing the dimensionality in optical systems. Nowhere is this more apparent than in the field of semiconductor laser diodes, demonstrated by the commercial success of the QW semiconductor laser (dimensionality reduced to two). It is then reasonable to assume that there are additional benefits to be gained by reducing dimensionality further to 1-D or even 0-D. 1-D systems are characterised by the quantum confinement of carriers in two directions, and 0-D systems display confinement in all three directions. The physical structures that display such dimensionality are commonly described as quantum wires, for 1-D systems, and quantum dots (QD) for 0-D systems.

It was first suggested in 1982 that the quantum confinement of the active region of a semiconductor laser in all three directions would significantly improve its performance (Arakawa, 1982). This was later confirmed by theoretical gain and threshold current density calculations carried out for a number of different material systems based on a laser using a box (measuring ~ 100 Å) for the active region. (Asada; 1986). However, it has only been recently that growth technologies have advanced sufficiently to allow quantum dot structures of such a scale to be formed. The main argument for reducing the dimensionality is that the resulting changes in the density of states (DOS) function have beneficial effects on the performance of a semiconductor laser.
Fig. 1.11 shows the change in the DOS function as the dimensionality of a quantum system is reduced. The transition from a 3-D bulk system to a 2-D QW system has the effect of reducing the DOS from a continuous dependence $N(E) \propto E^{1/2}$ to a step-like dependence, and is accounted for by the quantisation of motion of a particle in the QW in one direction (Dingle, 1975). Reducing the dimensionality further to 0-dimensions produces a DOS function with a number of discrete levels as shown in Fig. 1.11(d). A laser with such a DOS function for the active region would be anticipated to have increased temperature stability and a reduced threshold current density.

![Density of states](image)

**Fig 1.11** Density of states $N(E)$ for a (a) 3D, (b) 2D, (c) 1D and (d) 0D system (ideal cases)

The section in this work that examines lower dimensional systems (Chapter 6) is only concerned with quantum dot structures, so no more will be said on the subject of quantum wires. However, for further information on quantum wires the reader is referred to Gossard (Gossard, 1994). There are a number of techniques that can be used to form quantum dot structures. These can crudely be divided into selective
etching techniques, selective overgrowth techniques, and self-forming growth techniques.

Examples of selective etching techniques include electron beam lithography and wet etching techniques (Ils, 1993; Michel, 1997) and cyclotron resonance plasma etching (Vershuren, 1995; Bestwick, 1995). Example of selective overgrowth techniques are selective area overgrowth (Nagamune, 1994), self-limiting overgrowth (Fukui, 1996), and cleaved edge overgrowth (Wegscheider, 1997). It is also possible to form pseudo-QDs using various methods such as forcing local interdiffusion at QW interfaces (Brunner, 1992) and by inducing localised strain modulation with, for example, tungsten stressors (Yater, 1995).

The studies carried out in this work are made on QD islands grown by self-formed growth techniques. The QDs are formed by the relaxation of highly strained epitaxially grown layers, which result in the spatial modulation of the epitaxial layer thickness. This is known as the Stranski-Krastanow (SK) growth mode (Stranski, 1939). The SK growth mode and the type of material used to create self-formed QD structures are discussed in Chapter 6.
1.6 References

Adams A R 1986 *Electron. Lett.* 22 249
Alferov Zh I and Kazarinov R F 1963 Authors Certificate 181737 (U.S.S.R.)
Arakawa Y and Sakaki H 1982 *Appl. Phys. Lett.* 40 939
Brunner K, Bochelmann V, Abstreiter G, Walther M, Böhm G, Tränkle G and
Burnham R, Scifres D R and Streifer W 1982 Author Certificate 4309670 (U.S.)
Jpn. Soc. Apply. Phys., Tokyo
Dingle R 1975 *Festkorperprobleme (Advances in Solid State Physics)* (Pergamon-Vieweg, Braunschweig) 15 21
Franz W 1958 Z. Naturforsch 13 484
Quant. Electron.* 29 2977
Lett.* 9 366
Holonyak N, Jr. and Bevacqua S. F. 1962 *Appl. Phys. Lett.* 1 82
1989 *Electron. Lett.* 25 1123
Florez L T 1990 *Opt. Eng.* 29 1605
Electron.* 27 1332
Keldysh L V 1958 Soviet Physics JETP 34 788
Kroemer H 1963 Proc. IEEE 51 1782
Michel M, Forchel A and Faller F 1997 Appl. Phys. Lett. 70 393
O'Reilly E P 1989 Semicond. Sci. Technol. 4 121
O'Reilly E P and Adams A R 1994 IEEE J. Quant. Electron. 30 366
Sale T E 1995a IEE Proc. -Optoelectron. 142 37
Sale T E 1995b Vertical Cavity Surface Emitting Lasers (Research Studies Press Ltd.)
Schawlow A L and Townes C H 1958 Phys. Rev. 112 1940
Stillman G E and Wolfe C M 1977 See, for example, in Semiconductors and Semimetals (Academic Press, New York) p. 380
Tsu R and Esaki L 1973 Appl. Phys. Lett. 11 562
Varshni Y P 1967 *Physica* 34 149
Wannier G H 1937 *Phys. Rev.* 52 192
CHAPTER 2

Experimental Techniques

2.1 Introduction

This chapter describes the various experimental techniques used for the studies undertaken in this thesis. The main emphasis of the work focuses on the understanding and application of modulation spectroscopy, in the form of photomodulated reflectance (PR) spectroscopy, to a number of semiconductor materials and devices. Additional experimental techniques such as photoluminescence spectroscopy (PL), reflectance spectroscopy (R), and double crystal x-ray diffraction measurements (DCXRD) are used to complement the information provided by PR.

The fundamental purpose of performing PR and PL measurements is to reveal information about the electronic band structure of the material system under study. That is to say, to determine the energies of critical point interband transitions, or in the case of QW or QD systems, the critical point (CP) energies of inter sub-band transitions. There are a number of reasons why these data are desirable. Experimental confirmation of such information validates the growers’ ability to produce samples to the correct specification. In addition, theoretical models of novel systems often require experimental data for verification. Whilst both PR and PL can be used to determine the energies of CP
interband transitions, PR can provide additional information that PL cannot, such as the magnitude of an internal electric field within a sample, and, in the case of quantum confined systems, the energies of higher lying inter sub-band transitions. Of the other experimental techniques performed, reflectance spectroscopy was used for the work on VCSEL structures (Chapters 4 and 5) which, by their nature, have distinct reflectance responses. The reflectance spectra of these structures can be modelled, allowing certain structural information to be determined. DCXRD measurements were performed during the study of a series of tensilely strained MQW structures (Chapter 3). DCXRD measurements allowed additional information to be derived, to that given by PR and PL, by using a novel approach of fitting experimental data with simulated DCXRD spectra.

2.2 Photomodulated Reflectance

2.2.1 Modulation Spectroscopy and Photomodulated Reflectance

Modulation spectroscopy (MS) is the generic term given to a number of techniques where the spectral response of a material is modified by applying a repetitive perturbation. The types of perturbation can include modulating the material’s temperature (thermomodulation) (Matagui, 1968), applying stress (piezomodulation) (Tober, 1988), or applying an electric field (electromodulation) (Pollak, 1981). Under periodic modulation, the changes in optical response are examined as normalised differential changes in either the absorption or reflectance spectrum.

The form of MS used in this work is that of photomodulated reflectance (PR) which itself is a form of electroreflectance (ER). ER spectroscopy is performed by periodically applying an electric field to the sample. Alterations to the surface electric field produce changes in the complex dielectric function, which in turn affects the material’s reflectance response. A number of different methods can be used for the application of an electric field. These include, applying the field directly by forming Schottky barrier type contacts on the material (Aspnes, 1973), placing the sample in the space charge region of
a p-i-n diode (Glembocki, 1990), or placing the sample in a suitable electrolyte (Cardona, 1967). Other forms of ER include electron beam ER (EBER) (Herman, 1990), contactless ER (CER) in which the sample is placed between two capacitor plates (Aigouy, 1997), and photomodulated reflectance (PR) (Rowland, 1998).

PR uses a high intensity light source, usually a laser, to generate electron and hole pairs within a sample, thus requiring the light source photon energy to be greater than the bandgap energy of the material under investigation. These carriers migrate to the surface of the sample, modulating the surface electric field. PR is most effective when there is some degree of internal field already present in the sample that can be modulated.

### 2.2.2 Historical Development of ER Theory

Historically, PR theory was developed in terms of ER, and consequently will be described here in that context.

In 1958, Franz and Keldysh independently developed a theory that describes the effect of an electric field on the absorption profile of an insulating or semiconducting crystal (Franz, 1958; Keldysh, 1958). The effect of a field was shown to shift the absorption edge to a lower energy, or longer wavelength. This was explained as a quantum mechanical effect of electrons, in the presence of a field, being able to tunnel across the band gap due to the overlap of the evanescent tails of the electron and hole wavefunctions (Stillman, 1977). Further theoretical investigation confirmed the initial proposal of Franz and Keldysh, demonstrating that the absorption profile has an exponential tail off below the bandgap, as well as displaying oscillations in its magnitude at energies above the gap (Bulyanitsa, 1960; Callaway, 1962; Tharmalingham, 1963). These theoretical predictions were also demonstrated experimentally (Frova, 1965; Shacklee, 1965).

The electroreflectance effect was first reported in 1964 (Seraphin, 1964), with the effect of an electric field being described by its effect on the refractive index of a medium
(Seraphin, 1965), thus relating the Franz-Keldysh effect to reflection phenomena. Earlier theoretical calculations for the field-dependent optical absorption for direct transitions (Callaway, 1962; Tharmalingham, 1963) were extended to include arbitrary orientations of the electric field in an anisotropic solid (Aspnes, 1966). Following this, Aspnes calculated the effect of an electric field on the dielectric function of a material (Aspnes, 1967), and along with co-workers, Handler and Blosser, described the effect an electric field, in the non degenerate weak field approximation, as an Airy function convolution of the zero field dielectric function (Aspnes, 1968).

In an experimental observation of PR from germanium (Aspnes, 1970a), PR signals were seen to vanish for zero surface fields, indicating that for moderate light levels PR is due solely to ER. Aspnes later provided an asymptotic approximation to the convolution integral, describing the imaginary part of the dielectric function in the weak field limit with finite lifetime broadening (Aspnes, 1970b). In this approximation, the strength of the ER signal can be seen to scale quadratically with the magnitude of the field. This leads to a description of ER that shows that electric field modulation results in spectra that are approximately proportional to the third derivative with respect to photon energy of the unperturbed dielectric function.

### 2.2.3 Theory of Photomodulated Reflectance

**The optical absorption process**

This section describes, on a conceptual level, how optical measurements relate to the electronic structure of a solid. The absorption of a photon by the creation of an electron and hole pair is the fundamental process linking the band structure of a solid to its optical properties. This link is demonstrated by first considering the probability of an individual absorption process. The macroscopic optical properties are then related to the sum of all such processes at a given photon energy.
A monochromatic flux of photons entering an absorbing medium in a plane at $x = 0$ with an energy density $I(0)$ is reduced to $I(d)$ after penetrating to the plane at $x = d$ according to:

$$I(d) = I(0)e^{-\alpha d}$$ (2.1)

where

$$\alpha = \frac{\omega}{nc} \varepsilon_2(\omega)$$ (2.2)

is the absorption coefficient of the medium, and $\varepsilon_2$ is the imaginary part of the dielectric function

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon(\omega)$$ (2.3)

which describes the optical properties of the medium at all photon energies $E = h\omega$. The real and imaginary parts of this dielectric function are connected to the optical constants, $n$ and $k$, of the medium by:

$$\varepsilon_1 = n^2 - k^2 \quad \varepsilon_2 = 2nk$$ (2.4a,b)

This definition of the absorption process neglects losses due to scattering, etc. such that the absorption is solely caused by electronic transitions. Eqns. (2.1) and (2.2) show that the macroscopic quantity most related to the absorption process is that of $\varepsilon_2$, the imaginary part of the dielectric function.

The probability of a single photon absorption process can be described as follows, after Seraphin (Seraphin, 1972a):
The electromagnetic field of the incident wave stimulates the transition of an electron from an initial state with an energy $E_i$ and wave vector $k$ into a final state of energy $E_f$ and wave vector $k'$. When the electric field of frequency $\omega$ and polarisation is described as a time-dependent perturbation operator in the Hamiltonian of the system, the probability of finding the electron in the excited state is given by the matrix element of the perturbation. Per unit time, the number of transitions is:

$$\frac{dN}{dt} \sim |e \cdot M_{yt}|^2 \cdot \delta(E_f - E_i - \hbar \omega)$$

(2.5)

where $e.M_{yt}$ is the matrix element of the perturbing light wave with respect to the wave function of the initial and final states. The delta function stipulates that no transitions can occur unless the photon energy matches the energy difference between the initial and final states. Assuming that the creation of an electron and hole pair has no effect on the electronic states of the crystal, $E_i$ and $E_f$ will have the same values before and after the absorption process. The coupling of the polarisation vector, $e$, into the wavefunctions of the initial and final states imposes selection rules on the transition such that under certain polarisations of incident light some transitions are forbidden.

The conservation of momentum law imposes the condition that an electronic transition can only occur if:

$$k - k' + q = 0$$

(2.6)

where $q$ is the momentum of the absorbed photon. Since in the optical range this momentum is always small on the scale of the first Brillouin zone and therefore small compared to $k$ and $k'$ it is usually ignored. In this approximation, absorption can only occur between states that are located vertically above one another in the conventional $(E, k)$ diagram of the band structure. This is known as a direct transition.
The Joint Density-of-States Function and Critical Points

The connection between $\varepsilon_2$ and band structure parameters is established by assuming that the absorption is the sum of all the possible transitions between electronic states of the same $k$-vector and separated by the energy difference $E_f - E_i = \Delta E = \hbar \omega$.

$$\varepsilon_2(\omega) \sim \int_{BZ} d^3k \frac{2}{(2\pi)^3} |e \cdot M_{ik}|^2 \delta(\Delta E - \hbar \omega) \quad (2.7)$$

By assuming that the matrix element is the same for all pairs of states located vertically above each other, regardless of their location in the Brillouin zone, the joint density-of-states (JDOS) function, $J(\Delta E)$, can be defined as:

$$J(\Delta E) = \int_{BZ} d^3k \frac{2}{(2\pi)^3} \delta(\Delta E - \hbar \omega) \quad (2.8)$$

The JDOS function represents the simple counting of states within the Brillouin zone for which $E_f - E_i = \hbar \omega$. Thus

$$\varepsilon_2(\omega) \sim |e \cdot M_{ik}|^2 \cdot J(\Delta E) \quad (2.9)$$

Eqn. (2.8) can be transformed from a volume integral into a surface integral.

$$J(\Delta E) = \frac{2}{(2\pi)^3} \int_{\Delta E = \text{const}} dS \frac{dS}{|\nabla_k(\Delta E)|} \quad (2.10)$$

where $dS$ is the surface element on the isoenergetic surface $\Delta E = \text{const}$, and $\nabla_k(\Delta E)$ is the gradient of the separation of the initial and final states with respect to $k$. At certain points in $k$-space, the JDOS function experiences a singularity. This occurs whenever the
gradient, \( \nabla_k(\Delta E) \), equals zero. These singularities are known as critical points (CP) in the band structure and have considerable influence on the spectral profile of \( \varepsilon_2 \).

The JDOS function therefore has singularities wherever (Cardona, 1967)

\[
\nabla_k (E_f - E_i) = 0 \tag{2.11}
\]

This equation is satisfied at points of high symmetry in the Brillouin zone (\( \Gamma, X, \) and \( L \)) where \( \nabla_k(E_f) = \nabla_k(E_i) = 0 \). CPs can also be found at points where \( \nabla_k(E_f) \) and \( \nabla_k(E_i) \) do not equal zero, but eqn. (2.11) is still satisfied.

The type of CP depends upon the signs of the quadratic terms in the expansion of \( (E_f - E_i) \) as a function of \( k \).

\[
(E_f - E_i) = \frac{\hbar^2}{2m^*} \left[ \frac{k^2_x}{\mu_x^*} + \frac{k^2_y}{\mu_y^*} + \frac{k^2_z}{\mu_z^*} \right] + E_g \tag{2.12}
\]

There are four types of possible critical points for which eqn. (2.12) is satisfied, denoted \( M_0, M_1, M_2 \) and \( M_3 \) according as to whether all three, two, one, or none of the effective masses \( (\mu_x^*, \mu_y^* \) and \( \mu_z^*) \) are positive in eqn. (2.12). Through the course of this work, only interband transitions from \( M_0 \) type CPs at the Brillouin zone centre (\( \Gamma \)-point) are examined.

In the next section, the reflectance spectrum of a medium is shown to be a function of its complex dielectric function. Consequently, features can be seen in the reflectance spectrum that are due to CP structure in the imaginary part of the complex dielectric function, \( \varepsilon_2 \). This is demonstrated by Fig. 2.1, which shows a conventional reflectance spectrum of GaAs, along with the associated ER spectrum (Phillip, 1963). One of the key features of modulation reflectance techniques is that they suppress the broad and uninteresting background structure observed in conventional reflectance measurements,
and highlight structure due to CP interband transitions. Such transitions appear in modulated reflectance spectra as features with differential-like lineshapes.

![Fig. 2.1 Conventional reflectance and electro-reflectance spectra of GaAs at 300°K. (Phillip, 1963).](image)

**Photomodulated Reflectance of bulk materials**

This section describes how features in the normalised differential reflectance ($\Delta R/R$) spectrum, produced by PR, are related to modulation induced changes in the complex dielectric function $\varepsilon$. Consider the reflection of an electro-magnetic wave from the interface between two different, but homogenous media, in this case air and a dielectric material with a complex dielectric function $\varepsilon$. The reflection coefficient, $R$, is the ratio of intensities of the reflected, $I_{\text{ref}}$, and incident, $I_{\text{inc}}$, light:

$$R = \frac{I_{\text{ref}}}{I_{\text{inc}}}$$

(2.13)
Fresnel's reflection equation applies and for normal incidence light \( R \) has the form:

\[
R = \frac{\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2} - \left(2\varepsilon_1 + 2\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2}\right)^{1/2} + 1}{\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2} + \left(2\varepsilon_1 + 2\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2}\right)^{1/2} + 1}
\]

(2.14)

The formal expression for PR arises from total differentiation of eqn. (2.14) with respect to \( \varepsilon_1 \) and \( \varepsilon_2 \). This gives an expression for the normalised differential reflection:

\[
\frac{\Delta R}{R} = \text{Re}[(\alpha + i\beta)(\Delta\varepsilon_1 + \Delta\varepsilon_2)]
\]

(2.15)

where \( \alpha \) and \( \beta \), called the Séraphin coefficients, are functions of \( R \) and \( \varepsilon \) (Séraphin, 1966), given by:

\[
\alpha(E) = \frac{1}{R(E)} \left( \frac{\partial R(E)}{\partial \varepsilon_1(E)} \right)
\]

(2.16a)

\[
\beta(E) = \frac{1}{R(E)} \left( \frac{\partial R(E)}{\partial \varepsilon_2(E)} \right)
\]

(2.16b)

where \( E \) is the photon energy and \( \Delta\varepsilon_1 \) and \( \Delta\varepsilon_2 \) are the modulation induced changes in \( \varepsilon_1 \) and \( \varepsilon_2 \).

The Séraphin coefficients can be expressed in an implicit form for normal incidence light, and for convenience are expressed here in terms of the optical constants, \( n \) and \( k \) (Séraphin, 1972b).
\[ \alpha = \frac{2\gamma}{(\gamma^2 + \delta^2)} \]  
(2.17a)

\[ \beta = \frac{2\delta}{(\gamma^2 + \delta^2)} \]  
(2.17b)

\[ \gamma = \left(\frac{n}{n_0}\right)(n^2 - 3k^2 - n_0^2) \]  
(2.17c)

\[ \delta = \left(\frac{k}{n_0}\right)(3n^2 - k^2 - n_0^2) \]  
(2.17d)

where \( n_0 \) is the refractive index of the nonabsorbing medium of incidence, in this case air.

It is evident from these equations that the Seraphin coefficient for the imaginary part of the dielectric function, \( \beta \), is approximately zero near and below the fundamental absorption edge for bulk materials. Fischer and Seraphin have also expressed \( \alpha \) and \( \beta \) in terms of \( n \) and \( k \) for non-normal angles of incidence (Fischer, 1967).

Fig. 2.2 Seraphin coefficients \( \alpha \) and \( \beta \) for GaAs in the energy range of 0 to 5 eV, (Seraphin, 1966).
Fig. 2.2 shows the Seraphin coefficient for bulk GaAs in the energy range of 0eV to 5eV (Seraphin, 1966).

Field Regimes

To understand the lineshapes observed in ER and PR, it is necessary to consider the effect of the perturbing electric field on the dielectric function.

Schrödinger’s equation for a single electron is defined as

\[
\left( -\frac{\hbar^2}{2m_e} \nabla^2 + U(r) \right) \Psi = E\Psi
\]

(2.18)

where \( m_e \) is the mass of the electron, \( U(r) \) a potential, \( \Psi \) the wavefunction of the electron, and \( E \) the eigenstates of the equation. In an unperturbed periodic lattice, where the potential \( U(r) \) has the periodicity of the lattice, solutions to this equation have the form of a product of a plane wave and a function with the periodicity of the lattice, as described by Bloch’s theorem (Ashcroft, 1976),

\[
\Psi_{nk}(r) = e^{ik\cdot r} u_{nk}(r)
\]

(2.19)

The effect of the perturbing electric field can be considered as two separate mechanisms acting upon the unperturbed Bloch functions. The first is an interband mechanism that acts upon the periodic part, \( U_{nk}(r) \), of the Bloch functions. The second is an intraband, or one-band acceleration mechanism and is a result of the field-induced loss of translational invariance of the Hamiltonian in the field direction. This modifies the long range correlation part, \( e^{ik\cdot r} \), of the unperturbed Bloch functions.
ER and PR spectra are obtained in the range of externally applied fields where both interband and intraband mechanisms can be treated adequately by first-order perturbation theory. Perturbation theory implies the existence of two energies per mechanism: the characteristic energy of the perturbation, and a characteristic energy of the system.

For the interband mechanism the characteristic energy of the perturbation is $eF ao$, where $e$ is the charge on an electron, $F$ is the magnitude of the electric field, and $ao$ the lattice constant of the material. This represents the potential drop across the unit cell. The characteristic system energy is $Eg$, the energy separation between the pair of bands under consideration. Perturbation theory can be applied here whenever $eF ao << Eg$.

For the intraband mechanism, the characteristic energy of the perturbation is the electro-optic energy, $\hbar \Omega$. This represents the energy gained by a particle of mass $\mu^*$ when accelerated in a uniform field of force, $eF$, and is defined as

$$\hbar \Omega = \left( \frac{e^2 F^2 \hbar^2}{8 \mu^*} \right)^{1/3}$$

(2.20)

where $\mu^*$ is the reduced mass defined by eqn. (1.10). The characteristic system energy for the intraband mechanism is the phenomenological broadening, $\Gamma$, of the CP interband transition (Aspnes, 1973a). Perturbation theory can only be applied here when $\hbar \Omega << \Gamma$.

The relative magnitudes of the two pairs of characteristic energies lead to three ranges of ER and PR. These are summarised in Table 2.1.

For typical values $F = 100$ kV/cm, $a_0 = 6 \, \text{Å}$, and $\mu^* = 0.1 m_e$, the perturbation energy for the interband mechanism is calculated as $eF ao = 6 \, \text{meV}$, which compares to typical interband energies of the order of several eV. The electro-optic energy, $\hbar \Omega$, is calculated to be $21.2 \, \text{meV}$, which compares to typical values of the broadening parameter of 0.1 to 100 meV. From these values it is evident that the intraband mechanism determines the
low-field limit. In the low field limit, where $|\hbar \Omega| \leq \Gamma/3$, the lineshapes of the spectral features scale quadratically with the field size and are related to the third derivative of the unperturbed dielectric function. In the intermediate field limit, where $|\hbar \Omega| \geq \Gamma$, spectra are characterised by Franz-Keldysh oscillations (FKO) above the fundamental absorption edge. The high field limit occurs whenever $eFao \sim E_g$, and corresponds to a breakdown of the selection rules and Stark shifts of the energy bands.

<table>
<thead>
<tr>
<th>Range</th>
<th>Perturbation Energy versus System Energy</th>
<th>Identifying spectral characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>$</td>
<td>\hbar \Omega</td>
</tr>
<tr>
<td>Intermediate</td>
<td>$eFao \sim E_g$</td>
<td>Selection rules modified</td>
</tr>
<tr>
<td>(Airy convolution) (Franz-Keldysh)</td>
<td>$eFao \ll E_g$</td>
<td>Subsidiary (Franz-Keldysh) oscillations</td>
</tr>
<tr>
<td>low</td>
<td>$</td>
<td>\hbar \Omega</td>
</tr>
</tbody>
</table>

Table 2.1 Definition and experimental signatures of the three ranges of ER and PR spectra in terms of the relative strengths of the perturbation and characteristic system energies for both intraband and interband mechanisms.

The derivations of the following results are beyond the scope of the thesis. However, the main concepts will be listed as an aid to understanding the modelling of PR spectra. The results of the perturbation-induced change in the dielectric function are given for the two limiting cases of; the intermediate field regime, where $\Delta \varepsilon$ is formed from Airy functions and their derivatives, and the low field regime, where $\Delta \varepsilon$ is related to the third derivative of the unperturbed dielectric function, as given by Aspnes (Aspnes, 1980).
The Intermediate-Field Regime: The Franz-Keldysh Result

The Franz-Keldysh result for the effect of an electric field on the dielectric function can be calculated by a simple stationary state approach solved in the effective mass approximation as demonstrated by Tharmalingham (Tharmalingham, 1963) for an isotropic $M_0$ critical point.

A perturbation term is added to the one electron Hamiltonian given by eqn. (2.18). Solving this equation gives an expression for the wavefunction that has an Airy function component in the field direction. The imaginary part of the dielectric function, $\varepsilon_2$, under the influence of an electric field, can then be derived from this result, with the real part, $\varepsilon_1$, being calculated from $\varepsilon_2$ using the Kramers-Kronig transformation:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{[\omega']^2 - \omega^2} d\omega'$$ (2.21)

The result is expressed as the difference between the finite field and zero field limits and is given in terms of two functions $F(\eta)$ and $G(\eta)$ (Aspnes, 1966):

$$\Delta \varepsilon(E, F') = \frac{2e^2 \hbar^2}{m^2 E^2} \left| e M_{cv} \right|^2 \left( \frac{2\mu^*}{\hbar^2} \right)^{3/2} \left( \frac{\mu}{\hbar} \right)^{1/2} [G(\eta) + iF(\eta)]$$ (2.22)

where $M_{cv}$ is the momentum matrix element, and $\mu \theta$ is related to the electro-optic energy, $\hbar \Omega$, given by eqn. (2.20), as $(\mu \theta)^3 = 4(\hbar \Omega)^3$. The two functions $F(\eta)$ and $G(\eta)$ are defined as
\[ F(\eta) = \pi [Ai''(\eta) - \eta Ai''(\eta)] - \sqrt{-\eta} u(-\eta) \]  
\[ G(\eta) = \pi [Ai'(\eta)Bi'(\eta) - \eta Ai(\eta)Bi(\eta)] + \sqrt{\eta} u(-\eta) \]

where \( u(x) \) is the unit step function, \( Ai \) and \( Bi \) are Airy functions as defined by Aspnes (Aspnes, 1966), and \( Ai' \) and \( Bi' \) are their first differentials with respect to \( \eta \), and

\[ \eta = \frac{(E_s - E)}{\hbar \theta} \]

A consequence of eqn. (2.22) is the presence of Franz Keldysh oscillations (FKO) observed in PR spectra at energies above that of the CP transition. The period of these oscillations is a function of the electro-optic energy, and consequently is related to the size of the electric field, \( F \). The electric field \( F \) here simply refers to the largest field within the sample. This is an important fact that allows the size of any internal electric field within a sample to be determined as it will always be several orders of magnitude bigger than the size of the perturbing electric field used for modulation. In cases where the interband reduced mass is known, the magnitude of the internal electric field can be calculated by the graphical analysis of FKO's (Hughes, 1995) or by fitting the PR lineshape with Airy functions (Hall, 1997). For a full review of FKO analysis the reader is referred to (Shen, 1995).

The Low-Field Regime

The second important result follows from more fundamental derivations based on Bloch wavefunctions (Callaway, 1963; Aspnes 1968; Enderlein 1967). The result represents the effect of an electric field on the dielectric function as a convolution integral of an Airy function. It is possible to express this result in terms of a general energy band structure \( E_{cv}(k) \) as
\[ \Delta \varepsilon^\parallel (E, \Gamma, F) \equiv \frac{4 \pi e^2 \hbar^2 M^i_{vc} M^j_{cv}}{m^2 E^2} \left( \frac{2}{(2\pi)^3} \right) \int_{BZ} d^3k \int_0^\infty dse^{-Ts} \times \exp \left[ i(E - E_{cv}(k))s \right] \exp \left[ -\frac{i\hbar \Omega^3 s^3}{3} \right] - 1 \]  

(2.26)

This result is based on the assumption that the momentum matrix elements are independent of \( k \), and that the energy bands are locally parabolic. If the energy bands are assumed to be completely parabolic, eqn. (2.26) can be expressed in a closed form and the Franz-Keldysh expression given by eqn. (2.22) can be obtained.

The importance of this result can be seen when considering the limiting case of large lifetime broadening. It has been shown (Aspnes, 1970; Aspnes, 1972) that for the experimental situation where |\( \delta \Omega \) < \( \Gamma/3 \), eqn. (2.26) can be integrated to reveal the result for the low field limit,

\[ \Delta \varepsilon^\parallel (E, \Gamma, F) \equiv \frac{8 \pi e^2 \hbar^2 M^i_{vc} M^j_{cv}}{m^2 E^2} \left( \frac{2}{(2\pi)^3} \right) \int_{BZ} d^3k \frac{(\hbar \Omega)^3}{(E_{cv}(k) - E - i\Gamma)^4} \]  

(2.27a)

\[ \equiv \frac{(\hbar \Omega)^3}{3E^2} \frac{\partial^3}{\partial E^3} \left( E^2 \varepsilon^\parallel (\Gamma, E) \right) \]  

(2.27b)

Two important points are demonstrated by this result. Firstly, in the low field limit, an invariant lineshape is observed which scales quadratically with the applied field. Secondly, the field-induced change in the dielectric function, \( \Delta \varepsilon \), has a third derivative relationship with the unperturbed dielectric function \( \varepsilon \).
The experimentally measured PR signal, $\Delta R/R$ can be related to eqn. (2.26) by the following expression (Aspnes, 1973a)

$$\frac{\Delta R}{R} = \text{Re} \left[ C_s C_{ex} C_{in} e^i e^j \Delta \varepsilon^{ij} \right]$$ \hspace{1cm} (2.28)

where $e^i, e^j$ represent Cartesian components of the unit polarization vector, $\varepsilon$. The factor $C_s = \alpha + i\beta$ gives the Seraphin coefficients. $C_{ex}$ represents the electron-hole Coulomb interaction, and $C_{in}$ represents spatial inhomogeneities in the perturbing field.

### Photomodulated Reflectance of Microstructures

For bulk materials, in the limiting case of the low field regime, the change in the dielectric function, $\Delta \varepsilon$, due to an applied electric field, is related to the third derivative with respect to energy of the unperturbed dielectric function. However, for bound states such as excitons, impurities and quantum levels in an isolated QW, the lineshape of $\Delta \varepsilon$ has a first derivative nature. A derivation of $\Delta \varepsilon$ for an excitonic transition is given by Glembocki (Glembocki, 1992) and can be represented in a compact form as (Shanabrook, 1987):

$$\Delta \varepsilon \approx \left[ \frac{\partial \varepsilon}{\partial l} \frac{\partial l}{\partial F} + \frac{\partial \varepsilon}{\partial E_g} \frac{\partial E_g}{\partial F} + \frac{\partial \varepsilon}{\partial \Gamma} \frac{\partial \Gamma}{\partial F} \right] \Delta F$$ \hspace{1cm} (2.29)

where $E_g$ is the excitonic band gap, $\Gamma$ is a phenomenological broadening parameter, and $I$ is the integrated intensity of the excitonic transition. This representation of $\Delta \varepsilon$ is described as a first differential lineshape model (FDLM).
Chapter 2: Experimental Techniques

For MQW systems, interference effects between light reflected from different layers of the structure can complicate spectra and in some cases lead to additional, spurious features. In MQW systems, it has been shown (Shields, 1991) that changes in both the real and imaginary parts of the dielectric function can become important. It is also important to point out that for super-lattice systems, where the electron and hole wavefunctions overlap into adjacent QWs, the ER / PR lineshapes resumes a third derivative nature.

2.2.4 Lineshape Models

The lineshape modelling of PR data an essential part of the data analysis and allows the energies of CP transitions to be determined. The lineshape most commonly used to model both bulk CP transitions and confined-state QW transitions is that of Aspnes’s third derivative functional form TDFF (Aspnes, 1973b). If the band structure in the vicinity of a critical point is replaced with simple parabolic model, eqn. (2.27b) becomes

\[
\Delta \varepsilon^\theta (E, \Gamma, F) \equiv (\hbar \theta)^3 \frac{A}{(E - E_g + i\Gamma)^n}
\]

where \(A\) is an amplitude term, and the exponent \(n\) depends upon the dimensionality of the critical point (Aspnes, 1972). For a three dimensional CP, \(n = 2.5\) is used, for a two dimensional CP, \(n = 3\), and for bound excitonic states, \(n = 2\) is used.

Eqn. (2.30) can be incorporated into eqn. (2.28) if the terms \(C_{ex}\) and \(C_{in}\) in eqn. (2.28) are assumed to be constant. Conventionally the Séraphin coefficients are assumed to be energy independent and are represented by a phase term \(\phi\). This allows experimental spectra to be modelled as:
\[
\frac{\Delta R}{R} = \text{Re} \left[ \frac{Ce^{i\phi}}{(E - E_g + i\Gamma)^n} \right]
\]  
\hspace{1cm} (2.31)

where \( C \) is a constant.

When using the FDLM, the imaginary part of the dielectric function, \( \varepsilon_2 \), is assumed to have either a Lorentzian form (Shanabrook, 1987) or a Gaussian form (Shen, 1987), depending upon temperature and other scattering processes (Tang, 1989). The Lorentzian form for the dielectric function is suitable for low temperatures, whereas the Gaussian form is more appropriate for room temperature measurements. However, where the FDLM is used in this work, the Lorentzian form of \( \varepsilon_2 \) is used for simplicity as it permits a reduction in the number of first derivatives needed. Thus the complex Lorentzian form of the dielectric function is taken as

\[
\varepsilon(E) \approx \frac{I}{E - E_g - i\Gamma} = I \left( \frac{(E - E_g)^2 + i\Gamma}{(E - E_g)^2 + \Gamma^2} \right)
\]  
\hspace{1cm} (2.32)

In this special case, the following first derivatives are algebraically equivalent

\[
\frac{\partial \varepsilon_1}{\partial E_g} = \frac{\partial \varepsilon_2}{\partial \Gamma} \hspace{1cm} \frac{\partial \varepsilon_2}{\partial E_g} = -\frac{\partial \varepsilon_1}{\partial \Gamma}
\]  
\hspace{1cm} (2.33a, 2.33b)

For allowed QW transitions, the main contributions to the lineshape of \( \Delta \varepsilon \) are due to changes in the energy of the transition (Miller, 1984). However, for forbidden transitions, the main contribution to \( \Delta \varepsilon \) is due to the changes in the oscillator strength (Tang, 1991). This is a consequence of the modulating electric field allowing the selection rules to be relaxed. It is worth noting that the FDLM given by eqns. (2.29) and (2.32) used to model an allowed QW transition is algebraically equivalent to a TDFF, given by eqn. (2.31), suitable for an exciton \((n = 2)\).
Fig. 2.3 shows a comparison between the two fitting models described by eqns. (2.29) and (2.32) (FDLM), and by eqn. (2.31) (TDFF) used to fit a QW excitonic feature in the PR spectrum of a GaAs/Ga$_x$Al$_{1-x}$As MQW. It has been shown that it is interband excitonic transitions, rather than band to band transitions that are observed in the PR spectra of QWs (Shanabrook, 1987). However, as demonstrated in Fig. 2.3, it is still possible to fit the lineshapes of QW transitions at room temperature with TDFFs (with exponent $n = 3$). This is because although the TDFF is physically inappropriate to describe QW excitonic features in PR spectra, it mimics the first derivative of a dielectric function that has a Gaussian absorption profile (Shanabrook, 1987).

![Fig. 2.3 A comparison between the PR spectrum of a GaAs/Al$_x$Ga$_{1-x}$As MQW observed at 150K (dotted) and fits to the data using either eqns. (2.29) and (2.32), for a FDLM (dashed), or eqn. (2.31) for a TDFF ($n = 3$) of a 2-D CP (solid). (Shanabrook, 1987).]

2.2.5 Experimental Apparatus for PR Experiments

Here, the experimental apparatus used to acquire PR measurements is described. Two alternative arrangements were used, depending upon the desired angle of incidence of the incident probe beam. One arrangement allows the experimental angle of incidence to be varied between angles of $25^0 - 75^0$. A schematic for this arrangement is shown in Fig. 2.4a. The alternative arrangement allows PR measurements to be taken at normal
incidence to the sample’s surface, and is depicted in Fig. 2.4b. The samples investigated were mounted on either a rotating sample stage or, in the case of low temperature experiments, inside a cryostat.
Chapter 2: Experimental Techniques

Fig. 2.4a PR experimental arrangement for variable angle of incidence.

Fig. 2.4b PR experimental arrangement for measurements at normal incidence.
A 100W tungsten-halogen bulb provided a white light source for the incident probe beam. This was dispersed through a 0.5m Spex 1870 monochromator which has a 600 lines/mm grating blazed at 1μm. Typical slit widths used ranged from 200μm to 800μm, with an image height of 2mm. The probe light was focused onto the sample using two lenses, with focal lengths of 150mm, such that the incident light passed between the two lenses as a parallel beam. This enabled the incident beam to be manipulated by optical components placed between the two lenses such as an optical polariser or beam splitter.

The probe beam, once reflected off the sample, was refocused onto a detector using a single lens of focal length 60mm. The detector used was an InGaAs photodiode (A+G FD1000WX) which has a working spectral response range of 700nm – 1800nm. Fig. 2.5 shows a graph of the InGaAs detector and system response. A coloured glass high pass filter (>640nm) was used in front of the detector to reduce the amount of unwanted diffuse laser light from reaching it. For the modulating light source, a 2mW HeNe laser (632.8nm) was used which was mechanically chopped at the appropriate frequency. For certain experiments neutral density filters were used to reduce the laser’s intensity as required.

Fig. 2.5 Spectral response of system and InGaAs detector.
The signal received directly by the detector comprises two components. One is a d.c. component, \( I(\lambda)R(\lambda) \), originating from the reflected probe beam. The second component, \( I(\lambda)\Delta R(\lambda) \), is much weaker and a.c., and arises from the change in reflectance due to the periodic modulation of the sample’s surface electric field. The experimental system response \( I(\lambda) \) represents the spectral response of the detector combined with the wavelength dependence of the intensity of the light source. For the acquisition of the normalised differential reflectance, defined as \( \Delta R/R \), both the a.c. and d.c. components of the signal are recorded simultaneously. The \( \Delta R/R \) spectrum is calculated by the numerical division of the two signals to eliminate the \( I(\lambda) \) term. It is often necessary to remove a d.c. offset from the \( I(\lambda)\Delta R(\lambda) \) component prior to division. This offset is mainly a result of photoluminescence (PL) from the sample, also being modulated at the same frequency as the modulation source, the laser. Consequently, the PL is detected as part of the a.c. component of the signal.

A P.C. was used for controlling the spectrometer and for acquiring both the d.c. and a.c. detected signals. The d.c. output from the detector, \( I(\lambda)R(\lambda) \), was measured using a digital multimeter (Keithley 196) which communicated the information to the P.C. using a conventional RS232 interface. The a.c. component of the signal, \( I(\lambda)\Delta R(\lambda) \), was extracted using a lock-in amplifier (EG+G 5110) locked at the frequency of the modulating laser, and then sent to the P.C. via an additional digital multimeter.

For experiments taken at normal incidence, the reflected probe beam was diverted to the detector using a plate beam splitter (Melles Griot, R/T=50% at 850nm), as depicted in Fig. 2.4b. For experiments using selectively polarised probe light, an IR polariser (Meadowlark optics IR-1800) was placed between the two lenses prior to the beam splitter. For reduced-temperature experiments (77K - 300K), two types of cryostat were used. The first was a cold-finger liquid nitrogen cryostat with a single pure silica window. This cryostat was used for static temperature measurements at ~80K. As a consequence of this cryostat having only a single window, measurements were performed at, or near to normal incidence. The second cryostat used was a nitrogen exchange gas cryostat.
(Oxford Instruments DN704) with synthetic sapphire widows used in conjunction with a temperature controller (Oxford Instruments DTC2), and allowed the experimental temperature to be set in the range of 77K - 300K. Both types of cryostat were evacuated using a two stage rotary / diffusion pump system to attain a vacuum of $10^{-5}$ Torr.

As mentioned previously, the detected AR signal also contains a component due to the PL emitted by the sample. The presence of PL can cause problems for a number of reasons. The magnitude of the PL signal can be up to several orders of magnitude larger than that of the PR. Such a large PL signal prevents the sensitivity setting of the lock-in amplifier being set on a scale suitable for the size of the PR signal. In addition, owing to the large difference in sizes of the PL and PR signals, small fluctuations in the strength of the PL can actually be larger than the size of the PR signal itself, effectively masking it. These fluctuations in PL can arise from several effects such as slight temperature variations or variations in the laser intensity. One method of reducing the size of the PL signal is to simply reduce the power of the laser.

To acquire the AR signal, the experimental phase of the lock-in amplifier was initially optimised with respect to the PL signal. For simple structures, the maximum PR signal occurs at roughly the same optimum setting of the lock-in amplifier. However, for some experiments, measurements were made with the phase shifted by $90^\circ$ with respect to the PL, i.e. in quadrature. This became useful when examining more complicated multi-layered structures. Such structures often show some form of quadrature PR response and although the size of this signal is usually much weaker than the PR signal taken in phase with the PL, the overall signal to noise ratio can improve due to the reduction in PL. Other methods can be used to reduce the effect of the detected PL signal, such as front-end compensation (Yan, 1994) where a second a.c. signal, derived from the modulation source reference signal, is amplified and phase shifted in order to cancel out the signal of the PL. It is also possible to modulate both the probe beam and the pump beam in a technique known as double modulation (Ghosh, 1995). The pump and probe beams are modulated at differing frequencies, allowing the PR signal to be detected at the sum or
difference frequency of the two. Consequently the PL is no longer modulated at the detecting frequency of the experiment and, in principle, ceases to be a problem.

When both the $\Delta R$ and $R$ spectra have been recorded, any d.c. offset is subtracted from $\Delta R$ before the two spectra are divided to obtain $\Delta R/R$. The $\Delta R/R$ data are subsequently converted to an energy scale (in eV) before any line shape fitting is undertaken.

The line shapes of the experimental spectra in this work were fitted using mathematical models fitting software developed at Surrey\(^1\), and uses a Marquardt least squares algorithm.

### 2.3 Reflectance

This section examines the use of conventional reflectance (R) spectroscopy as a characterisation tool for multi-layered structures. For bulk materials and simple structures, the reflectance response is usually uninteresting, typically showing broad background features and only weak CP features, and reveals little information about the system under investigation. This is clearly demonstrated in Fig. 2.1, which shows the reflectance response of bulk GaAs. This is not true, however, when structures have been deliberately designed to have particular and detailed reflectance spectra, such as the material systems studied in Chapters 4 and 5, vertical cavity surface emitting laser (VCSEL) structures. These structures can contain in excess of two hundred layers, and consequently interference effects of rays reflecting from different interfaces in the structure result in the unique reflectance response characteristic of VCSELs.

#### 2.3.1 Experimental Apparatus

\(^1\) Dr. T. J. C. Hosea, Department of Physics, University of Surrey, Guildford, Surrey.
A conventional reflectance spectrum is acquired in the course of making a PR measurement. For details on the experimental equipment, the reader is referred to Section 2.2.5, Fig. 2.4a, which describes the PR apparatus. However, for making just straight reflectance measurements, the modulating laser and lock-in amplifier part of the experiment can be removed. This is a fairly crude method for acquiring the $R$ spectrum. It is also possible to measure the $R$ spectrum by using the now redundant chopper to modulate the probe beam prior to the sample. The a.c. reflectance signal is then extracted using the lock-in amplifier.

As described in Section 2.2.5, the signal received by the detector, $R(\lambda)I(\lambda)$, includes a factor $I(\lambda)$, which represents the spectral response of the detector combined with the wavelength dependence of the intensity of the light source. To obtain the true reflectance spectrum, $R(\lambda)$, this system response, $I(\lambda)$, needs to be measured. This is achieved by removing the sample and moving the detector in line with the probe beam such that it takes a direct measurement of the incident probe beam. Once $I(\lambda)$ has been acquired, a division of the two spectra, $R(\lambda)I(\lambda)$ and $I(\lambda)$, gives the reflectance response, $R(\lambda)$.

### 2.3.2 Modelling of Reflectance Spectra

If the nominal structure is known, it is possible to calculate the reflectance response of a particular system by using a transfer matrix approach, which is covered in detail in Chapter 4. By an iterative process of comparing experimental $R$ spectra with calculated spectra and then tailoring individual layer dimensions, it is possible, in some situations, to derive a best fit model for a given structure.

### 2.4 Photoluminescence
Photoluminescence (PL) uses a high-energy light source to photo-excite electrons into high lying conduction bands. The carriers then cascade down into the lowest available energy states by non-radiative processes. In bulk semiconductors, the carriers then recombine, emitting photons with energy corresponding approximately to the bandgap of the material. PL spectra typically show a broad spectral peak centred near the bandgap energy of the material. A certain amount of recombination does occur at energies higher than the bandgap due to thermal occupancy and band filling effects.

In QW systems, the carriers fall into the wells and recombine after dropping to the lowest lying confined sub-band. Owing to the fact that the heavy-hole and light-hole valence bands are no longer degenerate in QW systems, it is often possible to see two peaks in such a system, where one will appear as a weaker shoulder on the high energy side of the main PL emission peak.

In QD systems it is possible to observe PL from confined states other than that of the ground state. This is achieved by using a sufficiently high laser power, which saturate the lower-energy states of the dots. With increasing excitation powers, recombination begins to occur between higher excited confined states, making PL a useful tool for the characterisation of QDs.

For reviews focussing on PL as a characterisation technique for semiconductors, the reader is referred to (Lightowlers, 1990; Schroder, 1990).

### 2.4.1 Experimental Apparatus

A simple modification of the PR experimental apparatus described in Section 2.2.5 enables it to be used for PL measurements. Performing PL measurements in such a way has the added advantage of allowing measurements to be taken on exactly the same spot, on a particular sample, as the PR measurements were made.
The PL measurements acquired through the course of this work were usually performed immediately after taking a PR spectrum. Without disturbing either the sample, or the He-Ne laser, the white light source was removed from the front end of the spectrometer, and replaced with the InGaAs detector. Consequently the spectrometer was used in reverse, with PL emissions being focussed onto the detector after passing through the spectrometer. The He-Ne laser previously used to modulate the sample in the PR experiments was now used as the PL excitation source. The PL emissions are emitted at the frequency of the chopped laser and are detected using the lock-in amplifier. A schematic of the experimental arrangement is shown in Fig. 2.6.

Fig. 2.6 Schematic diagram of experimental apparatus used for photoluminescence measurements.
2.5 Double Crystal X-ray Diffraction

This section gives a brief overview of the spectroscopic technique known as high-resolution x-ray diffraction, or double crystal x-ray diffraction (DCXRD). This involves scattering x-rays off a particular set of Bragg planes of the crystal sample under investigation. Measurements are made of the intensity of scattered x-rays, and this intensity is recorded as a function of incident x-ray angle on the sample. The angle of incidence is varied by ‘rocking’ the sample through a chosen angle range, and the resulting spectrum is referred to as a rocking curve. The technique can resolve very small differences between the substrate and epi-layer lattice parameters.

2.5.1 Background of DCXRD

It was around 90 years ago that the phenomenon of x-rays diffraction in crystals was first discovered. This led to the development of Bragg’s law for diffraction in a crystal (Cullity, 1978) and also to Ewald’s dynamical theory for x-ray diffraction (Cruickshank, 1992). Following this, DuMond developed a theory showing that increased resolving power was attained when using successive reflections off a number of crystal surfaces (DuMond, 1937). For reviews on the subject of high-resolution x-ray diffraction the reader is referred to (Tanner, 1990; Wie, 1994; Fewster, 1995; Fewster, 1996).

As the name suggests, DCXRD uses two crystals to produce a spectrum. The x-rays are first reflected off a particular set of Bragg planes of a high quality reference crystal. This acts as a reference and produces, after the x-rays have passed through an aperture, a highly collimated and monochromatic beam. The second crystal is simply the sample under investigation.

2.5.2 DCXRD Experimental Apparatus

57
A Bede$^2$ Scientific model 150 double crystal diffractometer was used to acquire the DCXRD spectra in this work. This was controlled using a P.C. running Bede$^2$ DCC software. The x-rays were produced using a long fine focus Cu x-ray tube that was powered by a Philips PW 1180 generator running at 45kV and 35mA. A schematic diagram of the diffractometer is shown in Fig. 2.7. The reference was provided by a single crystal (111) silicon multi-reflection monochromator-collimator (from Bede), with x-rays being reflected off the Si (111) Bragg planes.

![Schematic diagram of the diffractometer used for DCXRD measurements.](image)

As all the samples examined in this work were grown in a (001) direction with respect to the substrate, it was possible to produce symmetrical rocking curves by using reflections off the (004) planes of the sample crystal. Symmetrical rocking curves were used for analysis, as these are more easily simulated than asymmetrical spectra.

### 2.5.3 Simulating DCXRD Spectra

$^2$Bede Scientific Instruments Ltd., Bowburn South Ind. Est., Bowburn, Durham, DH6 5AD.
For relatively simple structures, such as a single strained epitaxial layer grown on a substrate, it is possible to determine differences in layer lattice constants directly from a DCXRD spectrum. However, for multi-layered structures, such as those examined in this work, this proves to be impossible, as complex diffraction patterns are produced that cannot be analysed directly. Therefore to gain information about the sample under investigation, it is necessary to compare the experimental rocking curve with a simulated DCXRD spectrum. This way, structural information about a sample can be inferred by assuming the sample to have the structure that produces the closest match between experimental and simulated spectra.

DCXRD rocking curves are simulated using the dynamical theory of diffraction, as opposed to the classical kinematic theory that leads to the familiar Bragg equation. The
dynamical theory of diffraction was developed independently by Takagi (Takagi, 1962; Takagi, 1969) and Taupin (Taupin, 1964). Actual simulations were produced using Bede\textsuperscript{2} RADS software. The modelling of experimental rocking curves with theoretical simulations is covered in Chapter 3. Fig. 2.8 shows a typical DCXRD spectrum for a multi-layered structure, in this case a MQW sample with four QWs, along with the best-fit simulation. The high intensity peak can be seen which is due to reflections from the sample's substrate, whilst the peripheral satellite peaks are due to diffraction from additional layers in the structure.
2.6 References

Aspnes D E 1966 Phys. Rev. 147 554
Aspnes D E, Handler P and Blosser D F 1968 Phys. Rev. 166 921
Aspnes D E and Frova A 1969 Solid State Commun. 7 155
Aspnes D E 1970a Solid State Commun. 8 267
Aspnes D E 1970b Solid State Commun. 8 1145
Aspnes D E and Studna A A 1973a Phys. Rev. B 7 4605
Aspnes D E 1973b Surface Science 37 418
Bulyanitsa D S 1960 Soviet Physics JETP 11 868
Callaway J 1963 Phys. Rev. 130 549
Cullity B D 1978 Elements of X-ray Diffraction 2nd ed. (Addison - Wesley)
Dumond J W M 1937 Phys. Rev. 52 872
Fischer J E and Seraphin B O 1967 Solid State Commun. 5 973
Franz W 1958 Z. Naturforsh 13 484
Frova A and Handler P 1965 Phys. Rev. 137 A1857
Experimental Techniques

Electronics 1 1108

Hall D J, Hosea T J C and Lancefield D 1997 J. Appl. Phys. 82 3092
Keldysh L V 1958 Soviet Physics JETP 34 788
Phillip H R and Ehrenreich H 1963 Phys. Rev. 129 1550
Seraphin B O and Bottka N 1966 Phys. Rev. 145 628
Shen H and Dutta M 1995 J. Appl. Phys. 78 2151

62


Tanner B K 1990 *J. Cryst. Growth* 90 1315


Tang Y S 1991 *J. Appl. Phys.* 69 8298


Tharmalingham K 1963 *Phys. Rev.* 130 2204


Wie C R 1994 *Mat. Sci. & Eng.* R13 1

CHAPTER 3

PR, PL and DCXRD Studies of Tensilely Strained InGaAs/InGaAsP Quantum Well Structures

3.1 Introduction

The studies described in this chapter involve the examination and characterisation of a series of InGaAs/InGaAsP multiple quantum well (MQW) structures. Each structure has been grown with tensile biaxial strain in its InGaAs QW layers, with each successive structure in the series incorporating increased amounts of strain. There are seven structures in the series with the nominal strains of each structure ranging from 0.00% to 1.50% in steps of 0.25%. Of particular interest in this work are the effects of strain on the band structure in this material system, which is studied by the spectroscopic techniques of photomodulated reflectance (PR) and photoluminescence (PL). Double crystal x-ray diffraction (DCXRD) measurements are used to derive structural information about each particular sample.

The research has been undertaken for a number of reasons, the first of which is to develop an understanding of the effect that tensile strain has on the band structure of QW systems. This is achieved by observing the effect of tensile strain on the ground-state QW transitions $H_{11}$ and $L_{11}$. The energies of these two transitions are derived
from PR and PL measurements. The second reason for the work is to carry out a characterisation of the series of samples using all three techniques of PR, PL and DCXRD. Consequently, we should be able to make a useful comparison between the techniques of PR and PL, and assess their effectiveness in the characterisation of QW systems. In addition, such a characterisation allows one to assess the growers' ability to manufacture a sample to the correct specifications. The final reason for the work is to evaluate a theoretical model used to identify higher order QW transitions \( n, m > 1 \) observed in the PR spectra of these samples. This is then used as a complementary method for determining the structure of each sample to that of DCXRD characterisation.

This chapter is structured in the following manner. The remainder of this section gives an overview of the use of strain in semiconductor devices, followed by description of the nominal structures of the samples investigated. Details of the PR and PL measurements are then given. Following this, the DCXRD measurements are described along with their results. A theoretical model is then used to predict and identify the full manifold of both allowed and forbidden transitions observed in the PR spectra. Finally the effect of tensile strain on the ground-state QW transitions is examined.

3.1.1 Strain in QW Systems

It has long been recognised that incorporating strain into the QW layers of a semiconductor laser can lead to many benefits in terms of its performance. For example, Adams first suggested the advantages of growing QW lasers with built-in biaxial compression in the QW layers (Adams, 1986). Such lasers were shown to have higher quantum efficiencies, reduced threshold currents, and lower temperature sensitivities of the threshold current, compared to their unstrained predecessors. Introducing biaxial compression into the QWs of such a system has the effect of removing degeneracy and separating the heavy- and light-hole valence bands at the Brillouin zone centre (\( \Gamma \)-point). Consequently, the effective mass of the heavy-hole valence band is lowered, leading to a reduced density of states at the valence band.
edge. (Adams, 1986; Yablonovitch, 1988). This has the effect of reducing the carrier density required to reach lasing threshold, and of increasing the differential gain at threshold (Ghiti, 1989; Suemune, 1988).

In an unstrained QW, the highest lying valence band confined-state is due to the heavy-hole valence band. The effect of biaxial tensile strain, in bulk material, is to move the heavy-hole valence band to a lower energy than that of the light-hole valence band. This effect is described in Section 1.3.2, and is demonstrated in Fig. 1.7(b). In terms of confined-hole states in a QW, this has the initial effect of moving the heavy- and light-hole \((n = 1)\) confined states closer together until, at a particular strain, the two states become degenerate. Then, with increasing tensile strain, the heavy-hole confined state moves to a lower energy than that of the light-hole state, such that the light-hole state now becomes the highest lying confined valence band state. Semiconductor lasers, with biaxial tensile strain incorporated into their QW layers, have also been shown to have a reduced threshold current density and an increased differential gain (Thijs, 1994; Zah, 1991). However, the reason for improved performance in such lasers is no longer as simple to explain as in the case of a QW with compressive biaxial strain: it can be explained by considering the polarisation of the spontaneous emission. Photons emitted from the recombination of electrons with light-hole valence band confined states are more likely to be of the correct polarisation to contribute to lasing than from recombination with heavy-hole states (O’Reilly, 1994). Furthermore, strain plays an important role in many other optical components such as optical modulators and amplifiers.

3.1.2 InGaAs / InGaAsP Material System in Optical Devices

The InGaAs / InGaAsP ternary/quaternary alloy material system has proven to be of great technological importance in the field of optical fibre communications. Unstrained InGaAs / InGaAsP QW lasers grown on InP substrates are extensively used as light sources for emitting at the wavelength of 1.55 μm. This wavelength is one of the two key wavelengths (the other being 1.3 μm) used for transmission
through optical fibre networks. Tensile strain is also used extensively in InGaAs based laser devices. (Thijs, 1991; Krijn, 1992; Thijs, 1994; Silver, 1994).

The semiconductor optical amplifier has recently become a viable alternative to its more widely used contemporaries, such as the rare-earth ion doped fibre amplifiers. Semiconductor optical amplifiers are used as boosters between fibre-to-fibre interconnects, or as pre-amp stages before detection. Furthermore, they can also be used as wavelength converters for wavelength division multiplexing (WDM) (Dubovitsky, 1994).

One of the major problems associated with the design and application of semiconductor optical amplifiers is that of polarisation insensitivity. There is no way of controlling the polarisation of light entering an optical amplifier as it is usually delivered to the amplifier via a length of optical fibre. The fibre has the effect of randomising the orientation of the light travelling through it.

An optical mode travelling through a device with its electric field vector orientated in the in-plane direction, that is to say in the plane of the QW and perpendicular to the growth direction, is known as a transverse electric (TE) mode and interacts with electronic transitions involving both the heavy-hole and light-hole valence bands. However, an optical mode with its electric field orientated in the growth direction is known as a transverse magnetic (TM) mode and interacts only with transitions involving the light-hole valence band (O'Reilly, 1994). It is desirable then, for the realisation of polarisation insensitive optical amplifiers (PIOA), to have a situation where the energies of the ground state QW transitions \( H_{11} \) and \( L_{11} \) are degenerate. One purpose of this study is to determine the value of tensile strain at which the \( H_{11} \) and \( L_{11} \) transitions become degenerate for these structures. There are additional factors to be considered in the design of a PIOA such as matching the gain spectra of the TE and TM modes. For examples of the use of strain in PIOAs see: (Magari, 1991; Joma, 1993; Magari, 1994; Godefroy, 1995).

### 3.1.3 Samples
The samples investigated are a series of MQW laser substrate structures grown by low-pressure metal-organic vapour phase epitaxy (MOVPE) by Nortel Ltd. Each nominal structure contains four identical undoped In$_{x}$Ga$_{1-x}$As QWs, 95 Å wide, separated by 140 Å wide In$_{0.80}$Ga$_{0.20}$As$_{0.43}$P$_{0.57}$ barriers. The barriers are lattice matched to an $n+$ sulphur-doped InP substrate, and have a nominal room temperature bulk bandgap of 1.17 µm (1059 meV). There are seven structures in the series with the nominal In composition in the wells decreasing in steps from $x = 0.533$ to 0.316. Nominally, the samples have tensile strains ranging from 0.00% (lattice matched) to 1.50%, in steps of 0.25%.

<table>
<thead>
<tr>
<th>Layer/Designation</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>InP Cap</td>
<td>0.1 µm</td>
</tr>
<tr>
<td>In$<em>{0.80}$Ga$</em>{0.20}$As$<em>{0.43}$P$</em>{0.57}$ Barrier</td>
<td>0.15 µm</td>
</tr>
<tr>
<td>In$<em>{0.80}$Ga$</em>{0.20}$As$<em>{0.43}$P$</em>{0.57}$ Barrier</td>
<td>140 Å</td>
</tr>
<tr>
<td>In$<em>{x}$Ga$</em>{1-x}$As QW</td>
<td>95 Å</td>
</tr>
<tr>
<td>In$<em>{0.80}$Ga$</em>{0.20}$As$<em>{0.43}$P$</em>{0.57}$ Barrier</td>
<td>140 Å</td>
</tr>
<tr>
<td>In$<em>{x}$Ga$</em>{1-x}$As QW</td>
<td>95 Å</td>
</tr>
<tr>
<td>In$<em>{0.80}$Ga$</em>{0.20}$As$<em>{0.43}$P$</em>{0.57}$ Barrier</td>
<td>140 Å</td>
</tr>
<tr>
<td>In$<em>{x}$Ga$</em>{1-x}$As QW</td>
<td>95 Å</td>
</tr>
<tr>
<td>In$<em>{0.80}$Ga$</em>{0.20}$As$<em>{0.43}$P$</em>{0.57}$ Barrier</td>
<td>140 Å</td>
</tr>
<tr>
<td>In$<em>{x}$Ga$</em>{1-x}$As QW</td>
<td>95 Å</td>
</tr>
<tr>
<td>In$<em>{0.80}$Ga$</em>{0.20}$As$<em>{0.43}$P$</em>{0.57}$ Barrier</td>
<td>140 Å</td>
</tr>
<tr>
<td>In$<em>{x}$Ga$</em>{1-x}$As QW</td>
<td>95 Å</td>
</tr>
<tr>
<td>In$<em>{0.80}$Ga$</em>{0.20}$As$<em>{0.43}$P$</em>{0.57}$ Barrier</td>
<td>140 Å</td>
</tr>
<tr>
<td>In$<em>{x}$Ga$</em>{1-x}$As QW</td>
<td>95 Å</td>
</tr>
<tr>
<td>InP Buffer</td>
<td>-</td>
</tr>
<tr>
<td>InP Substrate</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.1 Schematic of the nominal structures of the seven tensilely-strained MQW samples studied. The nominal In composition of the QWs varied between $x = 0.533$ and 0.316, corresponding to tensile strains ranging from zero to 1.50%, respectively. The InGaAsP layers were nominally lattice-matched to the InP substrate, with a room-temperature bulk bandgap corresponding to a wavelength of 1.17 µm. The InP substrate was $n+$ type sulphur-doped while the buffer layer was doped to $n = 5 \times 10^{17} \text{cm}^{-3}$. All other layers are undoped.

Nortel Ltd. (formerly BNR Europe), London Road, Harlow, Essex.
The structures are referred to by their growth numbers, which are E874 (0.00%), E866 (0.25%), E868 (0.50%), E869 (0.75%), E870 (1.00%), E876 (1.25%), and E878 (1.50%), with the number in parentheses giving the value of strain. The substrate is buffered from the rest of the structure by an n-doped InP layer ($n \sim 5 \times 10^{17} \text{ cm}^{-3}$). Table 3.1 shows a schematic of the nominal structures. All the samples were initially capped with a 0.1 μm thick InP layer. However, this capping layer was removed prior to any optical experiments using a wet etching process. This was done to reduce the absorption of incident light.

Fig. 3.1a shows the tensile biaxial strain for an $\text{In}_x\text{Ga}_{1-x}\text{As}$ epi-layer grown pseudomorphically on InP as a function of the In/Ga ratio, $x$, in the ternary layer. Fig. 3.1b shows the corresponding unstrained bulk band gap for such a layer at room temperature. The unstrained bulk bandgap has been calculated using the binary constants given in Table 3.5 and the interpolation scheme described in (Krijn, 1990). The procedure used to calculate the strain is described in Section 1.3.2 (Van de Walle, 1989; Krijn, 1990).
Other researchers have investigated the series of structures studied in this chapter for a variety of purposes. Magneto-optical studies have been carried out by Martin et al. to investigate the effect of strain on the in-plane hole effective masses and on excitonic properties (Martin, 1994). In addition, Jones et al. have performed a thorough investigation of InP-based strained MQW lasers fabricated from these particular laser substrates (Jones, 1998). Hall et al. have performed PR measurements on a similar range of tensilely strained InGaAs/InGaAsP QW structures each containing only a single QW (Hall, 1998).

3.2 PR and PL Measurements

This section describes the PR and PL measurements performed on the series of tensilely strained MQW structures.

3.2.1 Experimental Details

The PR measurements were carried out at a modulation frequency of 333 Hz. chosen to avoid a multiple of the mains frequency, 50 Hz. The He-Ne modulation source was attenuated to a power of ~0.32 mW/mm² using appropriate neutral density filters. The probe beam was reflected off the sample at an angle of 55° ± 0.5° to the normal of the sample’s surface. Both scattered laser light and second order diffracted light from the monochromator were masked from the detector using a 640 nm high pass filter. The monochromator slits were set at 2 mm x 800 μm, giving an instrumental resolution of typically ~1.7 meV (full width at half maximum) in the energy range studied.

The 0.1 μm thick InP capping layer was etched off using a mixture of HCl : H₃PO₄ in a 1 : 9 ratio. This has an etch rate of ~ 0.3 μm/min, so samples were etched for approximately 20 secs. PR scans were taken over an energy range of 760 meV to 1420 meV. The constant background owing to PL detected in the ΔR signal was found to be relatively large and as a result it was advantageous to use long scan times to
achieve an appropriate signal to noise ratio. The maximum scan time for each full range spectrum was ~12 hours.

The corresponding PL measurements were taken using the experimental arrangement described in Section 2.4. Such an arrangement allows the PL measurements to be taken from the same position on each sample as the PR measurements. The PL measurements were taken over a shorter energy range of 760 meV to 960 meV. Individual PL scans were taken over a time scale of ~ 30 mins.

### 3.2.2 PR Measurements

![Diagram showing Franz-Keldysh oscillations (FKOs) and energy levels](image)

Fig. 3.2 Example of PR spectrum for sample E874. Arrows indicate features arising from the two ground-state QW transitions, $H_{11}$ and $L_{11}$, as well as from the InGaAsP barrier layers, and the InP substrate. Inset graph shows an expansion of the region displaying Franz-Keldysh oscillations (FKO).

A number of similar features can be observed in the PR spectra of all seven structures. Fig. 3.2 shows an example PR spectrum, taken for the nominally latticed matched
sample E874. A prominent feature can be seen at the higher energy end of the spectrum, which originates from the InP substrate. Another distinctive feature is observed in the spectra of all the samples at an energy of ~1050 meV. This feature originates from the InGaAsP barrier layers within each structure. On the higher energy side of this feature, a number of Franz-Keldysh oscillations (FKO) can be seen. These are shown more clearly in the inset figure. The presence of these oscillations indicates that there is an appreciable built-in electric field within each sample. The period of these oscillations is used later to determine the magnitude of the internal field. The spectral features observed at energies below the feature corresponding to the InGaAsP barrier layers arise from confined-state QW transitions. The two most prominent features are due to the two ground-state QW transitions, $H_{11}$ and $L_{11}$.

In all the samples, the InP feature was found to be at an energy of ~1350 meV. The InGaAsP barrier layer features were found to be at energies ranging from 1048 meV to 1057 meV. The energies of the barrier layers in each sample were found by fitting a third differential functional form (TDFF), as defined by eqn. (2.31), over the region of interest using an exponent $n = 2.5$. The fitted energies for the InGaAsP barrier layers in each sample are; E874 (1048 meV), E866 (1057 meV), E868 (1048 meV), E869 (1055 meV), E870 (1052 meV), E876 (1052 meV), and E878 (1054 meV).

**Estimating the size of the internal electric field from FKO analysis**

As stated earlier, it is possible to use the period of the decaying FKO oscillations present in each PR spectra to determine the magnitude of the internal electric field present in the structure (Shen, 1995; Hughes, 1995). In Section 2.2.3, a characteristic energy was defined by eqn. (2.20) and is referred to as the electro-optic energy, or $\hbar \Omega$ (Aspnes, 1973b). With knowledge of the electro-optic energy and the interband reduced mass of a system, eqn. (2.20) allows the magnitude of the internal electric field to be calculated.
In the intermediate-field regime the oscillatory behaviour at \( E > E_g \) can be described by an electro-optic function, whose asymptotic form (Aspnes, 1973a) can be written as:

\[
\frac{\Delta R}{R} = \cos \left[ \frac{4}{3} \left( \frac{E_j - E_g}{\hbar \Omega} \right)^{3/2} + \theta \right]
\]  

(3.1)

where FKO extrema occur at energies of \( E_j \) and \( j \) is the index of the extrema, \( \theta \) is a phase term, and \( E_g \) is the band edge transition energy. This leads to:

\[
\frac{2}{3} \left( \frac{E_j - E_g}{\hbar \Omega} \right)^{3/2} + \theta = j\pi
\]  

(3.2)

From this equation it is possible to form two alternate graphical plots to determine the value of \( \hbar \Omega \). In both cases, the value of \( \hbar \Omega \) is derived from the gradient of the plot. The first plot uses eqn. (3.2) to write:

\[
E_j = \hbar \Omega (F_j) + E_g
\]  

(3.3)

\[
F_j = \left[ \frac{3}{2} (j\pi - \theta) \right]^{2/3}
\]  

(3.4)

\( \hbar \Omega \) is then simply given by the gradient of the plot of \( E_j \) versus \( F_j \). This plot does not need prior knowledge of the value of \( E_g \), which is in fact given by the y-intercept of the plot. The phase factor \( \theta \) is supposed to depend upon the dimensionality of the critical point, \( d \), and is given as (Hughes, 1995):

\[
\theta = -\frac{\pi (d - 1)}{4}
\]  

(3.5)
Though it also depends on optical interference effects and is in effect essentially unknown. The limitation of this type of plot is the uncertainty in assigning correct values of \( j \) to experimental FKO extrema and in the assignment of \( \theta \). For these structures, a phase factor of \( \theta = \pi/2 \) was used for the analysis.

The second plot uses eqn. (3.2) as:

\[
(E_f - E_g)^{3/2} = \frac{3}{2}(\hbar \Omega)^{3/2}(j \pi - \theta)
\]  

This plot of \( (E_f - E_g)^{3/2} \) versus \( j \) requires that the value of \( E_g \) is known. The value of \( \hbar \Omega \) can then be calculated from the gradient of this plot, \( m \), using \( \hbar \Omega = (m^{2/3} / 2.81) \).

\( \hbar \Omega \) was calculated for each of the seven structures using an average of the two values obtained from the two types of plot. To calculate the electric fields, the reduced effective mass of the electron and heavy-hole pair was used, as defined by eqn. (1.10). The effective masses of the electron and heavy hole in the InGaAsP layers were calculated using a linear interpolation of the binary values given in Table 3.5, using the interpolation scheme described in (Krijn, 1991). The magnitudes of the fields calculated from the FKO plots are given in Table 3.2.

<table>
<thead>
<tr>
<th>sample</th>
<th>E874</th>
<th>E866</th>
<th>E868</th>
<th>E869</th>
<th>E870</th>
<th>E876</th>
<th>E878</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field</td>
<td>33</td>
<td>35</td>
<td>34</td>
<td>36</td>
<td>38</td>
<td>45</td>
<td>73</td>
</tr>
<tr>
<td>(kV/cm)</td>
<td>±15</td>
<td>±15</td>
<td>±15</td>
<td>±15</td>
<td>±15</td>
<td>±15</td>
<td>±15</td>
</tr>
</tbody>
</table>

Table 3.2  Internal electric field sizes calculated from graphical analysis of FKO's.

The PR spectra for all seven structures are plotted together in Fig. 3.3 from 760 meV to 1100 meV, thus showing the InGaAsP barrier feature in addition to all the confined-state QW transitions.

74
Fig. 3.3 Experimental room temperature PR spectra for the seven MQW samples. For clarity, the baselines of the spectra have been offset by factors of $4 \times 10^4$ units. Individual sections of each spectrum have been scaled according to the factor shown. Curves represent fits to data using eqn. (2.31). The thick and thin arrows indicate the fitted energies of the ground-state $H_{11}$ and $L_{11}$ transitions respectively. The dotted curves on far right show the InGaAsP barrier feature.
Individual spectra have been scaled as shown on the left of each graph. In addition, most midsections of each spectrum have been scaled separately as shown by the central column of numbers, to allow the weaker features arising from higher order QW transitions to be seen. Each spectrum has been offset from the previous one by a factor of $4.0 \times 10^{-4}$. The energy positions of the two ground state QW transitions, $H_{11}$ and $L_{11}$, as determined by lineshape fitting, are shown by the thick and thin arrows, respectively. Experimental data are shown as dots, whereas the fits to the data are given as solid lines. Each fit is composed of a number of TDFF oscillators, as defined by eqn. (2.31) using an exponent of $n = 3$. For excitonic states the correct exponent to use for a TDFF lineshape should be $n = 2$ (Aspnes, 1973b) However, it has been shown that using an exponent of $n = 3$ accurately mimics the correct lineshape at room temperature (Shanabrook, 1987). In fact, it was found that the fitting values of $E_g$ did not depend crucially on the value chosen for the exponent $n$. The results of the fitting are covered in more detail in Sections 3.4 and 3.5, and the $E_g$ values derived are given in Table 3.8.

As can be seen in Fig. 3.3, the ground-state QW transitions $H_{11}$ and $L_{11}$ both move to higher energies through the series as the amount of tensile strain in the wells increases. However, the $H_{11}$ transition increases in energy with increasing strain at a faster rate than the $L_{11}$ transition. Fig. 3.4 demonstrates this effect more clearly by displaying only the low energy region of each spectrum encompassing the $H_{11}$ and $L_{11}$ transitions. The lines in this figure have been drawn as a guide to eye. This behaviour will be examined more rigorously in Section 3.5 after the actual strain of each structure has been determined.

### 3.2.3 PL Measurements

Fig. 3.5 shows the PL and IPRI spectra of the series of structures. The PL spectra are shown as the thin set of lines. The ground-state QW transition energies estimated from the PL measurements are given in Table 3.3.
Fig. 3.4 Sections of PR spectra displaying the $H_{11}$ and $L_{11}$. Dashed lines have been drawn to demonstrate behaviour of the two transitions through the series.

Fig. 3.5 Modulus of PR, and PL spectra shown for the seven structures. IPRl and PL given as the thick and thin sets of lines, respectively.
For comparison, the results of the PR measurement have also been plotted in Fig. 3.5 as the thick set of lines. However, instead of displaying the PR data in the conventional $\Delta R/R$ form, the results have been represented as a series of 'modulus spectra', $|\text{PR}|$ (Hosea, 1995).

<table>
<thead>
<tr>
<th>Sample</th>
<th>E874</th>
<th>E866</th>
<th>E868</th>
<th>E869</th>
<th>E870</th>
<th>E876</th>
<th>E878</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{11}$ (meV)</td>
<td>789</td>
<td>817</td>
<td>844</td>
<td>868</td>
<td>885</td>
<td>908</td>
<td>923</td>
</tr>
<tr>
<td>$L_{11}$ (meV)</td>
<td>811</td>
<td>-</td>
<td>-</td>
<td>848</td>
<td>849</td>
<td>857</td>
<td>855</td>
</tr>
</tbody>
</table>

Table 3.3: Ground-state $H_{11}$ and $L_{11}$ transition energies as estimated from PL measurements.

Using the Kramers - Kronig relation described by eqn. (2.21), it is possible to transform an experimental PR spectrum into its modulus. The Kramers - Kronig relation is used to calculate a corresponding imaginary part of a spectrum from its experimental real part. Then by using both the real and imaginary parts, a $|\text{PR}|$ spectrum can be derived which effectively removes the unwanted phase information from the spectrum.

For example, the equation of a single TDFF as given by eqn. (2.31) can be written in the form:

$$\text{Re} \left[ \frac{Ce^{i\varphi}}{(E - E_g + i\Gamma)^n} \right] = \frac{C \cos(\theta + n \varphi)}{\left((E - E_g)^2 + \Gamma^2\right)^{n/2}}$$

(3.7)

where $\varphi$ is the phase angle of the complex number $E - E_g + i\Gamma$. Taking the modulus spectrum allows each feature in the experimental PR spectrum to be transformed from a multi-peaked differential-like feature into a simple single positive-definite peak, with the peak of the feature centred on $E = E_g$. Obviously this technique becomes less reliable for features that lie in close proximity to one another. However, it has been shown that the results of a modulus spectrum can still be reliable even if the $E_g$ values...
of a pair of TDFFs are separated by less than the sum of their individual $\Gamma$-parameters (Hosea, 1994).

It is clear from Fig. 3.5, that for some of the structures the energies of transitions $H_{11}$ and $L_{11}$, as defined by the peak positions in the PL and IPRl spectra, differ. In most cases the PL measurements show peaks at higher energies than those in the IPRl spectra. The energies given by PR are argued to be a more accurate representation of the true critical-point interband transitions as there are additional factors to be considered when interpreting PL spectra. Close to the band edges, the number of states available for recombination is relatively low, and consequently so is the PL emission. Thermal occupancy effects can then cause the emission to peak at energies above the critical-point energy. Additionally, the presence of one PL emission peak can have an influence on the lineshape of another peak in close proximity, effectively shifting its peak position.

The linewidths of features in the PL spectra are broader than those observed in the IPRl spectra, with linewidths typically of the order of 40 meV (FWHM). Linewidths of this magnitude are quite normal for room temperature PL measurements due to the thermal broadening of PL emission features by a few $kT$ ($kT = 25$ meV at 300K). Estera et al. have made optical studies on similar material systems (Estrera, 1991) and have observed comparable linewidths for room temperature PL measurements, ~45 meV (FWHM). Linewidths observed in the IPRl spectra are typically less, ranging from 8 meV to 48 meV (FWHM) with the average being 18 meV (FWHM). The half width half maximum (HWHM) of a IPRl feature is related to the associated TDFF linewidth, $\Gamma$, by $\text{IPRI}_{\text{FWHM}} = 0.766\Gamma$, for this particular system (Hosea, 1995). Hence, a IPRl feature with linewidth of 18 meV (FWHM) has an equivalent TDFF linewidth, $\Gamma$, of 12 meV. The linewidths of the IPRl spectra will be further examined in Section 3.5. Narrower linewidths are normally seen in PR spectra compared to PL spectra due to the different broadening mechanisms in the derivative PR technique. The linewidths of excitonic features in PR have been shown to be as narrow as 4 meV at 300 K (Qiang, 1992).
There is another interesting difference between the results given by PL and PR in the intensities of the two transitions, \( H_{11} \) and \( L_{11} \). In the set of PL measurements shown in Fig. 3.5, it can be seen that in all cases, the transition with the lower of the two energies gives rise to the largest emission peak. This is the expected result in a PL experiment, where the majority of carriers in the structure will fall into the lowest available energy state before recombining. Conversely, in the set of PR measurements, it is the \( H_{11} \) transition that always has the greater intensity, regardless of whether its actual energy lies above or below that of \( L_{11} \). The ratio of intensities of \( H_{11} : L_{11} \) was found to be in the range of \((1.2 - 6.1) : 1\). This phenomenon can be explained by an examination of the valence band Bloch functions. These can be expressed in terms of linear combinations of the orthogonal X, Y, and Z basis states, and the spin states (O'Reilly, 1994), where X and Y are co-ordinates in the plane of the QW, and Z is the basis state in the growth direction. Although these experiments have been performed with the probe beam incident at 55° to the sample, inside the sample the probe beam is refracted to a smaller angle of around 15° owing to the relatively high refractive index of the materials concerned. As a result, waves travelling inside the sample have electric field vectors polarised primarily in the in-plane X and Y directions. The heavy-hole valence band Bloch function is composed of only X and Y basis states, whereas the light-hole valence band Bloch function is predominantly Z-like. As a result, the light-hole band interacts less with the probe beam than the heavy-hole band does, and thus the \( L_{11} \) feature always appears weaker than that of the \( H_{11} \) transition in these spectra.

### 3.3 DCXRD Measurements

This section of work uses the technique of double crystal x-ray diffraction to derive structural information about each sample in the series. The actual compositions and thicknesses of both the InGaAs QW layers and the InGaAsP barrier layers are determined for each structure by modelling the experimental DCXRD spectra with theoretically simulated spectra.
3.3.1 Experimental Details

The DCXRD measurements were performed using the equipment described in Section 2.5, with spectra being taken over a typical angle range of 8000 arc seconds. Spectra were acquired using reflections from the (004) planes of the sample. In the structures investigated here, these planes are parallel to the surface, as the samples have been grown on InP substrates in a (001) orientation. Using reflections from these particular crystal planes has the effect of producing symmetrical diffraction spectra, which are more easily modelled. Individual spectra were acquired over typical time scales of 12 - 22 hours.

3.3.2 Modelling of DCXRD Spectra

Due to the complexity of DCXRD spectra of multilayer structures, it proves to be very difficult to infer any information about a structure directly from its DCXRD spectrum (Halliwell, 1984). However, it is possible to deduce the actual structure of a particular sample by comparing its experimental DCXRD spectrum with theoretically simulated spectra. The results of the modelling are taken to be the structures that give the closest match between simulated and experimental spectra. A similar approach was used by Choi and Fonstand for analysing DCXRD spectra of strained InGaAs MQWs (Choi, 1993).

The nominal structure of each sample was used as a starting point to generate an initial simulated spectrum, which was then compared with the experimental data. The quality of the fit of the simulation to experiment was determined by calculating the sum of the squares of the deviations between the logarithm of the experimental \(Y\) and simulated \(C\) x-ray counts:

\[ S^2 = \sum_i \left[ \log_{10}(Y_i) - \log_{10}(C_i) \right]^2 \]  

(3.8)
where $i$ is summed over the range of diffraction angle studied. The compositions and thicknesses of the layers in each structure were then varied, away from the nominal values, until the quantity $S^2$ was minimised. During the modelling process, $S^2$ was minimised with respect to only one varying parameter at a time. This was done for each freely varying parameter in turn. Then, when $S^2$ had been minimised with respect to each varying parameter, the whole cycle was repeated enough times to ensure that the absolute minimum of $S^2$ had been found.

In a given simulation, repeated layers within a structure were assumed to be identical in order to simplify the modelling process. Hence, the structural model consisted of four identical $In_xGa_{1-x}As$ QWs, separated by five identical $In_yGa_{1-y}As_zP_{1-z}$ barrier layers, all sandwiched between two other $In_yGa_{1-y}As_zP_{1-z}$ layers of the same composition. The thicknesses of the QW layers in any particular structure were assumed to be identical. The thicknesses of the $In_yGa_{1-y}As_zP_{1-z}$ layers within each model structure were all scaled from their nominal values according to a single independently varied parameter. Hence, a total of five parameters were varied, these being the thickness and In composition ($x$) of the QWs, and the thickness and In and As compositions ($y$ and $z$, respectively) of the remaining $In_yGa_{1-y}As_zP_{1-z}$ material layers.

The resulting layer thicknesses were rounded to the nearest 0.1 Å. The modelled compositions (taken to the nearest 0.1%) were used to determine the corresponding lattice constants of each layer. Strains were then calculated (to the nearest 0.1%) from these data using eqn. (1.5), by a linear interpolation of the binary material parameters given in Table 3.5.
Figs. 3.6a (top) and 3.6b (bottom) DCXRD spectra shown as dots for structures E874 and E866, respectively. Line shows the best-fit simulation. For clarity the experimental and theoretical data have been offset by one and two counts, respectively.
Figs. 3.6c (top) and 3.6d (bottom) DCXRD spectra shown as dots for structures E868 and E869, respectively. Line shows the best-fit simulation. For clarity the experimental and theoretical data have been offset by one and two counts, respectively.
Figs. 3.6e (top) and 3.6f (bottom) DCXRD spectra shown as dots for structures E870 and E876, respectively. Line shows the best-fit simulation. For clarity the experimental and theoretical data have been offset by one and two several counts, respectively.
Fig. 3.6g DCXRD spectrum shown as dots for structure E878. Line shows the best-fit simulation. For clarity the experimental and theoretical data have been offset by one and two counts, respectively.
### Table 3.4

The structural and compositional parameters of the seven samples, both nominal and those derived from DCXRD measurements. Tensile and compressive strains are represented by positive and negative values, respectively. Compositions \(x, y, \) and \(z\) refer to In\(_{x}\)Ga\(_{1-x}\)As QW layers and In\(_{y}\)Ga\(_{1-y}\)As\(_{z}\)P\(_{1-z}\) barrier layers. For the lattice-matched sample, each parameter is a mean value derived from two simulations. The numbers in parentheses represent slight final adjustments to the DCXRD values after theoretical modelling of structures (see Section 3.4).
3.3.3 Results

The experimental DCXRD spectra along with their associated best-fit simulations are shown in Figs. 3.6a-g. The data are graphed using a logarithmic scale for the x-ray counts for clarity. The theoretical and experimental data have been offset by one and two counts, respectively. Very good agreement between experiment and simulation was achieved by this method of modelling. The results of the modelling have been summarised in Table 3.4.

In all the structures, the nominally lattice matched InGaAsP barrier layers were found to be slightly compressively strained, with strains ranging from -0.01 % to -0.04 %. With regards to the InGaAs QW layers, the two structures in the series with the highest nominal strains, E876 and E878, were found to be significantly less strained than nominally intended. A possible explanation for this would be the onset of dislocations within the strained layers of these structures. Dislocations are expected to occur if a structure exceeds its critical thickness (see Section 1.3.2). As an approximation, this can be expected if the product of the strain, and the sum of the thicknesses of all the layers that are strained, exceeds the value of 200 Å.% (O'Reilly, 1989). The nominal strain-thickness products for samples E876 and E878 are 475 Å.% and 570 Å.%, respectively, which clearly exceed 200 Å.%, and consequently some degree of layer relaxation is anticipated for these two structures. However, this situation is argued to be unlikely, as subsequent measurements of laser threshold currents on these structures after they had been processed into full laser devices showed no evidence of strain relaxation (Smith, 1998). It is most likely then that these two samples were simply grown incorrectly, resulting in the relatively large deviations from the nominal strains.

In all cases, except for the nominally lattice matched sample, E874, it was possible to produce a single closest fit model structure with a unique set of structural parameters. However, for sample E874 it was possible to derive two different structural models, the simulations of which matched the experimental data equally well. This problem arises due to the intrinsic nature of the DCXRD spectrum for this structure. A typical DCXRD spectrum contains a high intensity peak arising from the combined
diffraction due to the substrate and other layers to which it is lattice matched. Surrounding this peak are a number of weaker satellite peaks which arise from the strained layers in the structure which have different lattice constants to that of the substrate. In fact, it is the presence of these satellite peaks in the DCXRD spectra that enables a spectrum to be modelled. In the case of sample E874, these satellite peaks are too weak to allow the spectrum to be modelled unambiguously. An additional problem arises for this structure E874 owing to an assumption in the model that all four QWs are identical. This is a good approximation for the higher strained samples, but for the nominally lattice matched sample, any small differences in strain between individual wells can be of similar magnitude to the actual strain in the wells themselves. The two closest fits to sample E874 gave alternative QW strains of +0.14 % or -0.14 %, so that, although the derived strain for this structure has been taken as the mean of the two values, 0.00 %, the uncertainty in the well strain is significantly larger than for the other samples.

### 3.4 Modelling the Full Manifold of QW Transitions Observed in the PR Spectra

The PR spectra of all seven samples in the series show a region of structure arising from confined-state QW interband transitions. These regions of spectra have been fit with an appropriate lineshape model to determine the energies of each of the transitions. A theoretical model was then used to identify each of the transitions observed in the experimental PR spectra. The compositions, strains and well widths determined by the DCXRD measurements, given in Table 3.4, were used as initial parameters for the model structures. However, the modelling process yielded a new set of refined structural parameters for each sample by matching experimentally determined confined-state QW transition energies with theoretically calculated ones.

#### 3.4.1 Theoretical Model
<table>
<thead>
<tr>
<th>Parameter</th>
<th>InAs</th>
<th>GaAs</th>
<th>InP</th>
<th>GaP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant, a (Å)</td>
<td>6.058</td>
<td>5.653</td>
<td>5.869</td>
<td>5.451</td>
</tr>
<tr>
<td>Bandgap $E_g$ (meV)</td>
<td>360</td>
<td>1420</td>
<td>1350</td>
<td>2740</td>
</tr>
<tr>
<td>Spin-Orbit splitting $A_0$ (meV)</td>
<td>380</td>
<td>340</td>
<td>114</td>
<td>80</td>
</tr>
<tr>
<td>Electron mass $(m_e/m_0)$</td>
<td>0.0223</td>
<td>0.0665</td>
<td>0.079</td>
<td>0.17</td>
</tr>
<tr>
<td>Heavy-hole mass $(m_{hh}/m_0)$</td>
<td>0.342</td>
<td>0.382</td>
<td>0.56</td>
<td>0.79</td>
</tr>
<tr>
<td>Light-hole mass $(m_{lh}/m_0)$</td>
<td>0.0255</td>
<td>0.08</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>Ave. valence band energy $E_{v,av}$ (meV)</td>
<td>-6680</td>
<td>-6840</td>
<td>-7040</td>
<td>-7060</td>
</tr>
<tr>
<td>Valence band hydrostatic deformation potential $a_v$ (meV)</td>
<td>1000</td>
<td>1160</td>
<td>1270</td>
<td>1700</td>
</tr>
<tr>
<td>Conduction band hydrostatic deformation potential $a_c$ (meV)</td>
<td>-5880</td>
<td>-8060</td>
<td>-6180</td>
<td>-9450</td>
</tr>
<tr>
<td>Elastic Constant $C_{11}$ ($10^{12}$ dyn cm$^2$)</td>
<td>0.83</td>
<td>1.18</td>
<td>1.02</td>
<td>1.41</td>
</tr>
<tr>
<td>Elastic Constant $C_{12}$ ($10^{12}$ dyn cm$^2$)</td>
<td>0.45</td>
<td>0.54</td>
<td>0.58</td>
<td>0.62</td>
</tr>
<tr>
<td>Shear deformation potential $b$ (meV)</td>
<td>-1800</td>
<td>-1700</td>
<td>-1500</td>
<td>-1500</td>
</tr>
<tr>
<td>Bandgap bowing parameter (meV)</td>
<td>380</td>
<td>790</td>
<td>280</td>
<td>210</td>
</tr>
<tr>
<td>(GaInAs)</td>
<td>(GaInP)</td>
<td>(InPAs)</td>
<td>(GaPAs)</td>
<td>(GaPAs)</td>
</tr>
<tr>
<td>Bandgap bowing parameter (meV)</td>
<td>800</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(GaInAsP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5 Room temperature binary material parameters used to calculate strained ternary InGaAs and quaternary InGaAsP material parameters. All parameters are linearly interpolated onto the ternary/quaternary composition space except bandgaps, which use the appropriate ternary/quaternary bowing parameters.

The model used to calculate the confined-state QW transition energies uses an effective mass formalism (Andreani, 1987) with the bulk valence band described by a three-band (heavy-hole, light-hole, and spin-split-off band) $k \cdot p$ Hamiltonian (O’Reilly, 1989). The conduction band confined states are assumed to be decoupled from the valence band states, an assumption which is valid due to the large band gaps of the materials studied here. The model includes coupling between the light-hole and spin-split-off bands but does not account for band non-parabolicity effects.
The material parameters used to model the strained MQWs are summarised in Table 3.5.

The formula used to map the binary compound parameters onto ternary composition space are given by Krijn (Krijn, 1992). The band alignments at the InGaAs and InGaAsP layers heterojunction interfaces have been determined using model solid theory (Van de Walle, 1989). The confined-states of the QWs were calculated using software developed at Surrey.

The model described so far is for a flat band situation, that is to say with no electric field present in the model structure. It is necessary for slight adjustments to be applied to the transition energies calculated by this model to account for the presence of electric fields, and for exciton binding energies.

The quantum confined Stark effect (QCSE)

The structures studied are from an intermediate stage in the fabrication of typical $p$-$i$-$n$ laser diodes (Jones, 1998). In a fully realised $p$-$i$-$n$ diode, there exists a charge depletion region between the $p$- and $n$- doped layers. This gives rise to an electric field across the active region of the device. Although the structures in this study contain only the $n$-doped layers, an electric field still exists through the structure. As described in Section 1.3.3, this field spatially localises electron and hole wave functions at opposite ends of the QW, lowering the average energy separation of the two wavefunctions. This leads to a red shift in the transition energies calculated from the simple flat-band model. This is known as the quantum confined Stark effect (QCSE) (Miller, 1984).

The graphical analysis of the FKO spectra in the PR spectra (Section 3.2.2) allowed magnitudes of the electric fields within each sample to be calculated. However, these values for the fields were not used to model the QCSE as the quality of the analysis proved to be unsatisfactory. In addition, the FKO behaviour depends upon the largest

---

4 Dr. M. Silver, Hewlett Packard, Whitehouse Road, Ipswich, IP1 5PB.
field in the structure, which may not reside in the region of the QWs. The size of the electric field across the QWs in each structure was calculated theoretically by numerically solving Poisson's equation, following the method of Whiteaway (Whiteaway, 1983) using software written by I. Morris\(^5\). In each structure, the Fermi level was assumed to be pinned at the surface of the sample at an energy of 750 meV below the conduction band edge. This value was taken from Schottky barrier height measurements on InGaAsP material similar to that studied here (Bhattacharya, 1981). All the parameters used in this calculation are given in Tables 3.4 and 3.5, with the exception of the material dielectric constants which are given elsewhere (Adachi, 1982).

Fig. 3.7 is an example of the calculated band profile for one of the structures, E866. All the structures were calculated to have nearly identical band profiles. The resulting field across the QW region is 21 kV/cm in all the structures. This calculated field size is in reasonable agreement with the values determined by FKO analysis, for the four lowest strained structures, E874, E866, E868, and E869, as given in Table 3.2. However, the FKO analysis suggests that the magnitudes of the electric fields in structures E870, E876, and E878, given in Table 3.2, are slightly larger than the theoretically calculated value of 21 kV/cm.

The magnitudes of the red shifts associated with the QCSE, for each particular confined-state transition, were then calculated by a finite element method (Ames, 1971), using software developed at Surrey\(^4\). It was found that the shifts resulting from a 21 kV/cm electric field were relatively insignificant. The effect of the QCSE was found to increase slightly with increasing strain through the series. The shifts for the ground state \(H_{11}\) transition for samples E874 and E878, that is the samples with the least and greatest amounts of strain were found to be 1.5 meV and 3.1 meV, respectively. The corresponding shifts for the \(L_{11}\) transition were 0.4 meV and 2.3 meV, respectively. The shifts due to the QCSE for higher-order QW transitions were found to have a similar increase with increasing strain, but were somewhat smaller in magnitude than those of the ground state transitions. Shifts of this order of magnitude

\(^5\) I. Morris, Dept. of Physics, University of Aberdeen, Aberdeen, AB24 3UE.
Chapters: PR, PL and DCXRD Studies of Tensilely Strained InGaAs/InGaAsP Quantum Well Structures

have been observed experimentally in a QW system for fields of a similar magnitude (Wang, 1995).

![Diagram of band profiles](image)

**Fig. 3.7** Example of conduction and valence band profiles calculated for sample E866. Gradient of band profiles determines the size of electric field present in sample.

**Exciton binding energies**

It is known that confined-state QW interband transitions observed in PR spectra are still excitonic in nature even at room temperature (Shanabrook, 1987). This is a result of increased binding energies due to quantum confinement. Exciton binding energies for the ground-state QW transitions, $H_{11}$ and $L_{11}$, were derived previously from magneto-optical studies on the present structures (Martin, 1994). These were used in the model here and are shown in Table 3.6 as Set A. For comparison, exciton binding energies have also been calculated using the fractional dimensionality approach described in Section 1.3.3 (Mathieu, 1992a; Mathieu, 1992b) and are given in Table 3.6 as Set B. The estimated uncertainty for both sets of binding energies is ±2meV.
Chapters: PR, PL and DCXRD Studies of Tensilely Strained InGaAs/InGaAsP Quantum Well Structures

<table>
<thead>
<tr>
<th>Sample</th>
<th>E874 (meV)</th>
<th>E866 (meV)</th>
<th>E868 (meV)</th>
<th>E869 (meV)</th>
<th>E870 (meV)</th>
<th>E876 (meV)</th>
<th>E878 (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SetA H_{11}</td>
<td>7</td>
<td>9</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>6</td>
<td>7</td>
<td>6</td>
<td>7</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>SetB H_{11}</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3.6 Exciton binding energies for ground state QW transitions $H_{11}$ and $L_{11}$. Set A gives values used in modelling, from (Martin, 1994). Set B values are calculated using a fractional dimensionality approach (Mathieu, 1992a; Mathieu, 1992b).

It can be seen that the fractional dimensionality technique calculates binding energies that are in close agreement with those determined experimentally by Martin et al. (Martin, 1994). However, the later method does not replicate the result of Martin et al. that, for the higher strained structures in the series, E869, E870, E876, and E878, the binding energy of the $L_{11}$ exciton is actually greater than that of the $H_{11}$ exciton. Although higher-order transitions are thought to have somewhat lower binding energies (Bastard, 1986) the difference is only slight. Thus, for the modelling of higher-order QW interband transitions, the ground-state exciton binding energies given by Set A were used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E874</th>
<th>E866</th>
<th>E868</th>
<th>E869</th>
<th>E870</th>
<th>E876</th>
<th>E878</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB well depth</td>
<td>107.3</td>
<td>91.7</td>
<td>76.9</td>
<td>67.1</td>
<td>51.1</td>
<td>40.0</td>
<td>28.0</td>
</tr>
<tr>
<td>HH VB well depth</td>
<td>190.1</td>
<td>176.4</td>
<td>163.6</td>
<td>155.2</td>
<td>142.2</td>
<td>133.6</td>
<td>124.1</td>
</tr>
<tr>
<td>LH VB well depth</td>
<td>192.4</td>
<td>197.8</td>
<td>204.5</td>
<td>210.2</td>
<td>218.1</td>
<td>224.1</td>
<td>230.9</td>
</tr>
<tr>
<td>CB offset $Q_c$ (%)</td>
<td>36.0</td>
<td>34.2</td>
<td>32.0</td>
<td>30.2</td>
<td>26.4</td>
<td>23.1</td>
<td>18.4</td>
</tr>
</tbody>
</table>

Table 3.7 Gives values of well depths for conduction band, and, heavy-hole and light-hole valence bands calculated by the theoretical model. Also given are the values of conduction band offset, $Q_c$.  

94
The theoretical model described earlier in this section predicted an unstrained barrier band gap of 1059.8 meV. Neglecting band tilting due to the presence of the internal electric field, the depth of the conduction band QW ranged from 107.3 meV (E874) to 28.0 meV (E878). The depth of the associated heavy-hole (light-hole) valence band QWs ranged from 190.1 (192.4) meV to 124.1 (230.9) meV respectively. The corresponding conduction band offset ratios, $Q_c$, as defined by eqn. (1.3), ranged from 36.0 % to 18.4 % respectively. These conduction band and valence band well depths, along with associated $Q_c$ values for the final modelled structures, are given in Table 3.7.

### 3.4.2 Identification of All Confined-State QW Transitions Observed in the PR Spectra

Each structure’s PR spectrum was fitted with an appropriate number of TDFF oscillators, as given by eqn. (2.31), across an energy range of 810 meV to 1040 meV. The number of TDFFs used was decided by examining the modulus of PR spectrum, $|PR|$, for each structure (calculated by the method outlined in Section 3.2.3.). It is difficult to perceive how many excitonic features are present in each spectrum from the examination of the PR spectra alone due to the overlapping of the numerous multi-peaked features. However, in a $|PR|$ spectrum the multi-peaked differential features are transformed into a number of single peaks, with each peak corresponding to a single confined-state QW interband transition. To a good approximation, the number of transitions present in each PR spectrum can be assessed by simply counting the number of clearly defined peaks in its associated $|PR|$ spectrum. The number of TDFFs used to fit the PR spectrum of each structure are; E874 (7), E866 (7), E868 (6), E869 (7), E870 (5), E876 (5), and E878 (6). As stated in Section 3.2.2, an exponent of $n = 3$ was used for each TDFF, as this mimics the correct lineshape for an excitonic feature in a room temperature PR spectrum (Shanabrook, 1987). All the PR spectra along with their associated fits can be seen in Fig. 3.3. The spectra have only been graphed over the energy range corresponding to the confined-state QW transitions and the InGaAsP barrier feature. Sections of each spectrum have been
expanded to allow weaker features, corresponding to the higher order transitions, to be seen more clearly.

Once all the spectra were fitted, the energies of the fitted TDFFs were compared with the theoretically calculated confined-state transition energies, as determined by the model outlined in Section 3.4.1. The structural parameters, such as strain, composition and well width, derived from the DCXRD measurements were used as starting values for each of the model structures.

For the three highest strained samples in the series, E870, E876, and E878, the agreement with experiment was very good and no further refinement to the model structures was considered necessary. However, for the four lowest strained samples in the series E874, E866, E868, and E869, the agreement between theoretically predicted and experimentally determined transition energies could be improved by allowing for further slight adjustments in some of the QW parameters derived from the DCXRD measurements shown in Table 3.3. The adjustments made are also shown in Table 3.3 as the values in parentheses, and have been taken into account when calculating the transition energies given in Table 3.8. The small set of slight refinements is justified by several facts. The DCXRD simulations were based on the approximation that repeated layers in the structures were assumed to be identical and thus treated as such. Such an approximation may lead to discrepancies between the different types of measurements if, in fact, the wells are not completely identical. As optical-frequency waves penetrate the structures differently from x-rays, the individual PR signals from each of the four slightly different QWs may be weighted differently in comparison to the corresponding DCXRD signals. This would lead to different conclusions about the QW composition and strain from the results of the two techniques. Other imperfections in the wells themselves may also be the cause of discrepancies between the two techniques. For example, non-abrupt interfaces may affect the PR and DCXRD signals in different ways. If a slightly non-rectangular or graded profile is modelled using a rectangular QW, the width deduced may differ slightly from the true width of the well. Consequently the PR and DCXRD measurements would lead to different conclusions about the value of the effective width for the QW.
A full list of the all the confined-state transitions identified in the series of PR spectra is given in Table 3.8. This table gives both the theoretically calculated transition energies, taking into account exciton binding energies and the QCSE, and the energies of the fitted TDFF functions, given by eqn. (2.31), used to fit the experimental data. The uncertainties in the experimentally determined transition energies are shown by the numbers in parentheses and are equal to half the values of the half width at half maximum (HWHM) of the fitted TDFFs. This information is displayed graphically in Figs. 3.8a-g, for structures E874 to E878 respectively. Each graph shows the experimental PR spectrum as dots, overlaid by the fit to the data, which is shown as a solid line. Each fit is the sum of all the individual TDFFs used to fit a particular spectrum. A horizontal and vertical line positioned above the PR spectrum represents each fitted TDFF. The energy, $E_g$, and the amplitude, $C/F^2$, of the TDFF are represented by the position and length of the vertical line, respectively. The horizontal line represents the full width at half maximum (FWHM), of the TDFF. A number of annotated arrows are positioned below the PR spectrum in each figure. These show the energy positions of the theoretically calculated confined-state QW transitions, as derived by the model.
### Table 3.8 Summary of the confined-state QW interband transition energies for the seven structures studied. Energies given are both those calculated theoretically, and observed experimentally in the PR spectra. The tensile strains are those given by the final modelled structures. All energies are in meV. Figures in parentheses give the uncertainty in the experimental transition energies and are equal to half the value of the FWHM of the fitted TDFFs.
Figs. 3.8a (top) and 3.8b (bottom)  Fitting and analysis of full manifold of QW transitions for samples E874 and E866. Curve is a least-square fit using a number of TDDF oscillators. The length and position of vertical lines give the intensity, \(\frac{C}{T}\) and \(E_g\) of the fitted TDDF components, respectively. The horizontal lines at the same position represent the FWHM of the fitted TDDF. Arrows represent the corresponding transition energies obtained from the theoretical model.
Chapter 3: PR, PL and DCXRD Studies of Tensilely Strained InGaAs/InGaAsP Quantum Well Structures

Figs. 3.8c (top) and 3.8d (bottom) Fitting and analysis of full manifold of QW transitions for samples E868 and E869. Curve is a least-square fit using a number of TDFF oscillators. The length and position of vertical lines give the intensity, $C/T^2$, and $E_g$ of the fitted TDFF components, respectively. The horizontal lines at the same position represent the FWHM of the fitted TDFFs. Arrows represent the corresponding transition energies obtained from the theoretical model.
Figs. 3.8c (top) and 3.8d (bottom) Fitting and analysis of full manifold of QW transitions for samples E868 and E869. Curve is a least-square fit using a number of TDFF oscillators. The length and position of vertical lines give the intensity, $C/I^3$, and $E_g$ of the fitted TDFF components, respectively. The horizontal lines at the same position represent the FWHM of the fitted TDFFs. Arrows represent the corresponding transition energies obtained from the theoretical model.
Chapter 3: PR, PL and DCXRD Studies of Tensilely Strained InGaAs/InGaAsP Quantum Well Structures

For the nominally lattice matched sample, E874, the best agreement between the theoretical model and experimental data was achieved using a slightly increased In composition of $x = 0.534$ for the $\text{In}_x\text{Ga}_{1-x}\text{As}$ wells, in comparison to the DCXRD values given in Table 3.3. This composition confirms that the wells are indeed almost lattice-matched with a minimal compressive strain of -0.01%. For samples E874 and E866, the two least strained samples, the well width was reduced slightly from the DCXRD value of 103 Å to 100 Å (these values apply to both samples). For the remaining samples in the series, the well widths were found to be in good agreement with the DCXRD determined values.

For structures E866, E868, and E869, the QW In compositions were increased slightly from the DCXRD values to $x = 0.496$, 0.457, and 0.427, respectively, corresponding
to slightly reduced tensile strains of 0.26%, 0.53%, and 0.73%, respectively. For the remaining three samples in the series, E870, E876, and E878, no adjustments to the In composition in the wells were necessary to achieve the best agreement between the theoretically calculated and experimentally determined.

Some additional interesting facts may be noted from the results of the modelling shown in Table 3.8. Several forbidden transitions are identified, which is now a common occurrence in the PR spectra of QWs (Bhattacharya, 1981). The removal of the parity selection rule in the model allows for the possibility of many transitions; however, in general, not all of these are observed. The reason not all these predicted transitions are observed is not well understood, but such transitions may be extremely weak or broad, effectively masking their presence in room temperature PR spectra. Here, for instance, although the forbidden \( H_{13}, H_{14}, \) and \( H_{15} \) transitions are identified in many of the spectra, there is no evidence of their presence in the PR spectrum of structure E874. This may be seen clearly by examining Fig. 3.8a in the region of the corresponding predicted energies for \( H_{13}, H_{14}, \) and \( H_{15}, \) although the transition that is identified as \( L_{12} \) is close enough to \( H_{14} \) that the TDFF could be described as either, or a combination of both. Furthermore, for this structure, only the model predicts the existence of the forbidden transitions \( H_{21}, H_{24}, \) and \( H_{25} \) at energies of 864 meV, 974 meV, and 1030 meV, respectively, but again there is no unambiguous evidence of these in its PR spectrum. However, sample E874 was the only structure in which the \( H_{22}, L_{22}, \) and \( H_{23} \) transitions were predicted, and these were observed. Similarly, although the \( H_{12} \) transition is identified in the spectra of four of the samples; E874, E866, E869, and E878, there is no evidence for its presence in the spectra of samples E868, E870, E876.

The values of \( Q_c \) as determined by the model solid theory (Van de Walle, 1989) are shown in Table 3.7, and can be seen to decrease with increasing tensile strain. This effect is evident in the experimental results, as no transitions from the \( m = 2 \) conduction sub-band are observed for samples with deduced strains of 0.26% (E866) or greater. This is due to the fact that electron states in this sub-band are no longer confined in this range of strain. Similarly, increasing the amount of tensile strain reduces the number of confined hole states in the valence band, such that the \( n = 5 \) heavy-hole valence sub-band ceases to be confined at a certain value of strain. The
$H_{15}$ transition is not predicted or observed for any of the structures with deduced strains of 1.17% (E876) or above.

### 3.5 The Effect of Tensile Strain on the Ground-State QW Interband Transitions $H_{11}$ and $L_{11}$

This section examines the effect of tensile strain on the two ground-state QW transitions $H_{11}$ and $L_{11}$, in terms of both the energies, and the linewidths of these transitions.

#### 3.5.1 Energies of Ground-State QW Interband Transitions $H_{11}$ and $L_{11}$

The energies of the two lowest confined state QW transitions, $H_{11}$ and $L_{11}$, are plotted as a function of strain in Fig. 3.9a. Each structure has been plotted according to its strain deduced from the modelling process, given by the values in parentheses in Table 3.4 where different from the DCXRD values. The strains used for each sample are those deduced from the modelling process, and are given by the strains in parentheses in Table 3.4 where different from the DCXRD values. The energies of the two transitions for each structure as determined by PL are shown as hollow triangles, except for structures E866 and E868 where only the $H_{11}$ transition energy could be determined from the PL measurements. The energies derived from fitting eqn. (2.31) to the PR spectrum of each structure are shown as filled circles. For the PR measurements, the uncertainties in both the energies and strains are also shown, as vertical and horizontal error bars respectively. The uncertainties in strain are taken as the differences between the modelled values of strain and those derived from DCXRD measurements, except in the case of structure E874 (nominally lattice matched) where the uncertainty in the DCXRD derived value of strain was used, as this is larger.
Fig. 3.9a (top) Graph of ground state $H_{11}$ and $L_{11}$ QW transition energies as a function of deduced strains for series of structures. Energies derived from PR, PL, and theory indicated by circles, triangles, and squares, respectively.

Fig. 3.9b (bottom) Graph of splitting of $H_{11}$ and $L_{11}$ transitions as a function of deduced strains. In both figures, short dashed lines are linear regressions to theoretical values. Long dashed lines indicate position of degeneracy of $H_{11}$ and $L_{11}$ as determined from theory.
Also shown in Fig. 3.9a are the theoretically predicted energies of transition $H_{11}$ and $L_{11}$. These are shown as open squares. The dashed lines through the data points are simple linear regression to the theoretically predicted energies. It can clearly be seen that for the ground state transitions $H_{11}$ and $L_{11}$, a good agreement is achieved between the theoretical calculated energies and the energies given by PR measurements.

It is evident from Fig. 3.9a that the $H_{11}$ and $L_{11}$ transitions increase in energy with increasing tensile strain. This is consequence of the fact that the bulk band gap of the InGaAs QWs increases with decreasing In concentration, which corresponds to increasing tensile strain. In addition, the onset of strain has the effect of bringing the $H_{11}$ and $L_{11}$ transitions closer together in energy until they become degenerate at a certain value of strain. Then, with increasing amounts of tensile strain, the two transitions pass through degeneracy and become increasingly separated. This is demonstrated in Fig. 3.9b.

Fig. 3.9b shows the splitting of the $H_{11}$ and $L_{11}$ transitions, as given by PR, PL and the theoretical model. This figure also demonstrates the good agreement between the PR measurements and the theoretical model. Also shown on both Fig. 3.9a and Fig. 3.9b by the set of long dashed lines is the theoretically predicted point of degeneracy of the $H_{11}$ and $L_{11}$ transitions. This is taken to be the crossing point of the fitted theory lines, in Fig. 3.9a, and as the point of zero splitting in Fig. 3.9b. The $H_{11}$ and $L_{11}$ transitions are anticipated to become degenerate at a tensile strain of 0.36 % ± 0.02 %, which corresponds to an In composition of the In$_x$Ga$_{1-x}$As QWs of $x = 0.481 ± 0.003$.

### 3.5.2 Linewidths of Ground State QW Transitions $H_{11}$ and $L_{11}$ as Determined by |PR|

This section examines the linewidths of the ground state QW transitions as a function of strain. Fig. 3.10 shows the linewidths (FWHM) of the $H_{11}$ transitions in the series of |PR| spectra, as graphed in Fig. 3.5. The |PR| spectra have been used to determine the linewidths instead of PR spectra as the linewidths of fitted TDFFs in the PR
spectra can be influenced by TDFFs of neighbouring transitions. This is the case for structures E874, E866, and E878 and can be seen in Figs. 3.8(a), 3.8(b), and 3.8(g), respectively. In Fig. 3.10, the dotted line is a simple linear regression to the data points. As can be seen in the figure, generally the linewidths of the $H_{11}$ transition increase with increasing tensile strain. This effect is also evident for the $L_{11}$ transition, although not as obvious as for $H_{11}$, and for this reason only the $H_{11}$ linewidths have been graphed.

![Graph of the linewidths of ground-state QW transition $H_{11}$ as a function of deduced strain. Linewidths taken as FWHM of IPR spectra. Line is simple linear regression to data points.](image)

The most probable cause of the linewidth broadening is an increase in interface roughness that occurs with increasing strain in the wells. A similar effect has been observed by Simes et al. in electroabsorption and PL measurements on InGaAs / InGaAsP single QW structures (Simes, 1993). They propose that broadening occurs with increasing strain owing to a roughening of the QW growth surface, as a result of a strain-enhanced transition from a two-dimensional layer-by-layer growth regime to a three-dimensional one.
3.6 Summary

The non-destructive techniques of photomodulated reflectance, photoluminescence, and double crystal x-ray diffraction have been used to characterise a series of seven tensilely strained laser structures. The PL and PR measurements were used to derive the energies of the two ground-state QW transitions, \( H_{11} \) and \( L_{11} \). Furthermore, the PR measurements have revealed additional information about each structure. This includes the observation of a number of, both allowed and forbidden, higher-order QW transitions, as well as features arising from the InGaAsP barrier layers and the InP substrate. Also the PR measurements have been used to give an indication of the internal electric field size in each structure from analysis of the barrier FKOs.

The DCXRD studies, even though the structures were complex, were able to determine structural parameters such as compositions, strains and layer thicknesses, by a systematic comparison of simulated and experimental spectra. QW widths were found to be \( 99 \pm 2 \, \text{Å} \), only slightly wider than nominal \( 95 \, \text{Å} \). The In composition, \( x \), of the \( \text{In}_x\text{Ga}_{1-x}\text{As} \) QWs ranged from \( x = 0.534 \) to \( x = 0.337 \) for the structures E874 to E878, respectively. These values were close to nominal except in the case of the two highest strained structures, E876 and E878, where the In composition is a few percent higher than expected, so the strains were about 0.1 \% less than nominal. The DCXRD measurements also showed that the \( \text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z} \) quaternary barrier material is almost lattice matched to the InP substrate as intended, with a slight compressive strain of around \(-0.03 \pm 0.01 \%\). The In and As compositions, \( x \) and \( y \), were found to be \( y = 0.807 \pm 0.002 \) and \( z = 0.432 \pm 0.001 \). The barrier widths were calculated to be \( 143 \pm 6 \, \text{Å} \), close to the nominal \( 140 \, \text{Å} \).

The PR spectra were fit with eqn. (2.31) to determine the energies of both the ground-state and higher-excited state QW interband transitions. The identification of the various allowed and forbidden transitions for each sample was achieved by comparing the experimentally derived transition energies with those given by a theoretical model. The three-band model was based on an effective mass formalism (Andreani, 1987) and used the structural and compositional information derived from the DCXRD measurements. Band alignments at heterojunction interfaces were calculated using
model solid theory (Van de Walle, 1989). The model also accounted for contributions due to exciton binding energies and the quantum confined Stark effect. The built-in electric fields in the structures were determined by the numerical solution of Poisson’s equation, and these values agreed well with those deduced from the analysis of the barrier FKOs. Only slight adjustments to the DCXRD derived structural parameters were necessary to achieve a good agreement between the experimental and theoretical transition energies.

The behaviour of the ground-state heavy- and light-hole QW transitions has also been demonstrated, showing not only that the ground-state heavy hole transition, $H_{11}$, is more intense in the PR spectra than the corresponding light hole transition, $L_{11}$, but also that its energy rises more rapidly with increasing tensile strain than $L_{11}$. Consequently, at a certain tensile strain, the heavy-hole ground-state transition moves to an energy above that of the light-hole transition. The two transitions are degenerate near 0.36% strain. Furthermore, the linewidths of the ground-state transitions, as given by corresponding features in the IPRI spectra, can be seen to increase with increasing tensile strain. This has been attributed to an increasing roughness of the QW heterojunction interface owing to an increased strain in its QW layers.
3.7 References

Adachi S 1982 J. Appl. Phys. 53 8775
Adams A R 1986 Electron. Lett. 22 249
Aspnes D E and Studna A A 1973a Phys. Rev. B 7 4605
Aspnes D E 1973b Surface Science 37 418
Krijn M C P 1991 Semicond. Sci. Technol. 6 27
998
O’Reilly E P 1989 Semicond. Sci. Technol. 4 121
Shen H and Dutta M 1995 J. Appl. Phys. 78 2151
Silver M and O’Reilly E P 1994 IEEE J. Quant. Electron. 30 547
Yablonovitch E and Kane E O 1988 J. Lightwave Technol. 6 1292
CHAPTER 4

Photomodulated Reflectance and Conventional Reflectance Studies of Vertical Cavity Surface Emitting Lasers

4.1 Introduction

This chapter investigates a typical type of semiconductor laser known as the vertical cavity surface emitting laser (VCSEL) and uses photomodulated reflectance (PR) and conventional normalised reflectance (R) as a means of characterising such structures. Two particular VCSEL structures are investigate here and in Chapter 5, and are referred to as RMB627 and RMB1048. PR and R are used to investigate the behaviour of the cavity mode (CM) with the experimental angle of incidence. Such behaviour can be used to differentiate between features in the PR spectra of VCSELs arising from the CM, and from the confined-state QW transitions. R spectra are calculated for RMB1048 using a transfer matrix method, and are used to model the experimental R spectra enabling certain structural information to be inferred.

The remainder of this chapter is organised as follows: This section re-introduces the concept of the VCSEL and gives a background to its use and commercial application. This is followed by a description of the two VCSEL structures, RMB627 and RMB1048. The basic features observed in the PR spectra of these VCSELs are then
described. Finally, the experimental R spectra of RMB1048 are modelled, and the errors in the Ga and Al growth fluxes for this structure are derived.

### 4.1.1 Review of VCSELS

This section gives a brief overview of the applications of VCSELS along with various techniques currently used for their characterisation. The concept of the vertical cavity surface emitting laser has already been introduced in Section 1.4. However, as a reminder to the reader, some of the key features of a VCSEL will be described again.

One of the fundamental features of any working laser device is the Fabry–Pérot cavity, which encompasses the gain medium of the laser. This forces a coherent build up of photon population within the cavity. A VCSEL differs from a conventional semiconductor laser in that the Fabry–Pérot cavity is orientated ‘vertically’, in other words, along the growth direction. The vertical orientation of the cavity has a number of advantages and disadvantages in terms of producing a working laser device. One advantage with this orientation of the cavity is that it is possible to closely pack numerous individual VCSEL devices together on a single wafer, thus allowing large-scale arrays of VCSEL devices to be constructed relatively easily. However, owing to restraints on the maximum layer thickness achievable by epitaxial growth techniques, the length of the cavity in a VCSEL must be greatly reduced compared with a conventional semiconductor laser. Generally, a VCSEL cavity is just a few multiples in length of its actual lasing wavelength. As a result, mirrors with a very high reflectivity are required to enclose the cavity if the cavity is to have a positive round trip gain. In fact, mirrors of such high reflectivity are possible in the form of distributed Bragg reflector (DBR) stacks. DBRs are composed of repeated identical pairs of semiconductor layers, with each layer being a quarter of the lasing wavelength in optical thickness. The two layers in each pair are formed from materials with differing refractive indices to ensure that the travelling optical wave sees an interface between the two layers and is partially reflected. A schematic diagram of a VCSEL is given in Fig. 1.9(b). For more information of the construction
of a VCSEL, the reader is referred to Section 1.4 (Geels, 1991; Jewell, 1991; Geels, 1993; Sale, 1995a).

There are other important advantages of VCSELs over conventional semiconductor lasers, aside from the ability to form large-scale arrays on a single wafer. VCSELs have less divergence of the emitted light because of a larger aperture. Furthermore, owing to the shape of the aperture, the beam profile is circular, and as a result is more easily coupled to an optical fibre.

VCSEL arrays of 64 (8 × 8) independently accessible elements have been fabricated on a single chip (Von Lehman, 1991). Larger arrays, with up to 1024 (32 × 32) individually accessible devices have also been created on chip, using matrix addressing to access individual elements (Orenstein, 1991). In addition, VCSEL arrays with novel properties have been created such as 2-D phase locked arrays (Orenstein, 1992; Warren, 1992). Such VCSELs have elements operating in a single coherent mode and are used as high brightness sources. Also 2-D multiple wavelength arrays have been fabricated (Chang-Hasnain, 1991a) for use in applications such as wavelength division multiplexing (Maeda, 1991; Chang-Hasnain, 1991b) and optical interconnects (Hasain, 1992; Wong, 1995).

An important factor determining whether or not a VCSEL device will actually work correctly is the accuracy of its growth. There are essentially three components of a VCSEL, each having its own working wavelength. The first is the Fabry–Pérot cavity and its associated cavity mode (CM) wavelength, designated as \( \lambda_{CM} \). There is also the working wavelengths of the two DBR stacks, which are denoted as \( \lambda_{DBR} \). Finally, the QW (or QWs) used as the active gain medium has a particular wavelength associated with the ground-state transition of the well, which is described as \( \lambda_{QW} \).

In a working VCSEL it is essential that the following criterion is met:

\[
\lambda_{CM} = \lambda_{QW} = \lambda_{DBR}
\]

(4.1)
This requirement must be satisfied to within 1% for a device to function correctly (Jewell, 1991).

For this reason, the characterisation of VCSEL structures plays an essential role in the fabrication of working laser devices, both \textit{in situ}, during the growth of the wafer, as well as after growth prior to any device formation.

A variety of techniques are used for the characterisation of VCSEL structures. Conventional reflectance responses of VCSEL structures are used to characterise both the Bragg stack layers and the cavity resonance. This can be done either \textit{in situ} during growth (Bacher, 1992) in order to evaluate the quality of both DBR stacks separately, or post VCSEL fabrication (Faist, 1989; Christensen, 1992; Choquette, 1997; Okamoto, 1997). Photoluminescence (PL) is used to determine the energies of the confined-state transitions of the QW layers. The wavelength associated with the particular QW transition used for optical gain must satisfy eqn. (4.1) in order for the VCSEL to work. Unfortunately, a direct PL measurement of a fully realised VCSEL structure can be misleading. The optical mode of the cavity has a strong influence on the PL emission, making it hard to determine the true energy of the QW transition. The PL emission is strongly modulated by the surrounding cavity, so it consequently occurs at the energy of the CM rather than at the energy of the QW transition. This problem is overcome either by growing the associated QW layers and surrounding structure separately, and using this as a reference for the growth process (Schneider, 1992; Mars, 1997), or by temporarily interrupting the growth before the top DBR layers have been grown (Amano, 1998), or by etching away the top BDR stack after growth. Gramlich \textit{et al.} have demonstrated that it is possible to use PL to probe the QW layers of a fully realised VCSEL structure by measuring the in-plane PL emissions which are unaffected by the cavity interaction (Gramlich, 1995). However, such measurements are difficult and require specialised optics.

Other characterisation techniques used include double crystal x-ray diffraction (Christensen, 1992) and spectroscopic ellipsometry (Maracus, 1993; Herzinger, 1996), both of which are used to determine the thickness and composition of the DBR layers. Pyrometric interferometry (Grothe, 1993; Houng, 1994) is often used \textit{in situ} during growth to ensure that individual DBR layers are grown to the correct
Chanter 4: 

Phntomodulated Reflectance and Conventional Reflectance Studies of VCSELs 

thickness. Modulation spectroscopy has been used to a limited extent in the investigation of VCSELs in the form of contactless electroreflectance (Pollak, 1995; Moneger, 1996). These workers examined a test InGaAs/GaAlAs/GaAs VCSEL structure grown with an incomplete top DBR stack that contained only 10 repeat periods. Furthermore, they were unsuccessful in obtaining a PR signal from this test VCSEL. PR measurements have been performed successfully on a fully realised GaAs/GaAlAs VCSEL structure at 110K by Berger et al (Berger, 1995; Berger, 1996). However, in order to acquire room temperature PR measurements, they used an incomplete structure containing only the bottom BDR and 98% of the cavity.

4.1.2 I.R. VCSEL Samples 

The work in this chapter and Chapter 5 is developed using PR and R to investigate two different VCSEL structures, which are referred to as RMB1048 and RMB627. Both structures are based on an InGaAs/GaAs/AlAs/AlGaAs material system grown on (100) GaAs n+ substrates by solid source molecular beam epitaxy (Sze, 1985). Details of the growth are given elsewhere (Sale, 1992; Sale, 1995b). Both structures were designed for a working I. R. wavelength of $\lambda = 1 \mu m$.

The nominal structure of RMB1048 consists of 278 layers and it has an overall thickness of $\sim 7.8 \mu m$. A schematic diagram of the nominal structure of this sample is given in Table 4.1. For the active gain of this structure, a single compressively-strained In$_{0.23}$Ga$_{0.77}$As QW of 85 Å is used, embedded in an undoped cavity region made of GaAs. The optical length of the cavity region is $\sim \lambda$ and the QW is positioned in the centre, at the antinode of the cavity optical field. The top DBR is p-type with Be used as the dopant, and consists of 16 repeats of a set of multiple layers. The repeated set comprises four layers: GaAs, AlAs, and two thinner intermediate ternary layers of Al$_{0.5}$Ga$_{0.7}$As and Al$_{0.5}$Ga$_{0.5}$As. These intermediate layers help reduce the resistivity of the stack without compromising the DBR’s reflectivity. This is achieved by a combination of the modulation doping in the DBR, and by the fact that these layers reduce the band offsets at the interfaces between the GaAs and AlAs.
layers (Sugimoto, 1992; Kurihara, 1993). The bottom BDR is $n$-type, using Si as a dopant and is identical to the top DBR, only with 28 repeats.

<table>
<thead>
<tr>
<th>repeats</th>
<th>layer thickness (Å)</th>
<th>material</th>
<th>dopant</th>
<th>concentration ($10^{18}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
<td>GaAs</td>
<td>Be</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>949</td>
<td>GaAs</td>
<td>Be</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.3}$Ga$</em>{0.7}$As</td>
<td>Be</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.5}$Ga$</em>{0.5}$As</td>
<td>Be</td>
<td>5.0</td>
</tr>
<tr>
<td>16</td>
<td>676</td>
<td>AlAs</td>
<td>Be</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.3}$Ga$</em>{0.7}$As</td>
<td>Be</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.3}$Ga$</em>{0.7}$As</td>
<td>Be</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>507</td>
<td>GaAs</td>
<td>Be</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.3}$Ga$</em>{0.7}$As</td>
<td>Be</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.3}$Ga$</em>{0.7}$As</td>
<td>Be</td>
<td>5.0</td>
</tr>
<tr>
<td>1</td>
<td>664</td>
<td>AlAs</td>
<td>Be</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>AlAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1436</td>
<td>GaAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>In$<em>{0.23}$Ga$</em>{0.77}$As</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1436</td>
<td>GaAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>AlAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>664</td>
<td>AlAs</td>
<td>Si</td>
<td>1.0</td>
</tr>
<tr>
<td>28</td>
<td>100</td>
<td>Al$<em>{0.5}$Ga$</em>{0.5}$As</td>
<td>Si</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.5}$Ga$</em>{0.5}$As</td>
<td>Si</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>507</td>
<td>GaAs</td>
<td>Si</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.5}$Ga$</em>{0.5}$As</td>
<td>Si</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.5}$Ga$</em>{0.5}$As</td>
<td>Si</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>676</td>
<td>AlAs</td>
<td>Si</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>Al$<em>{0.3}$Ga$</em>{0.7}$As</td>
<td>Si</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Al$<em>{0.3}$Ga$</em>{0.7}$As</td>
<td>Si</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>GaAs</td>
<td>Si</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Substrate</td>
<td>GaAs</td>
<td>Si</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 4.1 The nominal structure of sample RMB1048. Grouped layers are repeated according to values given. Also shown are layers thicknesses, compositions and doping parameters (Be: $p$-type, Si: $n$-type).
Table 4.2  The nominal structure of sample RMB627. Grouped layers are repeated according to values given. Also shown are layers thicknesses, compositions and doping parameters (Be: p-type, Si: n-type).

<table>
<thead>
<tr>
<th>repeats</th>
<th>layer thickness (Å)</th>
<th>material</th>
<th>dopant</th>
<th>concentration ((10^{18} \text{ cm}^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1323</td>
<td>GaAs</td>
<td>Be</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>~220</td>
<td>Super Lattice</td>
<td>Be</td>
<td>10</td>
</tr>
<tr>
<td>718</td>
<td>AlAs</td>
<td>Be</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>609</td>
<td>GaAs</td>
<td>Be</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>~220</td>
<td>Super Lattice</td>
<td>Be</td>
<td>10</td>
</tr>
<tr>
<td>609</td>
<td>AlAs</td>
<td>Be</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>Al(<em>{0.5})Ga(</em>{0.5})As</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1294</td>
<td>GaAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>In(<em>{0.22})Ga(</em>{0.77})As</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1343</td>
<td>GaAs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>In(<em>{0.22})Ga(</em>{0.77})As</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1343</td>
<td>GaAs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>In(<em>{0.22})Ga(</em>{0.77})As</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1294</td>
<td>GaAs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>200</td>
<td>Al(<em>{0.5})Ga(</em>{0.5})As</td>
<td>Si</td>
<td>10</td>
</tr>
<tr>
<td>616</td>
<td>GaAs</td>
<td>Si</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>Al(<em>{0.5})Ga(</em>{0.5})As</td>
<td>Si</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>532</td>
<td>GaAs</td>
<td>Si</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Substrate</td>
<td>GaAs</td>
<td>Si</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

The nominal structure of RMB627 consists of 329 layers and has an overall thickness of ~6.7 μm, as given in Table 4.2. This structure is designed such that the cavity has an optical length of ~2λ; as a consequence, the optical field has three antinodes in the cavity region. Three compressively-strained In\(_{0.22}\)Ga\(_{0.77}\)As QWs, each 85 Å, are used to provide the gain in the active region and are positioned to coincide with each of the three antinodes of the cavity optical field. The top DBR in this structure consists of 14 repeats of a AlAs, GaAs, and a superlattice layer, and is p-type with Be used as the dopant. The superlattice layer is made up of a number of individual layers each between 2 - 10 monolayers in thickness. Half of this superlattice set of layers consists of alternating GaAs and Al\(_{0.5}\)Ga\(_{0.5}\)As layers, and the other half of Al\(_{0.5}\)Ga\(_{0.5}\)As and AlAs layers. The inclusion of this superlattice grading, and the modulation doping of
the whole DBR, is again to reduce the resistivity of the stack sufficiently whilst maintaining its optical reflectivity. The bottom DBR does not use a superlattice layer and instead has 28 repeats of a GaAs and Al$_{0.5}$Ga$_{0.5}$As layer combination. The bottom uses modulation doping to lower its resistivity and is $n$-type with Si used as the dopant.

### 4.2 Photomodulated Reflectance of a VCSEL

In this section, as well as in Section 4.3, RMB1048 is studied to investigate some of the basic features and concepts observed in the PR spectroscopic study of VCSEL structures. RMB1048 is studied because the energy of the cavity mode does not coincide with that of the ground-state QW transition, $H_{11}$, as it should do. In Chapter 5, it is shown that this is a consequence of an incorrect calibration during the growth of the structure. However, this consequence is particularly convenient for the present study as it allows the cavity and QW modes to be investigated independently.

#### 4.2.1 Experimental Details

PR spectra of RMB1048 were taken using the experimental apparatus described in Section 2.2 and shown in Fig. 2.4a. The 2 mW He-Ne laser was chopped at a frequency of 333 Hz. The spectrometer slit was 2 mm $\times$ 800 $\mu$m giving a typical resolution of 3.6 meV (FWHM) across the energy range studied. PR scans were taken both in phase with the PL of the sample, as well as $90^\circ$ out of phase (in quadrature), over an energy range of 1.03 eV to 1.77 eV. Spectra were taken at incident angles of $15^\circ$ to $75^\circ$ in steps of $15^\circ$ and care was taken to perform measurements at the same position on the sample each time. Individual spectra were typically taken over $\sim$1 hour. The corresponding normalised reflectance (R) spectra were then obtained by the method outlined in Section 2.3.
4.2.2 Identification of Confined-State QW Transitions and Cavity Mode Features in the PR Spectrum of a VCSEL

The sample RMB1048 is useful as an introduction to the work in this chapter as a number of distinct and separate features are observed in its PR spectrum. Fig. 4.1 shows both the PR and corresponding R spectrum taken of structure RMB1048 at an incident angle of 45°. The PR spectrum shown was taken with the phase of the lock-in amplifier set at 90° out of phase with the PL. The R spectrum shows a high reflectance stop-band, which is due to the high reflectivity of the DBR stacks across this spectral range. In the centre of this stop-band can be seen a dip which arises from the optical mode of VCSEL cavity and is consequently referred to as the cavity mode (CM). This feature in the reflectance spectrum has a corresponding feature in the PR
spectrum and is clearly present in the PR spectrum shown in Fig. 4.1. The origin of this feature in the PR spectrum of a VCSEL is described in Chapter 5. The clear feature observed in the PR spectrum at an energy of 1.190 eV is due to the ground-state QW transition, $H_{11}$, in contrast to the R spectrum where there is no information about the confined-state QW transitions. Also present in the PR spectrum are Franz-Keldysh oscillations (FKO) and these will be used to give an estimation of the size of the built-in electric field within the structure.

Fig. 4.2 shows five PR spectra for sample RMB1048 taken at the same position on the sample. The spectra have been taken over a range of incident angles, ranging from $15^\circ$ to $75^\circ$ in steps of $15^\circ$, with the lock-in amplifier set to the phase of the PL. Fig. 4.3 shows the corresponding PR spectra but with the phase of the lock-in amplifier set at $90^\circ$ out of phase with the PL. Generally, for the PR of simple structures, the strongest PR signal is obtained at the same phase as the PL. In this VCSEL structure, however, there is still an appreciable PR signal present at $90^\circ$ out of phase with the PL. Taking spectra at this phase setting has the obvious advantage of greatly reducing the amount of unwanted PL being detected and, as a consequence, the overall signal to noise ratio is improved. This is apparent in Figs. 4.2 and 4.3, especially at energies above 1.5 eV where the sensitivity of the InGaAs detector is greatly reduced.

Oscillatory behaviour is clearly visible in all of the PR spectra, in both Figs. 4.2 and 4.3, at energies above ~ 1.40 eV. This results from FKOs in the GaAs layers in the structure. The period of these oscillations is used to give an estimation of the built-in electric field within the samples by means of graphical analysis, as described in Section 3.2.2 (Hughes, 1995; Shen, 1995). Using the two alternative graphical methods outlined in Section 3.2.2, the average value for the built-in electric field was determined to be $18.0 \pm 0.8$ kV/cm. As expected, this value was found to be independent of the angle of incidence at which the spectrum was taken. As RMB1048 is doped on both sides of the structure, one can place a theoretical limit on the maximum size of the built-in field, by taking a potential energy difference of 1.42 eV across the cavity region and calculating the potential gradient.
Fig. 4.2 PR spectra of sample RMB1048 detected in phase with PL. Experimental angles of incidence are given by values on the right. PR spectra show structure due to confined-state QW transition, $H_{11}$, CM and FKOs. Individual spectra have been offset by factors of $1 \times 10^3$. Small sections of the spectra are magnified by the factor given.
Fig. 4.3  PR spectra of sample RMB1048 detected 90° out of phase with PL. Experimental angles of incidence are given by values on the right. PR spectra show structure due to confined-state QW transition, \textit{H}_{11}, CM and FKOs. Individual spectra have been offset by factors of \(1 \times 10^3\). Small sections of the spectra are magnified by the factor given.
If the undoped cavity region is taken to be 3157 Å wide then the theoretical upper
limit of the field size is calculated to be 45 kV/cm. This discrepancy between the
upper theoretical estimate for the built-in field, and the value determined
experimentally is quite common (van Hoof, 1989) and is thought to be because of
photovoltage effects. This is in agreement with studies performed by Berger et al.
(Berger, 1996).

There are two distinct features in all the spectra shown in Figs. 4.2 and 4.3. The
former lies at an energy of 1.185 eV and is attributed to the ground-state QW
transition, \( H_{11} \). This feature remains at a constant energy independent of incident
angle. However, the latter feature can be seen to increase in energy with angle of
incidence. This latter feature moves from 1.250 eV, for an incident angle of 15\(^\circ\), to an
energy of 1.290 eV for an incident angle of 75\(^\circ\), and is due to the optical mode of the
cavity. This demonstrates the usefulness of PR as a characterisation technique for
VCSELs. Thus, with a limited number of experiments, it is easy to determine which
of the features in a PR spectrum of a VCSEL are due to confined-state transitions
within a QW, and which feature is due to the CM. This enables the values of \( \lambda_{QW} \) and
\( \lambda_{CM} \) in eqn. (4.1) to be determined relatively easily from the examination of a PR
spectrum.

As a simple approximation, the angular dependence of the cavity mode can be
modelled by considering a cavity of mean refractive index, \( n \), with an effective
thickness, \( d \), enclosed by two reflecting surfaces. With the condition that the rays
reflecting from the front and back surfaces of the cavity must destructively interfere,
the wavelength of the cavity mode, \( \lambda_{CM} \), can be shown to be:

\[
\lambda_{CM} = \frac{2d}{m} \sqrt{n^2 - \sin^2 \theta_i}
\]

(4.2)

where \( \theta_i \) is the external angle of incidence and \( m \) is an integer.

This angular dependence of the CM feature also allows its energy at normal incidence
to be inferred without having to perform measurements actually at normal incidence.
This is achieved by plotting \((\lambda_{CM})^2\) against \(\sin^2(\theta_i)\), and extrapolating the graph to normal incidence. This wavelength, or energy, is of particular interest, of course, as it corresponds to the energy of the CM in a working VCSEL.

In some samples, it is also possible to move the CM feature to a different energy simply by performing the measurement on a different point on the sample. Such position tuning of the CM is made possible because of growth irregularities that occur as a result of the MBE growth. Growth variations across the wafer lead to a gradual variation of the effective cavity length, with the cavity being thickest in the centre of the wafer and thinner towards the edges.

For structure RMB1048 it was not possible to bring the ground-state QW transition, \(H_{11}\), and the CM feature, into resonance using either position tuning or the angle dependence of the CM to alter its energy. In structure RMB1048, the condition set by eqn. (4.1) for a working VCSEL is not satisfied, one can conclude that it would be impossible to make a device from this sample which worked at room temperature conditions. However, it has been shown that it is possible to bring the CM into resonance with the \(H_{11}\) transition in this sample by using either high pressure (Klar, 1998) or low temperature (Klar, 1999) to shift the \(H_{11}\) transition to a higher energy.

Some additional points of interest arise from a closer inspection of Figs. 4.2 and 4.3. In both figures, the feature originating from the QW transition, \(H_{11}\), is an order of magnitude weaker in the spectra taken at 15° and 30°, compared to those at higher angles of incidence. The reason for this behaviour becomes apparent after the associated normalised reflectance (R) spectra are examined. The set of R spectra is shown in Fig. 4.5, in Section 4.3.3, and in the same figure the energy of the \(H_{11}\) transition is indicated by the dashed line. In the case of the spectra taken at 15° and 30° we can see that the position of the \(H_{11}\) transition lies under the broad high reflectance stop band of the DBRs. This makes optical penetration of the incident probe beam more difficult at this energy, and as a result the signal from the QW layer is greatly reduced for these two spectra. As the experimental angle of incidence is increased, the high reflectance stop-band moves to higher energies, reducing the attenuation of the incident probe light at the energy of the \(H_{11}\) transition.
It is also evident that the magnitude of the CM feature is greater between the experimental angles of incidence of 30° to 60°, than for the spectra taken at 15° and 75°. This is a consequence of the CM being near resonance with a higher-order QW transition in the spectra taken from 30° to 60°. This is discussed in more detail in Chapter 5.

4.3 Reflectance Studies of VCSELs

This section examines the transfer matrix method for modelling the reflectance spectrum of a multi-layered structure. Using this technique, the R spectra of RMB1048, corresponding to the PR spectra described in Section 4.2, will be modelled, enabling certain structural parameters to be derived. The experimental details concerning the acquisition of all the data shown in this section are given elsewhere. For RMB1048, these can be found in Section 4.2.1, and for RMB627, in Section 5.3.1.

4.3.1 Transfer Matrix Theory

This section describes how the transfer matrix method, or the Jones matrix method, is used to calculate the reflection response of a multi-layered structure (Klein, 1986). If the thickness and dielectric function of each individual layer in a particular structure are known, then it is possible to calculate the reflection spectrum of the whole structure by means of matrix multiplication. This technique is of particular importance as it takes into account all multiple reflections within any particular layer.

Consider a multi-layered structure consisting of \( N \) layers, with the final layer, representing the substrate, being of infinite thickness. This is represented schematically in Fig. 4.4, which shows such a structure with light being incident on the system from left to right, at an initial incident angle of \( \theta_i \).
The incident medium is usually taken to be air and hence $n_I = 1$. In any particular layer, $j$, within the structure, the optical field can be considered as consisting of two components, $E_R$ travelling to the right, and $E_L$ travelling to the left. The total optical field in layer $j$ is written as a vector:

$$E_j = \begin{pmatrix} E_{IJ} \\ E_{Rj} \end{pmatrix}$$  \hspace{1cm} (4.3)

For light crossing a given interface, such as between layers $i$ and $j$, we define the reflection and transmission coefficients, $\rho_{ij}$ and $\tau_{ij}$, as:

$$\rho_{ij}(s) = -\frac{\sin(\theta_i - \theta_j)}{\sin(\theta_i + \theta_j)} \hspace{1cm} \tau_{ij}(s) = \frac{2\sin\theta_j \cos\theta_i}{\sin(\theta_i + \theta_j)}$$  \hspace{1cm} (4.4a,b)

for s-polarised light, where $\theta_i$ and $\theta_j$ are the angles of the incident and transmitted light rays at the interface between layers $i$ and $j$, and,
\[ \rho_{\theta}(p) = \frac{\tan(\theta_i - \theta_j)}{\tan(\theta_i + \theta_j)} \]

\[ \tau_{\theta}(p) = \frac{2 \sin \theta_j \cos \theta_i}{\sin(\theta_i + \theta_j) \cos(\theta_i - \theta_j)} \]  

(4.5a,b)

for \( p \)-polarised light.

This enables us to transform the field components, eqn. (4.3), on the right of any particular interface to those on the left by using an interface transition matrix, defined as:

\[
H_{ij} = \frac{1}{\tau_{ij}} \begin{pmatrix} 1 & \rho_{ij} \\ \rho_{ij} & 1 \end{pmatrix}
\]  

(4.6)

In crossing a given layer from left side to right, a phase factor \( e^{i\beta} \) is introduced. The exponent is defined as:

\[ \beta_j = \frac{2\pi}{\lambda_0} n_j d_j \cos \theta_j \]  

(4.7)

for layer \( j \), where \( d_j \) and \( n_j \) are the thickness and refractive index, respectively, and \( \lambda_0 \) is the wavelength of the light ray in a vacuum. This enables a layer propagation matrix to be defined:

\[
L_j = \begin{pmatrix} e^{-i\beta_j} & 0 \\ 0 & e^{i\beta_j} \end{pmatrix}
\]  

(4.8)

The important boundary condition used to derive the optical field components travelling in both directions, at any interface within the system, is that in the final medium there can be no reflected optical field travelling to the left. Therefore,

\[
E_N = \begin{pmatrix} 0 \\ E_{RN} \end{pmatrix}
\]  

(4.9)
With this boundary condition, the optical field components at the first interface of any structure can be calculated by simply multiplying the appropriate combination of interface transition with the layer propagation matrices, to arrive at a matrix that represents the whole structure.

\[ E_1 = H_{12} L_2 ... L_{N-1} H_{N-1,N} E_N \]  
\[ E_1 = S_{1N} E_N \]  

The stack matrix \( S_{1N} \) contains the combined effect of all the layers including multiple reflections:

\[ S_{1N} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \]  

The amplitude reflection coefficient for the entire stack, \( \rho_s \), can be derived by using the boundary condition of eqn. (4.9) along with eqns. (4.3, 4.11, and 4.12).

\[ \rho_s = \frac{E_{L1}}{E_{R1}} = \frac{S_{12}}{S_{22}} \]  

The intensity reflectance, \( R \), is then simply:

\[ R = |\rho|^2 \]  

Generally, the reflectance, \( R \), is calculated separately for both \( s \)- and \( p \)-polarisations of the incident light. For randomly polarised incident light, the average of these two spectra may be taken. Thus, the reflectance can be calculated for any complex multilayered structure so long as the complex dielectric function of all the constituent materials is known across the energy range of interest. With knowledge of the
complex dielectric function, the coefficients $\rho_j$, $\tau_j$, and $\beta_j$ can be calculated for any particular layer.

### 4.3.2 Polarisation Effects on the R and PR Spectra of VCSELs

This section investigates the effect that the polarisation of the incident light has on the reflectance spectrum of a VCSEL. Reflectance spectra were calculated for sample RMB627 using the transfer matrix method outlined in Section 4.3.1. Fig. 4.5a shows the reflectance spectra calculated for both $s$- and $p$-orientations of polarised light, incident on the sample at $60^\circ$. The $s$-polarisation R spectrum is shown as the light grey line and the $p$-polarisation is shown as the black line, highlighting several differences. Firstly, the CM dip centres on different energies according to which polarisation of light is incident. In fact, the $p$-polarisation CM centres at a slightly higher energy than the $s$-polarisation, about 2 meV for an incident angle of $60^\circ$. Secondly, the two CM dips are of different depths, with the dip in the $s$-polarisation spectrum having almost zero reflectance at its centre point.

These two facts are confirmed experimentally in Fig. 4.5b. This figure shows the normalised reflectance spectra taken of sample RMB627. The spectra are from a series of data examined in Chapter 5. The $s$-polarisation R spectrum is shown as the light grey line and the $p$-polarisation is shown as the black line. The R spectra correspond to measurements made at an experimental incident angle of $60^\circ$, and correspond to the PR spectrum shown in Fig. 5.2f, at a micrometer setting of 3.0. Both Fig. 4.4a and 4.4b demonstrate that at this angle of incidence ($\theta = 60^\circ$), the CM dip in the R spectrum measured with $s$-polarised light is centred about 2 meV lower in energy than for the spectrum with $p$-polarised light. The asymmetrical lineshape of the CM dip in Fig. 4.4b is owing to the influence of the confined-state transition, $H_{21}$, within the QW layer of the structure. This feature is addressed in more detail in Section 5.3.2.
Chapter 4: Photomodulated Reflectance and Conventional Reflectance Studies of VCSELs

Fig. 4.5a (top) R spectra of RMB627 with nominal layer dimensions, calculated for s- and p-polarisations of light using transfer matrix formalism.

Fig. 4.5b (middle) R Spectra of RMB627, taken at 60° incidence using s- and p-polarised light. Spectra correspond to PR spectrum 3.0, in Fig. 5.2f, Section 5.3.2.

Fig. 4.5b (bottom) PR spectra of RMB627 corresponding to R spectra shown in Fig. 4.5a. Spectra taken 90° out of phase with PL.
Fig. 4.5c shows the PR spectra measured using $s$- and $p$-polarised light, corresponding to the two R spectra graphed in Fig. 4.5b (RMB627 at an incident angle of 60° and a micrometer setting of 3.0). Again, the $s$-polarisation spectrum is shown as a grey line, and $p$-polarisation as the black line. It is obvious that the different positions of the CM dip, as shown in the reflectance spectra (Fig. 4.5b), have a consequential effect on the lineshapes of the corresponding PR spectra.

### 4.3.3 Modelling and Fitting of VCSEL Reflectance Spectra

Fig. 4.6 shows a series of R spectra of sample RMB1048 taken at different experimental angles of incidence. The R spectra, shown as dots, have been taken at incident angles of 15° to 75° in steps of 15°, and are the R spectra corresponding to the AR/R spectra displayed in Figs. 4.2 and 4.3. All the R spectra show a high reflectance stop band, in the centre of which lies a dip due to the optical mode of the cavity. The position of the CM dip is indicated by an arrow for the spectrum taken at 75° incidence. The high reflectance stop-bands are approximately 0.32 eV wide and are flanked on each side by a number of subsidiary interference peaks. The position of the ground-state QW transition, $H_{11}$, as determined from the PR spectra (Figs. 4.2 and 4.3) is indicated by a dashed line. It is evident from this figure that the energy of the $H_{11}$ transition lies underneath the high reflectance stop-band for the spectra taken at incident angles of 15° and 30°. The method by which the experimental R spectra are modelled will be described next, and the solid lines in Fig. 4.5 represent the final lineshape fits to the spectra.

The series of experimental R spectra of RMB1048 were modelled in the following manner. Theoretical R spectra were calculated for the nominal structure of RMB1048 as defined in Table 4.1, using the transfer matrix method described in Section 4.3.1. Transfer matrix calculations were performed using software developed at Surrey¹.

¹ Dr. T. J. C. Hosea, Department of Physics, University of Surrey, Guildford, Surrey, GU2 5XH.
Chapter 4: Photomodulated Reflectance and Conventional Reflectance Studies of VCSELs

Fig. 4.6 R spectra of RMB1048. Experimental angle of incidence given by values on the right of figure. Solid lines show best fits to data, calculated using transfer matrix method. Dashed line indicates position of $H_{11}$ transition as defined by PR spectra in figs. 4.2 and 4.3. Position of CM is also shown for spectrum at 75°. Spectra have been offset by factors of 1.
Chapter 4: Photomodulated Reflectance and Conventional Reflectance Studies of VCSELs

The complex dielectric functions used in the calculation were taken from the database of commercial software used to drive a spectroscopic ellipsometer (SE), produced by J A Woollam Co., Inc⁶. In the case of the In_{0.23}Ga_{0.77}As QW layer, the complex dielectric function of the bulk material was used, but with the absorption spectrum shifted by an appropriate amount to account for the effect of quantum confinement.

To produce a realistic R spectrum from these ideal spectra calculated by the transfer matrix method, several additional factors need to be taken into account. The first factor is evident from the studies in Section 4.3.2, which showed that R spectra, calculated for orthogonal polarisations of incident light, differ. Tests made on the spectrometer probe light showed that it is composed of equal proportions of s- and p-polarised light. Therefore, in order to produce a theoretical R spectrum with no polarisation dependence, R spectra were calculated for both polarisations and then averaged in equal ratios.

The second factor can be seen from the examples of the theoretical R spectra calculated for structure RMB627 shown in Fig. 4.5a for an incident angle of 60°. These clearly demonstrate that the CM dip is both narrower and deeper than the CM dip in the corresponding experimentally measured spectrum at 60°, shown in Fig. 4.5b. If the finesse of the cavity, \( F \), is defined as,

\[
F = \frac{E_{\text{CAV}}}{(2 \times W)}
\]

(4.15)

where \( W \) is the width of the cavity dip (FWHM), then the associated finesse of the cavity can be calculated for both the experimental and theoretical R spectra. The experimental R spectrum for RMB627 taken at 60° incidence using s-polarised light, (Fig. 4.4b) has a depth of ~0.27 and a width of ~17 meV. With \( E_{\text{CAV}} \sim 1.224 \text{ eV} \), the CM finesse in the experimental spectrum is ~36. However, for the theoretically R spectrum of RMB1048 calculated for the same angle of incidence and polarisation of

---

⁶ J A Woollam Co., Inc. Spectroscopic Ellipsometers and Thin Film Characterisation, 645 M St., Suite 102, Lincoln, NE 68508. USA.
light (Fig. 4.5a), the CM was found to have a depth of \(-0.9\) and a width of \(\sim 4.1\) meV, which leads to a much greater CM finesse of \(\sim 156\).

There are three different causes as to why the actual CM finesse in an experimental spectrum is less than observed in the theoretically calculated spectrum. In each case, the reduction in the CM finesse is due to an effective broadening of the CM dip. The first, and least significant, is due to the effect of the finite instrumental energy-resolution (FWHM \(\sim 3.6\) meV). The second is that the incident and reflected beams have an angular spread of approximately \(9^\circ\). This variation of incident angle has a consequential effect on the energy of the CM, as may be seen from eqn. (4.2). Finally, the finite size of the image of the probe beam on the sample's surface results in a variation in the energy of the CM. This effect is of particular significance for sample RMB1048 where the positional variation of the energy of the CM across the wafer is \(\sim 5\) meV/mm. At normal incidence the image of the probe beam has a width of 800 \(\mu\)m in the direction of the variation. However, at an incident angle of \(75^\circ\), the image width becomes \(\sim 3.2\) mm and results in an energy variation of the CM of \(\sim 16\) meV.

The combined effects of all these factors can be accounted for here by convoluting a theoretical R spectrum with a Gaussian broadening function with FWHM \(\sim 8\) meV.

The lineshape fits shown in Fig. 4.6 were calculated using both the polarisation averaging and accounting for the 'smearing' due to the above three effects. Initially, theoretical R spectra were calculated for the nominal structure of RMB1048, shown in Table 4.2. Generally, the theoretical calculations produced R spectra which had a CM dip positioned at too low an energy compared with the experimental data. With the quality of fit between experimental and theoretical spectra being determined by a least squares function, a better agreement was initially achieved by simply scaling all the layer thicknesses in the structure by an appropriate factor. However, Mortaza and Campbell (Mortaza, 1995) have shown that it possible to model the R spectra of Bragg stacks by evaluating different variations in the layer thicknesses, based on the assumption that incorrect flux calibrations were used during the growth of the structure. The full series of spectra were fitted by first modelling the R spectra taken at \(15^\circ\) incidence. This was in fact achieved by allowing only two parameters to be varied independently. These were the growth fluxes of the Ga and Al, as the structure
is grown in an As overpressure. The quality of the fits did not depend on the
parameters of the QW layer, so this was not varied and kept at the nominal thickness.
The calculated errors in the Ga and Al fluxes led to alterations in the layer thicknesses
in individual layers given in Table 4.2. Once the errors in the Ga and Al growth
fluxes had been established for the spectra taken at 15° incidence, it was possible to
model all the other R spectra, in Fig. 4.6 with the same flux errors.

The theoretically calculated R spectra are shown in Fig. 4.6 as the solid lines, and as
can be seen, a very good agreement was achieved between experiment and theory
throughout the series. The best agreement was achieved with the Ga and Al fluxes at
94.7% and 102.9% of their nominal values, respectively. These are within the
tolerances of the MBE growth. This effectively represents a reduction in all the GaAs
layer thicknesses by 5.3%, and an increase in all the AlAs layer thicknesses by 2.9%.
The 100 Å Al0.3Ga0.7As and Al0.5Ga0.5As layers are slightly thinner, by 2.8 Å and 1.2
Å, respectively.

The results of the theoretical modelling, as well as the experimental data, are shown
in Fig. 4.7, which demonstrates the angular dependence of the CM energy. Shown on
the graph are the energies of the CM according to the R spectra (as squares), AR/R
spectra in phase with the PL (circles), and AR/R spectra 90° out of phase with the PL
(triangles). Also demonstrated is the angular dependence of the CM energy according
to the transfer matrix method, shown by the dashed lines. This has been done for the
Ga and Al fluxes at (97%, 97%), (95%, 103%), and (100%, 100%) of the nominal
values. The solid line on the graph shows the CM dependence according to eqn. (4.2).
This figure validates the simple dependence of the CM energy with incident angle,
given by eqn. (4.2). Furthermore, from this graph it is possible to calculate the
anticipated energy position of the CM at normal incidence, and this was deduced to
occur at 998.5 nm (1.242 eV). From the fit using eqn. (4.2) the mean refractive index,
\( n \), of the cavity is calculated to be \(-3.48\) and the effective cavity thickness, \( d \), is
calculated to be \(-2870\) Å (using the appropriate value for \( m \), in this case, of 2).
Chapter 4: Photomodulated Reflectance and Conventional Reflectance Studies of VCSELs

Fig. 4.7 Results of theoretical modelling of R spectra of RMB1048, shown in Fig. 4.6. Graph shows the angular dependence of the CM wavelength. Solid and dashed lines show dependence according to eqn. (4.2) and transfer matrix calculation, respectively. Squares, circles, and triangles show CM positions according to R spectra (Fig. 4.3), in phase PR spectra (Fig. 4.1), and out of phase PR spectra (Fig. 4.2), respectively.
4.4 Summary

This chapter has shown that PR and R spectroscopy can be useful characterisation tools for the investigation of VCSEL structures. A number of features are present in the PR spectrum of a VCSEL structure including the usual Franz-Keldysh oscillations which can be used to determine the built-in electric field within a structure. In addition, features are observed that arise from both the ground-state transition of the QW layers, as well as from the optical mode of the cavity itself. The energy of the CM feature is shown to depend upon the experimental angle of incidence, a fact that allows it to be distinguished from critical-point features.

A typical normalised reflectance spectrum of a VCSEL exhibits a large high reflectance stop band, with a small dip in the centre arising from the optical mode of the cavity. In fact, it is owing to the modulation of this dip that a corresponding feature is observed in the PR spectrum. It is possible to calculate a reflectance spectrum of a VCSEL structure using a transfer matrix formalism, so long as the complex dielectric functions of all the constituent materials are known across the energy range of interest. Such a method also accounts for all multiple reflections within each layer. Theoretical calculations along with experimental data show that at non-normal incidence, the R and PR spectra of a VCSEL have a dependence on the polarisation of the incident light.

Experimental R spectra have been modelled with theoretical spectra calculated using the transfer matrix method. Such modelling allows the deviations of the layer thicknesses from their nominal values to be derived, and can be expressed as errors in the Ga and Al growth fluxes. For Sample RMB1048 the Ga and Al growth fluxes were found to be 94.7% and 102.9% of their nominal values.
4.5 References

Choquette K D and Hou H Q 1997 Proceedings of the IEEE 85 1730
Grothe H and Boebel F G 1993 J. Cryst. Growth 127 100
Solid State Commun. 107 97
Klein M V 1986 Optics 2nd Ed. (New York, Wiley)
Phys. 73 21
Mars D E, Rosser S J, Kaneko Y, Nakagawa S, Takeuchi T and Yamada N 1997 J.
Crystal Growth 175 365
Mortaza S and Campbell J C 1995 J. Appl. Phys. 77 3641
Okamoto H, Tadokoro T, Kondo Y and Nakao M 1997 Jpn. J. Appl. Phys. 36 5365
Orenstein M, Chang-Hasnain C J, Wullert J, Carrion L, Stoffel N G, Florez, L T and
Harbison J P 1991 Electron. Lett. 27 437
Lett. 60 1536
1121
4 1192
Sale T E 1995a IEE Proc. -Optoelectron. 142 37
Growth 124 763
Shen H and Dutta M 1995 J. Appl. Phys. 78 2151
Electron. Lett. 28 384
Sze S M 1985 Semiconductor Devices, Physics and Technology (New York: Wiley)
54 608
and Harbison J P 1991 *Electron. Lett.* **27** 583


CHAPTER 5

Lineshape Model for the PR Spectrum of a VCSEL

5.1 Introduction

In the previous chapter the PR spectrum of a VCSEL was shown to exhibit features arising from both the ground-state transition of the QW layers, and the optical mode of the cavity. Furthermore, these features could clearly be treated as distinct when they are located at well-separated energies. However, as will be shown here, the PR lineshape of these two features becomes increasingly complex, as they move closer in energy, and is no longer a simple sum of the lineshapes of the individual features. Here, an appropriate model is developed for describing such a PR lineshape. The use of the model is demonstrated on sets of spectra, taken at differing angles of incidence, where each series in the set shows the cavity mode (CM) feature moving through resonance with the ground-state QW transition. Following this, the model is used in a novel way to calculate the modulated change in the imaginary part of the dielectric function of the QW layers, \( \Delta \varepsilon_2 \), free from any effects of the VCSEL cavity. The results of this spectrum are compared with a conventional PR spectrum taken of the exposed QW layers of the same sample after removing the top DBR. The model is also demonstrated on PR spectra where the CM interacts with higher-order QW transitions. Finally, the measured energies of the confined-state QW transitions are
Chapter 5: Lineshape Model for the PR Spectrum of a VCSEL

compared with those calculated by a theoretical model based on an effective mass formalism.

5.2 Lineshape Model for a Confined-State QW Transition in Resonance with the Cavity Mode

This section develops a model that can be used to describe the PR spectrum of a VCSEL structure where the features due to the optical mode of the cavity and a confined-state QW transition are close to, or in, resonance. The model is based on the assumption that, unlike simple QW structures, the Seraphin coefficients of the QW layers in a VCSEL structure are no longer simple slowly-varying functions, but instead have detailed structure localised near the energy of the CM.

5.2.1 Calculating the Seraphin Coefficients of a VCSEL Structure

Some of the formulae in this section have already been given in Chapter 2, but are repeated here for convenience.

The lineshape of a PR spectrum is described by eqn. (2.15):

\[
\frac{\Delta R}{R} = \alpha \Delta \varepsilon_1 + \beta \Delta \varepsilon_2
\]  

(2.15)

with the Seraphin coefficients, \( \alpha \) and \( \beta \), consequently being described by eqns. (2.16a, 2.16b) (Seraphin, 1966):

\[
\alpha(E) = \frac{1}{R(E)} \left( \frac{\partial R(E)}{\partial \varepsilon_1(E)} \right) \quad \beta(E) = \frac{1}{R(E)} \left( \frac{\partial R(E)}{\partial \varepsilon_2(E)} \right)
\]  

(2.16a, b)
Chapters: ____________

For bulk semiconductors, the Seraphin coefficients are often generally considered to be slowly varying functions that are virtually energy independent in the region of critical point features (Shanabrook, 1987; Shen, 1987; Tang, 1991). The Seraphin coefficients, as depicted in Fig. 2.1 for bulk GaAs, can be obtained analytically from eqns. (2.16a, 2.16b) by differentiating the expression for $R$ acquired from Fresnel's equations (Seraphin, 1966; Fischer, 1967).

It is also possible to calculate the Seraphin coefficients numerically when the above approach is not possible. The transfer matrix method described in Section 4.3.1 is used to calculate the reflectance ($R$) spectrum of the particular structure (Hosea, 1995a; Hosea, 1995b). A small perturbation, $\Delta \varepsilon_1$, or $\Delta \varepsilon_2$, is then added to the real, or imaginary, part of the dielectric function, respectively, to allow a perturbed $R$ spectrum to be calculated. The rate of change in the reflectance with respect to $\varepsilon_1$ or $\varepsilon_2$ can then be calculated as

$$\frac{\partial R}{\partial \varepsilon_1} \approx \frac{R(\varepsilon_1 + \Delta \varepsilon_1) - R(\varepsilon_1)}{\Delta \varepsilon_1}$$
$$\frac{\partial R}{\partial \varepsilon_2} \approx \frac{R(\varepsilon_2 + \Delta \varepsilon_2) - R(\varepsilon_2)}{\Delta \varepsilon_2}$$

(5.1a, b)

As we are interested in the Seraphin coefficients of the QW layers in these structures, the perturbations are applied to the dielectric functions of these layers in the calculation. The Seraphin coefficients, $\alpha$ and $\beta$, of the QW layers can then be calculated using eqns. (2.16a) and (2.16b), respectively.

Using this approach, the Seraphin coefficients were calculated for the VCSEL structures RMB1048 and RMB627. Figs. 5.1a, 5.1b, and 5.1c show a number of different stages in the calculation of the Seraphin coefficient $\alpha$ for RMB1048. Similarly, Figs. 5.2a-c, 5.3a-c, and 5.4a-c show different stages in the calculation of $\beta$ for RMB1048, $\alpha$ for RMB627, and $\beta$ for RMB627, respectively.

Fig. 5.1a shows $R$ spectra calculated for RMB1048. The $R(\varepsilon_1)$ and $R(\varepsilon_1 + \Delta \varepsilon_1)$ spectra are shown as the solid and dashed lines, respectively. In all the calculations performed, a value of 0.26 was chosen for both $\Delta \varepsilon_1$ and $\Delta \varepsilon_2$. However, in calculating the $R(\varepsilon_1 + \Delta \varepsilon_1)$ spectrum shown in Fig. 5.1a, a value of 1.3 was used for $\Delta \varepsilon_1$ to
exaggerate the effect of the perturbation. As the figure demonstrates, perturbing $\varepsilon_1$ effectively modulates the refractive index of the QW layer. This alters the effective optical length of the cavity and consequently alters the energy of the CM dip. Fig. 5.1b depicts the rate of change in the reflectance with respect to $\varepsilon_1$, as given by eqn. (5.1a). Fig. 5.1c shows the Séraphin coefficient $\alpha$, calculated for RMB1048 using eqn. 2.16a, as the solid line. The dashed line in this figure represents the lineshape used to model $\alpha$ given by eqn. (5.2a), and is discussed later.

Figs. 5.2a-c follow the calculation of $\beta$ for RMB1048, with Fig. 5.2 displaying the $R(\varepsilon_2)$ and $R(\varepsilon_2 + \Delta\varepsilon_2)$ lineshapes. This figure demonstrates that perturbing $\varepsilon_2$ has the effect of altering the optical absorption of the QW layer, and as a result affects the shape and depth of the CM dip. Fig. 5.2b shows the rate of change of $R$ with respect to $\varepsilon_2$, as given by eqn. (5.1b). Fig. 5.2c shows the Séraphin coefficient $\beta$, calculated for RMB1048 using eqn. (2.16b), as the solid line. The dashed line shows the lineshape used to model $\beta$, given by eqn. (5.2b). It is worth noting that even though the $\partial R/\partial\varepsilon_2$ spectrum in Fig. 5.2b has an unusual lineshape, after dividing through by $R$, the Séraphin coefficient $\beta$ becomes a single negative peak.

Figs. 5.3a-c, and 5.4a-c, represent the same stages in the calculation of $\alpha$, and $\beta$, respectively, for RMB627. The calculated coefficient $\alpha$ was found similar for both of the structures. However, the Séraphin coefficient $\beta$ calculated for the QW layers of RMB627 was found to be different from that of RMB1048. This is evident from comparing Figs. 5.2c and Fig. 5.4c. The Séraphin coefficient $\beta$ for RMB627, as shown in Fig. 5.4c, is found to be a positive peak with small negative protruding side lobes. This is a consequence of the additional effects of there being three QW layers, in the cavity of sample RMB627, instead of the single QW in RMB1048. Indeed, if the calculation is repeated for structure RMB627 using only a single QW in the cavity region, a similar result to that of RMB1048 is obtained for the lineshape of $\beta$. 

145
Chapter 5: Lineshape Model for the PR Spectrum of a VCSEL

Fig. 5.1a (top left) Solid, and dashed, lines show $R(\varepsilon_1)$, and $R(\varepsilon_1 + \Delta \varepsilon_1)$, respectively, calculated for RMB1048 using the transfer matrix method.

Fig. 5.1b (bottom left) Shows $dR/d\varepsilon_1$ spectrum calculated for RMB1048 using eqn. (5.1a).

Fig. 5.1c (top right) Solid line represents Séraphin coefficient $\alpha$ calculated for QW layer of RMB1048 using eqn. (2.15a). Dashed line shows the real part of a complex Lorentzian lineshape used to model $\alpha$ as given by eqn. (5.2a).
Fig. 5.2a (top left) Solid, and dashed, lines show $R(\varepsilon_2)$ and $R(\varepsilon_2 + \Delta\varepsilon_2)$, respectively, calculated for RMB1048 using the transfer matrix method.

Fig. 5.2b (bottom left) Shows $dR/d\varepsilon_2$ spectrum calculated for RMB1048 using eqn. (5.1b).

Fig. 5.2c (top right) Solid line represents Seraphin coefficient $\beta$ calculated for QW layer of RMB1048 using eqn. (2.15b). Dashed line shows the real part of a complex Lorentzian lineshape used to model $\beta$ as given by eqn. (5.2b).
Fig. 5.3a (top left) Solid, and dashed, lines show $R(\varepsilon_1)$, and $R(\varepsilon_1 + \Delta \varepsilon_1)$, respectively, calculated for RMB627 using the transfer matrix method.

Fig. 5.3b (bottom left) Shows $dR/d\varepsilon_1$ spectrum calculated for RMB627 using eqn. (5.1a).

Fig. 5.3c (top right) Solid line represents Séraphin coefficient $\alpha$ calculated for QW layer of RMB627 using eqn. (2.15a). Dashed line shows the real part of a complex Lorentzian lineshape used to model $\alpha$ as given by eqn. (5.2a).
Fig. 5.4a (top left)  Solid, and dashed, lines show $R(\epsilon_2)$, and $R(\epsilon_2 + \Delta \epsilon_2)$, respectively, calculated for RMB627 using the transfer matrix method.

Fig. 5.4b (bottom left)  Shows $dR/d\epsilon_2$ spectrum calculated for RMB627 using eqn. (5.1b).

Fig. 5.4c (top right)  Solid line represents Seraphin coefficient $\beta$ calculated for QW layer of RMB627 using eqn. (2.15b). Dashed line shows the real part of a complex Lorentzian lineshape used to model $\beta$ as given by eqn. (5.2b).
The analysis shows that the Seraphin coefficients for QW layers of these structures are no longer broad, slowly-varying functions, but instead have a well defined structure centred near the energy of the CM, which extends over a limited range of energies.

The Seraphin coefficients of the QW layers of both VCSEL structures have a similar lineshape to that of a complex Lorentzian, as defined in eqn. (2.32). Consequently, the Seraphin coefficients are represented in this model by the real and imaginary parts of a complex Lorentzian:

\[
\alpha(E) = \alpha_0 \frac{(E - E_{cm})}{(E - E_{cm})^2 + \Gamma_{cm}^2} \quad \beta(E) = \beta_0 \frac{\Gamma_{cm}}{(E - E_{cm})^2 + \Gamma_{cm}^2} \quad (5.2a, b)
\]

where \(E_{cm}\) and \(\Gamma_{cm}\) are the energy position and half-width of the CM, and \(\alpha_0\) and \(\beta_0\) are amplitudes. The dashed lines in Figs. 5.1c and 5.3c represent eqn. (5.2a) with suitable values of \(\alpha_0, E_{cm}\), and \(\Gamma_{cm}\) such that eqn. (5.2a) fits the calculated lineshape of \(\alpha\) as closely as possible. Similarly in Figs. 5.2c and 5.4c the dashed line represents eqn. (5.2b) and models the lineshape of \(\beta\).

### 5.2.2 Lineshape for the Modulated Change in the Complex Dielectric Function of the QW layers

The lineshape of a PR spectrum follows the form given by eqn. (2.15). For the modulation induced changes in the real, \(\Delta \varepsilon_1\), and the imaginary, \(\Delta \varepsilon_2\), parts of the complex dielectric function of the QW layers, the model uses the first derivative lineshape form given by eqn. (2.29) (Shanabrook, 1987; Glembocki, 1992). In this model, a Lorentzian form for the dielectric function is used for simplicity (Shanabrook, 1987). For further details of this model see Section 2.2.4.
Allowed Transitions

For an allowed confined-state QW transition, the lineshapes of \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) can be described by the linear combination of the first derivatives of a complex Lorentzian with respect to energy-position and linewidth (Shen, 1987; Klar, 1995) (see Section 2.2.4). The complex Lorentzian lineshape is given by eqn. (2.32) and can be expressed in terms of its real and imaginary components:

\[
\varepsilon_1 = I_{qw} \frac{(E - E_{qw})}{(E - E_{qw})^2 + \Gamma_{qw}^2}, \quad \varepsilon_2 = I_{qw} \frac{\Gamma_{qw}}{(E - E_{qw})^2 + \Gamma_{qw}^2} \tag{5.3a, b}
\]

where \( I_{qw} \) and \( E_{qw} \) denote the intensity and energy-position of the confined-state QW transition, and \( \Gamma_{qw} \) is its HWHM. The partial derivatives with respect to energy have the form:

\[
\frac{\partial \varepsilon_1}{\partial E_{qw}} = I_{qw} \frac{(E - E_{qw})^2 - \Gamma_{qw}^2}{((E - E_{qw})^2 + \Gamma_{qw}^2)^2} \tag{5.4a}
\]

\[
\frac{\partial \varepsilon_2}{\partial E_{qw}} = I_{qw} \frac{2 \Gamma_{qw} (E - E_{qw})}{((E - E_{qw})^2 + \Gamma_{qw}^2)^2} \tag{5.4b}
\]

The partial derivatives with respect to linewidth have the form:

\[
\frac{\partial \varepsilon_1}{\partial \Gamma_{qw}} = I_{qw} \frac{-2 \Gamma_{qw} (E - E_{qw})}{((E - E_{qw})^2 + \Gamma_{qw}^2)^2} \tag{5.5a}
\]

\[
\frac{\partial \varepsilon_2}{\partial \Gamma_{qw}} = I_{qw} \frac{(E - E_{qw})^2 - \Gamma_{qw}^2}{((E - E_{qw})^2 + \Gamma_{qw}^2)^2} \tag{5.5b}
\]

Hence, for an allowed transition, \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) take the form:
where the angle $\theta$ accounts for the degree of mixing between the two types of first derivative. An angle of $\theta = 0^\circ$ would correspond purely to a first derivative with respect to $E_{qw}$, whereas an angle of $\theta = 90^\circ$ would describe purely a first derivative with respect to $\Gamma_{qw}$.

For describing the lineshape of a PR spectrum near, or at, resonance of a single confined-state QW transition with the CM, it is not necessary to include the intensity coefficient, $I_{qw}$, in eqns. (5.6a, b). In such a situation, just the expression inside the large set of brackets may be used. This is because intensity coefficients are already accounted for by $\alpha_0$ and $\beta_0$ in the expressions for the Seraphin coefficients given by eqns. (5.2a, b). However, for some spectra examined here, the CM is close to resonance with more than one confined-state QW transition, and in such a case the intensity term, $I_{qw}$, must be included to account for the relative strengths of the transitions.

**Forbidden Transitions**

For a forbidden confined-state QW transition, the lineshapes of $\Delta \varepsilon_1$ and $\Delta \varepsilon_2$ can be described by the first derivative of a complex Lorentzian with respect to intensity (Shen, 1987; Klar, 1995) (see Section 2.2.4).
\[ \Delta \varepsilon_1(E) = \frac{\partial \varepsilon_1}{\partial I_{qw}} = \frac{E - E_{qw}}{(E - E_{qw})^2 + \Gamma_{qw}^2} \]  

(5.7a)

\[ \Delta \varepsilon_2(E) = \frac{\partial \varepsilon_2}{\partial I_{qw}} = \frac{\Gamma_{qw}}{(E - E_{qw})^2 + \Gamma_{qw}^2} \]  

(5.7b)

**CM Feature in Resonance with a Confined-State QW Transition**

From a combination of the above equations it is now possible to model the PR spectrum of a VCSEL where the CM is near, or in resonance with, a confined-state QW transition. For an allowed QW transition, a lineshape combining eqns. (2.15), (5.2a, b), and (5.6a, b) is suitable. For the lineshape of a CM feature near or at resonance with a forbidden QW transition, a combination of the eqns. (2.15), (5.2a, b), and (5.7a, b) should be used.

This model is similar to those used to describe a conventional PR spectrum where there are, for example, two confined-state QW transitions that overlap, in so much that it uses two oscillator functions. However, for QW transitions, the PR lineshape is in fact the sum of the oscillatory lineshapes of the two individual transitions. However, in the present case the lineshape is the product of the two individual oscillatory lineshapes. This leads to two contrasting situations. The first is when the two features are far apart, such as in the PR spectra of sample RMB1048 shown in Figs. 4.2 and 4.3. In such a case, each feature is simply represented by its own lineshape, which is only slightly modulated by the tail-end of the lineshape of the other feature, and this is similar to the situation obtained for two typical PR lineshapes which are summed. The second situation is when the two features move closer in energy, and is demonstrated in Section 5.3.2. In this case, a large enhancement of the PR lineshape is observed, as predicted by the new lineshape model where the two oscillators are multiplied together.
5.3 Application of the Model for Resonance Between the CM and Ground-State QW Transition

Here, the new model is used to examine the behaviour of the PR lineshape of a VCSEL as the CM is moved through resonance with the ground-state QW transition. For some of the spectra shown, the model is extended to allow for the situation where the CM is near resonance with more than one confined-state transition.

5.3.1 Experimental Details

Sample RMB627 is used to demonstrate the new VCSEL PR model. Details on the structure of this sample can be found in Section 4.1.2. This structure has been chosen since, unlike structure RMB1048, the ground-state QW transition, $H_{11}$, and the CM are in close proximity in energy at ambient conditions. All the measurements in this section are performed at room temperature with selectively polarised probe light. There are six sets of spectra, taken at incident angles, $\theta_i$, of 0°, 20°, 30°, 40°, 50° and 60°. Each set contains ~13 individual PR spectra taken at various positions on the sample along a straight line running from the centre of the wafer to the edge. The sample was mounted on a micrometer, such that each consecutive spectrum was taken 0.5 mm from the previous one. The position on the sample was changed so that the CM feature was effectively moved in energy through resonance with the ground-state transition of the QW, $H_{11}$. The ground-state transition is known to be $H_{11}$ from the theoretical modelling of the structure and is discussed in more detail in Section 5.6. The angle and position were changed to move the CM in energy whilst keeping the position of $H_{11}$ constant. For all sets of spectra, measurements were taken using both s- and p-orientations of polarised light. However, only the spectra taken with s-polarised light will be described (See Section 5.3.2 for explanation).

The He-Ne laser was chopped at a frequency of 333 Hz and attenuated to ~ 0.8 mW. Measurements were performed with the phase of the lock-in amplifier set at 90° out of phase with the PL. The measurements at normal incidence were performed using the apparatus shown in Fig. 2.4b, which included a polariser positioned prior to the
beam splitter. Spectra for the normal incidence series were taken over an energy range of 1.17 eV to 1.32 eV, and used a spectrometer slit of 2 mm x 400 μm, giving an instrumental resolution of 1.7 meV (FWHM) across this energy range. The remaining series of spectra, taken at non-normal incidence, were performed using the apparatus depicted in Fig. 2.4a, and included a polariser in between the two lenses positioned before the sample. For the series of spectra taken at 20°, 30°, 40°, 50° and 60°, measurements were performed from 1.14 eV to 1.28 eV, using a spectrometer slit of 2 mm x 200 μm, giving an instrumental resolution 0.8 meV (FWHM) across this energy range.

5.3.2 Results

Each set of PR spectra at a particular angle of incidence consists of individual spectra taken at different positions on the sample. Only the spectra taken with s-polarised light have been described here as no additional information can be gained from the spectra taken using p-polarised light. Each set of spectra is shown in the following figures: Fig. 5.5a (θi = 0°), Fig. 5.5b (θi = 20°), Fig. 5.5c (θi = 30°), Fig. 5.5d (θi = 40°), Fig. 5.5e (θi = 50°), and Fig. 5.5f (θi = 60°). The experimental data are shown as dots and the values on the right of each individual spectrum indicate the associated vernier setting (in mm) on the sample micrometer. Each individual PR spectrum has been scaled by the value shown on the left of the spectrum. In each figure, starting at the bottom left and moving upwards, the CM feature is seen to move upwards in energy, such that it passes through the position of the $H_{11}$ transition at ~ 1.223 eV. An important feature, present in each of the series of spectra, is that close to resonance there is a great enhancement of the PR lineshape. For this particular sample, this enhancement is by a factor of ~ 40, and occurs near the following vernier settings: Fig. 5.5a (at position 3.5 mm), Fig. 5.5b (at position 3.5 mm), Fig. 5.5c (at position 2.0 mm), Fig. 5.5d (at position 5.0 mm), Fig. 5.5e (at position 4.0 mm), and Fig. 5.5f (at position 1.5 mm).

Each PR spectrum was fitted using the model described in Section 5.2.2. The fits are shown as the sets of solid lines in Figs. 5.5a - 5.5f. The spectra were fit using the
model suitable for a CM interaction with an allowed QW transition, and thus uses eqns. (2.15), (5.2a, b), and (5.6a, b). However, as will be discussed later, this model was extended for some of the spectra, in the series taken at 60° incidence, to account for the CM being in resonance with more than one QW transition. In the majority of cases, only a single QW transition, \( H_{11} \), is near resonance with the CM, and consequently the intensity term, \( I_{qw} \), in eqns. (5.6a, b) is neglected. Therefore, only seven independently varying parameters were used to model the PR lineshape for these spectra. These are \( \alpha_0, \beta_0, E_{cm}, \Gamma_{cm}, E_{qw}, I_{qw}, \) and \( 0 \). It was found that within each series, the only parameter that varied significantly was the energy of the CM, \( E_{cm} \).
Fig. 5.5a  Series of PR spectra of RMB627 showing CM moving through resonance with $H_{11}$ transition. Measurements were taken at normal incidence, using s-polarised light, and at $90^\circ$ out of phase with PL. Data are shown as dots. Solid lines show fits. Spectra scaled by the values on the left. Position of probe beam on sample given by the values on the right (in mm). Individual spectra have been offset by factors of $3 \times 10^3$. 
Fig. 5.5b  Series of PR spectra of RMB627 showing CM moving through resonance with $H_{11}$ transition. Measurements were taken at $20^\circ$ incidence, using s-polarised light, and at $90^\circ$ out of phase with PL. Data are shown as dots. Solid lines show fits. Spectra scaled by the values on the left. Position of probe beam on sample given by the values on the right (in mm). Individual spectra have been offset by factors of $3 \times 10^3$. 
Fig. 5.5c  Series of PR spectra of RMB627 showing CM moving through resonance with $H_{11}$ transition. Measurements were taken at 30° incidence, using $s$-polarised light, and at 90° out of phase with PL. Data are shown as dots. Solid lines show fits. Spectra scaled by the values on the left. Position of probe beam on sample given by the values on the right (in mm). Individual spectra have been offset by factors of $3 \times 10^3$. 

$\theta_i = 30^\circ$
Fig. 5.5d  Series of PR spectra of RMB627 showing CM moving through resonance with $H_{11}$ transition. Measurements were taken at 40° incidence, using s-polarised light, and at 90° out of phase with PL. Data are shown as dots. Solid lines show fits. Spectra scaled by the values on the left. Position of probe beam on sample given by the values on the right (in mm). Individual spectra have been offset by factors of $3 \times 10^3$. 
Fig. 5.5e Series of PR spectra of RMB627 showing CM moving through resonance with $H_{11}$ transition. Measurements were taken at 50° incidence, using s-polarised light, and at 90° out of phase with PL. Data are shown as dots. Solid lines show fits. Spectra scaled by the values on the left. Position of probe beam on sample given by the values on the right (in mm). Individual spectra have been offset by factors of $3 \times 10^3$. 

\( \theta_I = 50^\circ \)
Fig. 5.5f  Series of PR spectra of RMB627 showing CM moving through resonance with $H_{11}$ transition. Measurements were taken at $60^\circ$ incidence, using $s$-polarised light, and at $90^\circ$ out of phase with PL. Data are shown as dots. Solid lines show fits. Spectra scaled by the values on the left. Position of probe beam on sample given by the values on the right (in mm). Individual spectra have been offset by factors of $3 \times 10^{-3}$. Arrows indicate the position of the $H_{21}$ transition at $\sim 1.246$ eV.
Generally, for the series taken at experimental angles of incidence from 0° to 50° (Figs. 5.5a to 5.5e), the fits to the data are very good, with the exception of one or two individual spectra within each series. However, the lineshape model proved to be less successful in fitting the spectra taken at 60° incidence (Fig. 5.5f) for a number of reasons. The first, which will be discussed in more depth later, is that the CM feature increases in width with the angle of incidence, and at 60° incidence a Lorentzian profile is no longer a good approximation to its lineshape (see Fig. 5.5f).

The second reason is that in certain PR spectra, the CM feature begins to move into resonance with a higher-order QW transition. The presence of this second QW transitions begins to appear in the series taken at 50° incidence, shown in Fig. 5.5e, and can be seen as a small high-energy shoulder in the spectra labelled 6.0 and 6.5. This additional feature becomes even more pronounced in the series taken at 60° (Fig. 5.5f) in the spectra labelled 3.5 to 5.0. In fact, it proved to be impossible to fit these four spectra with the model described so far, and it was necessary to extend the model to account for the presence of an additional QW transition.

In order to model the PR spectrum of the CM feature interacting with two QW transitions, it was necessary to use two sets of equations to describe the changes in the complex dielectric function due to modulation, one set for each transition. The first transition, $H_{11}$, is still described by eqns. (5.6a, b), and the respective changes in the dielectric function are referred to as $\Delta \varepsilon_{1QW(1)}$ and $\Delta \varepsilon_{2QW(1)}$. The confined-state QW transitions for both structures are theoretically modelled later in Section 5.6, and this predicts that the second QW feature, observed in some of the PR spectra of the series at 60°, is the transition $H_{21}$. This transition is nominally parity-forbidden, and consequently the modulated changes in the dielectric function, $\Delta \varepsilon_{1QW(2)}$ and $\Delta \varepsilon_{2QW(2)}$, are described by eqns. (5.7a, b). Furthermore, it is now important to include the intensity term, $I_{qw}$, in eqns. (5.6a, b) for describing $\Delta \varepsilon_{1QW(1)}$ and $\Delta \varepsilon_{2QW(1)}$, as the two transitions have different strengths.

The model still uses eqn. (5.2a, b) to describe the Seraphin coefficients of the QW layers, but eqn. (2.15) is amended to account for both transitions by becoming
\[ \frac{\Delta R}{R} = \alpha (\Delta E_{1,qw(1)} + \Delta E_{1,qw(2)}) + \beta (\Delta E_{2,qw(1)} + \Delta E_{2,qw(2)}) \quad (5.8) \]

This model has ten freely varying parameters, which are: \( \alpha_0, \beta_0, E_{cm}, \Gamma_{cm}, I_{qw(1)}, E_{qw(1)}, \Gamma_{qw(1)}, \theta(1), E_{qw(2)}, \) and \( \Gamma_{qw(2)} \). This extended model was used to fit the four spectra in the series measured at 60° incidence (Fig. 5.5f), labelled 3.5 to 5.0. The energy position of the second fitted QW transition has been indicated in these four spectra by the arrows, and is labelled \( H_{21} \).

The mean values of the fitting parameters \( \alpha_0, \beta_0, \Gamma_{cm}, E_{qw}, \Gamma_{qw}, \) and \( \theta \), used in the model for the CM in resonance with the ground-state QW transition, along with their standard errors are given for each series of spectra in Table 5.1. The mean values and standard errors of the additional parameters used in the fitting of spectra 3.5 - 5.0, in the series at 60° incidence, are given in Table 5.2.

<table>
<thead>
<tr>
<th>Series (°)</th>
<th>( \alpha_0 ) (10(^{-10}) eV)</th>
<th>( \beta_0 ) (10(^{-10}) eV)</th>
<th>( \Gamma_{cm} ) (meV)</th>
<th>( E_{qw} ) (eV)</th>
<th>( \Gamma_{qw} ) (meV)</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0.3 ± 0.021</td>
<td>-3.8 ± 0.19</td>
<td>1.9 ± 0.021</td>
<td>1.223 ± 0.00014</td>
<td>4.8 ± 0.079</td>
<td>-2° ± 3.0°</td>
</tr>
<tr>
<td>20°</td>
<td>0.5 ± 0.021</td>
<td>-3.3 ± 0.16</td>
<td>2.8 ± 0.057</td>
<td>1.224 ± 0.00021</td>
<td>4.7 ± 0.071</td>
<td>4° ± 2.9°</td>
</tr>
<tr>
<td>30°</td>
<td>0.8 ± 0.033</td>
<td>-3.0 ± 0.08</td>
<td>3.2 ± 0.079</td>
<td>1.224 ± 0.00017</td>
<td>5.3 ± 0.092</td>
<td>5° ± 2.0°</td>
</tr>
<tr>
<td>40°</td>
<td>0.7 ± 0.023</td>
<td>-3.6 ± 0.14</td>
<td>3.4 ± 0.069</td>
<td>1.221 ± 0.00015</td>
<td>5.3 ± 0.100</td>
<td>7° ± 3.8°</td>
</tr>
<tr>
<td>50°</td>
<td>0.7 ± 0.036</td>
<td>-2.8 ± 0.05</td>
<td>3.2 ± 0.050</td>
<td>1.223 ± 0.00014</td>
<td>4.7 ± 0.050</td>
<td>19° ± 2.2°</td>
</tr>
<tr>
<td>60°</td>
<td>0.4 ± 0.025</td>
<td>-1.6 ± 0.26</td>
<td>3.8 ± 0.510</td>
<td>1.223 ± 0.00017</td>
<td>3.1 ± 0.050</td>
<td>-18° ± 1.3°</td>
</tr>
</tbody>
</table>

Table 5.1 Mean values and standard errors of fitting parameters used to model the PR spectra of RMB627 taken at various angles of incidence and positions, shown in Figs. 5.5a - f.
The following observations are general and apply to each series of spectra, regardless of its angle of incidence. The standard errors in the energy-position and linewidth of the $H_{11}$ transition, and in the linewidth of the CM, are all 0.2 meV or less, except for the linewidth of the CM in the series taken at $60^\circ$, which was found to be somewhat larger at ~ 0.5 meV. The most likely cause of this anomaly is the fact that two different models are used to fit the spectra in the series at $60^\circ$ incidence. In this series, the fact that in one of the models, the CM, is interacting with two confined-state transitions instead of one, will influence the value obtained for $\Gamma_{cm}$ in eqns. (5.2a, b). The term $\beta_\theta$ is larger than $\alpha_\theta$ in all cases, by a factor ranging from ~ 4 for the series taken at $30^\circ$, $50^\circ$ and $60^\circ$, to more than an order of magnitude for the series taken at normal incidence. This shows that the majority of the PR signal arises from the product of $\beta$ and $\Delta\varepsilon_2$. The derivative mixing term, $\theta$, has mean values which are close to zero with standard errors of less than 4°. This means that in most cases, the majority of the lineshape of the modulated dielectric function comes from the first derivative of a complex Lorentzian with respect to energy, rather than linewidth. That is to say that eqns. (5.6a, b) have their main contribution from eqns. (5.4a, b). This result is in agreement with previous studies of QW samples (Theis, 1988).

The quality of the fit to the spectra in each series was generally very good. However, some fits were noticeably poorer such as those in which the CM and $H_{11}$ transition were closest to resonance. These were spectra 4.0 and 4.5 in the series at $0^\circ$ (Fig. 5.5a), spectrum 4.5 in the series at $20^\circ$ (Fig. 5.5b), and spectrum 5.5 in the series at $50^\circ$ (Fig. 5.5e). It may be that these spectra were difficult to fit because the model assumes a Lorentzian profile for the dielectric function, and consequently the $H_{11}$ transition is purely excitonic in nature, which is not strictly true at room temperature.

Table 5.2  Mean values and standard errors of additional fitting parameters used in the amended model used to fit PR spectra of RMB627 at $60^\circ$ incidence where CM in resonance with more than one confined-state QW transition. Used in the fitting of spectra 3.5 - 5.0 in Fig. 5.5f.

<table>
<thead>
<tr>
<th>Series ($\theta_i$)</th>
<th>$I_{qw(1)}$</th>
<th>$E_{qw(2)}$ (eV)</th>
<th>$\Gamma_{qw(2)}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$60^\circ$</td>
<td>0.86 ± 0.038</td>
<td>1.246 ± 0.001</td>
<td>5.0 ± 0.43</td>
</tr>
</tbody>
</table>
(Shen, 1987). However, the more likely cause of the discrepancies between the experimental spectra and modelled lineshapes is that the lineshape used to represent the Séraphin coefficients is an inadequate approximation in the case of this structure. The problem lies with the coefficient $\beta$, and as can be seen in Fig. 5.4c. The complex Lorentzian lineshape used, given by eqn. (5.2b), does not account for the small negative side lobes that flank the main peak. These side lobes are likely to be the cause of the additional structure seen in some of the spectra of RMB627 which the model has difficulty in fitting.

The mean values of some of the parameters given in Table 5.1 show a behaviour that is dependent upon the experimental angle of incidence. The most obvious is the linewidth of the CM, $\Gamma_{cm}$, which increases from a value of 1.9 meV, in the series taken at normal incidence, to 3.8 meV, in the series taken at 60° incidence. This behaviour is expected and easily explained. One of the main contributing factors to the linewidth of the CM feature is its change in energy across the finite width of the image of the spectrometer slit on the surface of the sample. As the experimental angle of incidence is increased, the projection of the slit image also increases in width, resulting in an increase in $\Gamma_{cm}$. For sample RMB627, the rate of change in energy of the CM is determined to be $\sim 7$ meV/mm (see Figs. 5.7a-f). At 20° incidence, the 200 $\mu$m image width has a projected width of $\sim 210 \mu$m, which corresponds 1.5 meV broadening in the energy of the CM across the width of the image. At 60° the projected image width is $\sim 400 \mu$m, corresponding to a shift of 2.8 meV. In addition to the linewidth of the CM, the derivative-mixing parameter, $\theta$, also appears to increase with increasing angle of incidence. This would indicate that as the experimental angle of incidence is increased, an increasing amount of the linewidth-derivative of a complex Lorentzian contributes to the lineshape of the modulated dielectric function.

Fig. 5.6 displays the normalised reflectance spectra corresponding to the series of PR spectra taken at 0° incidence and 60° incidence. The numbers on the right of each graph indicate the vernier position the measurements were made at. The energies of both the $H_{11}$ and $H_{21}$ transitions, as determined from the PR measurements, are shown on the graphs by arrows. Both graphs demonstrate how the CM moves in energy with position on the sample. Also the effect that the ground-state transition has on the
depth of the CM dip can clearly be seen in the R spectrum at normal incidence. As the CM moves to a higher energy than the $H_{11}$ transition, the optical absorption in the cavity is increased, and this causes the CM dip to alter shape and become deeper. In addition, the presence of the $H_{21}$ transition can be seen to affect the shape of the CM dip in the R spectra taken at $60^\circ$ incidence.

The energies of the CM and both the $H_{11}$ and $H_{21}$ QW transitions, derived from the fitting of each individual PR spectrum, are plotted as a function of position on the sample in Figs. 5.7a to 5.7f, corresponding to incident angles of $0^\circ$ to $60^\circ$, respectively. The energies of the CM, $E_{cm}$, are shown as filled circles; the energies of the $H_{11}$, and $H_{21}$, transitions are shown as open circles, and filled triangles, respectively.

The energy of the $H_{11}$ transition is found to be $1.223 \pm 0.0002$ eV, with a linewidth of $4.7 \pm 0.1$ meV. The $H_{21}$ transition, as derived from spectra 3.5 to 5.0 of the series at $60^\circ$ incidence (Fig. 5.5f), was found to have an energy of $1.246 \pm 0.001$ eV with a linewidth of $5.0 \pm 0.4$ meV. These linewidths are typical of excitonic features observed in PR spectra at 300 K (Qiang, 1992). The rate of change of energy of the CM with position on the sample was calculated to be $7$ meV/mm.
Fig. 5.6 R spectra of RMB627 taken at normal incidence (left) and at 60° incidence (right). Position of the probe beam on the sample is given by the values on the right (in mm). The arrows indicate the positions of the $H_{11}$ and $H_{21}$ transitions.
Figs. 5.7a-f  Energies of CM and both $H_{11}$ and $H_{21}$ QW transitions of RMB627, derived from fitting of the PR spectra shown in Figs. 5.4a-f. Energies are plotted as a function of probe beam position on the sample (in mm). Angle of incidence for each series is shown in the top left corner. Energies of CM, $H_{11}$, and $H_{21}$, shown as filled circles, open circles, and filled triangles, respectively.
5.4 A Novel Application of the Lineshape Model to Calculate $\Delta \varepsilon_2$

This section uses a novel application of the lineshape model, developed in Section 5.2, to plot the energy dependence of the modulated change in the imaginary part of the dielectric function, $\Delta \varepsilon_2$, for the QW layers of structures RMB627 and RMB1048. The $\Delta \varepsilon_2$ spectrum thus calculated is free from any effects of the VCSEL cavity. For sample RMB627, it is only possible to derive $\Delta \varepsilon_2$ across the energy region of the ground-state QW transition, $H_{11}$. However, for sample RMB1048 it is possible to do this over a much larger energy range, encompassing a number of higher-order QW transitions.

Once the $\Delta \varepsilon_2$ spectrum is acquired, it is fitted with an appropriate lineshape model to derive the energies of the confined-state QW transitions. For sample RMB1048, two additional and complementary methods are employed to derive the same confined-state QW transition energies, to compare with those given from the derivation of the $\Delta \varepsilon_2$ spectrum. The first of these methods is to use the new VCSEL PR lineshape model, given in Section 5.2, to fit a number of VCSEL PR spectra where the CM moves through resonance with one of the higher-order QW transitions. The second is to take a conventional PR spectrum of the exposed QW layers in sample RMB1048 after removal of the top DBR stack.

5.4.1 Deriving $\Delta \varepsilon_2$

For both the structures investigated in this chapter, a common lineshape has been used to model the Seraphin coefficients of the QW layers in the structures. Unlike the broad slowly-varying functions that describe bulk materials (Seraphin, 1966), the Seraphin coefficients of a VCSEL structure exhibit a detailed structure, localised at the energy of the CM. The significant point of interest, which is common to both VCSEL samples, is that the Seraphin coefficient $\alpha$ is approximately zero at the energy of the CM. In addition, the value of the Seraphin coefficient $\beta$ becomes
greatly enhanced at the same energy. This leads to the conclusion that, at the energy of the CM, the value of $\Delta R/R$ is given by only the product of $\beta$ and the imaginary part of the modulated dielectric function, $\Delta e_2$. Thus, at the energy of the CM, eqn. (2.15) reduces to:

$$\left. \frac{\Delta R}{R} \right|_{cm} = \beta_{\text{max}} \Delta e_2(E_{cm})$$

(5.9)

where $\beta_{\text{max}}$ represents the enhanced value of $\beta$ at this energy, given from eqn. (5.2b) as:

$$\beta_{\text{max}} = \frac{\beta_0}{\Gamma_{cm}}$$

(5.10)

Thus the value of $\Delta R/R$ in any PR spectrum, at the energy of the CM, gives a value proportional to $\Delta e_2$ at the same energy. The energy of the CM can be determined directly from the corresponding R spectrum as the position of the lowest value of $R$ within the CM dip. This is demonstrated in Fig. 5.8, which shows an example of an individual PR spectrum and its associated R spectrum of sample RMB627 taken at normal incidence. The arrows on the figure indicate how the R spectrum is used, first to obtain a value for $E_{cm}$; then, the associated value of $\Delta R/R$ at this energy is acquired from the PR spectrum. The cavity mode can then be tuned to another energy by either altering the experimental angle of incidence or changing position on the sample. Repeating this procedure, as many times as is necessary, a spectrum of $\Delta e_2$ can be plotted with each single point being derived from a separate pair of associated PR and R spectra. Although this technique is time consuming, it allows the modulated change in the imaginary part of the complex dielectric function of the QW layers to be determined free from any effects of the VCSEL cavity. The technique does, however, make the assumption that $\beta_{\text{max}}$ does not vary significantly over the energy range investigated. This point is raised again later.
5.4.2 Experimental Details

The $\Delta \varepsilon_2$ spectrum for sample RMB627 was derived, over a fairly limited energy range of 1.19 eV to 1.24 eV. The PR, and associated R, spectra were taken at normal incidence using the apparatus described in Section 2.2.5 and depicted in Fig. 2.4b. The He-Ne laser was chopped at a frequency of 333 Hz and appropriate neutral density filters were used to reduce the power to 0.8 mW. The spectra were taken with the lock-in amplifier set at $90^\circ$ out of phase with the PL. Individual spectra were taken
over an energy range of 1.15 to 1.27 using a spectrometer slit of 2 mm × 200 µm, giving an instrumental resolution of ~0.8 meV across this energy range. Each consecutive pair of PR and R spectra were taken 0.1 mm apart on the sample, which corresponds to a change in the cavity mode energy of ~0.7 meV. Sixty-five pairs of PR and R spectra were taken over a 6.5 mm radial length of sample.

Similarly, the Δε₂ spectrum for sample RMB1048 was determined, but over a wider energy range of 1.20 eV to 1.34 eV. In order to vary the energy of the CM across this larger energy range, it was necessary to utilise both the angular dependence and the position dependence of the CM energy. The section of RMB1048 was sufficiently long, around 22 mm, to allow this wide energy range to be covered. The experiments were performed in four stages with the sets of individual PR and R spectra taken at experimental angles of incidence of 0°, 25°, 30°, and 45°. The sets taken at 0° and 30° incidence were acquired close to the centre of the wafer, whilst those at 25° and 45° were taken near the wafer’s edge. Spectra were taken as described above for RMB627. A spectrometer slit of 2 mm × 400 µm was used over the energy ranges of 1.17 eV to 1.27 eV; and, 1.27 eV to 1.41 eV, gave typical instrumental resolutions of ~1.6 meV and ~2.0 meV, respectively. One hundred and forty pairs of PR and R spectra were needed to map out the Δε₂ spectrum.

### 5.4.3 The Derived Δε₂ Spectra

The derived Δε₂ spectra for RMB627 and RMB1048 are shown in Figs. 5.9a and 5.9b, respectively. In Fig. 5.9a, the data points for Δε₂ of RMB627 are shown as filled circles, and it was possible to plot enough data points to encompass all of the ground-state QW transition, H₁₁. These data were fitted using eqn. (5.6b), shown as the solid line. This lineshape was used, instead of the more conventional third differential functional form (TDFF) (Aspnes, 1973) such as is used to model the spectra investigated in Chapter 3, as it allows the linewidths and derivative mixing parameters to be directly compared with the values obtained from applying the VCSEL PR lineshape model developed in Section 5.2.
The values derived for $E_{qw}$, $I_{qw}$, and $\theta$ are given in Table 5.4, in Section 5.6, and are labelled as “$\Delta \varepsilon_2$ spectrum” results. These can be compared with the mean values obtained from the fitting of the series of individual PR spectra for the same sample, given in Table 5.1, in Section 5.3.2. The results obtained at normal incidence series are repeated in Table 5.4 and labelled as “VCSEL-PR model”. The energies of the ground-state QW transition, $H_{11}$, obtained from the “$\Delta \varepsilon$ spectrum” and “VCSEL-model” results are found to be in close agreement. However, the broadening and asymmetry of the lineshapes obtained from the two techniques were found to be different. The linewidth of $H_{11}$ derived from the fitting of the $\Delta \varepsilon_2$ spectrum is found to be twice that calculated from the “VCSEL-PR model” of Section 5.3.2. Also the mean value of the first derivative mixing parameter, $\theta$, as calculated from the VCSEL-PR model was found to be close to zero, i.e. the main contribution to the lineshape of the modulated dielectric function is from the first derivative of a complex Lorentzian, with respect to energy. However, the fitting to the $\Delta \varepsilon_2$ spectrum gave a derivative mixing parameter of $\theta = -47^0$, indicating that the lineshape is made up of almost equal contributions of first derivatives with respect to energy and linewidth, and this is reflected in the asymmetrical lineshape observed for the $H_{11}$ transition in Fig. 5.9a. The differences between the values obtained from the two types of fitting are likely to be caused by the indirect nature by which the parameters have been obtained, and the fact that the two methods account for the influence of the cavity in different ways.
Fig. 5.9a (top) Derived $\Delta \varepsilon_2$ spectrum of sample RMB627 at normal incidence shown as dots. Solid line shows fit using eqn. (5.6b).

Fig. 5.9b (bottom) Derived $\Delta \varepsilon_2$ spectrum of sample RMB1048. Spectrum comprises four sections taken at $0^\circ$, $25^\circ$, $30^\circ$, and $45^\circ$ incidence, shown as filled triangles, filled circles, open triangles, and open squares, respectively. Normal incidence data have been scaled by factor of 0.1.
Fig. 5.9b shows the calculated $\Delta \varepsilon_2$ spectrum for sample RMB1048. The spectrum consists of four sections, taken at the incident angles of $0^\circ$, $25^\circ$, $30^\circ$, and $45^\circ$, and are shown as filled triangles, filled circles, empty triangles, and empty squares, respectively. The section of the spectrum taken at normal incidence shows a section of the $H_{11}$ transition, and has been scaled by a factor of 0.1. All four sections of the spectrum merge correctly without the need to scale any individual section. This confirms that $\beta_{\text{max}}$, in eqn. (5.9), does not vary greatly over the whole energy range. (There is in fact a small variation of $\beta_{\text{max}}$ across the wafer, and this is discussed in Section 5.5.2). The solid line in Fig. 5.9b represents the lineshape fit of the $\Delta \varepsilon_2$ spectrum for sample RMB1048. The spectrum was modelled assuming there to be four higher-order confined-state QW transitions between the energies of 1.21 eV to 1.34 eV. From the theoretical modelling work described in Section 5.6, it is known that these transitions are $H_{12}$, $H_{13}$, $H_{21}$, and $H_{22}$. The transitions $H_{12}$ and $H_{21}$ are 'forbidden' and are consequently modelled using eqn. (5.7b) and a scaling factor. The transitions $H_{13}$ and $H_{22}$, however, are 'allowed' and therefore modelled using eqn. (5.6b). The values derived for $E_{qw}$, $I_{qw}$, and where applicable, $\theta$, are given in Table 5.4, and labelled "$\Delta \varepsilon_2$ spectrum". In addition, the tail end of the $H_{11}$ transition was also modelled using eqn. (5.6b). As only part of this transition is captured in the spectrum, only the intensity parameter, $I_{qw}$, was allowed to vary in the fitting. The remaining parameters were held at the following values: $E_{qw} = 1.189$ eV (this is the value obtained from PR spectra of RMB1048 shown in the previous chapter, Figs. 4.2 and 4.3); $I_{qw} = 5$ meV (typical value for the broadening at 300K); and $\theta = 0^\circ$.

These fitted parameters for each QW transition of RMB1048 are discussed in the next section, where they are compared with the values obtained from the fitting with the VCSEL-PR model, and later in Section 5.5 (where they are compared with the values obtained from the PR spectrum of an etched sample).
5.4.4 Modelling of CM Interaction with Higher-Order QW Transitions

In Section 5.3.2, the VCSEL-PR model developed in this Chapter was used to fit a PR spectrum showing the CM interacting with the ground-state QW transition, $H_{11}$. Such PR spectra can be modelled using a combination of eqns. (2.15), (5.2a, b), and (5.6a, b). A similar interaction process occurs when the CM passes through resonance with higher-order QW transitions. An indication of this was first observed in Chapter 4, Section 4.2.2, and can be seen in Figs. 4.2 and 4.3 where the shape of the CM feature changes between the spectra at 60° and 70°.

To demonstrate the effect of the CM moving through resonance with higher-order QW transitions, some of the PR spectra used earlier to derive the Δε2 spectrum of sample RMB1048 were fitted with the appropriate VCSEL PR lineshape model. Two sets of spectra were chosen, one set showing the CM moving through resonance with the $H_{22}$ transition, and the other showing resonance with the $H_{21}$ transition. These two particular transitions were chosen as they demonstrate how the CM interacts with both an 'allowed' higher-order QW transition ($H_{22}$), and a 'forbidden' higher-order QW transition ($H_{21}$).

Fig. 5.10 shows ten PR spectra of the CM feature moving through resonance with the $H_{22}$ transition. These data come from the set of spectra taken at an incidence angle, $\theta_1 = 45°$, and are taken across an energy range of 1.28 eV to 1.36 eV. The solid lines show the fits to the data using the VCSEL-PR model described in Section 5.2.2, appropriate to the CM interacting with an 'allowed' QW transition, and consequently uses eqns. (2.15), (5.2a, b), and (5.6a, b). The mean values of the parameters derived from this modelling are given in Table 5.4, and are labelled "VCSEL-PR model". The dashed line shows the derived position of the QW transition $H_{22}$. 

177
Fig. 5.10 Series of spectra of RMB1048 showing the CM moving through resonance with the 'allowed' $H_{22}$ transition. Experimental data are shown as dots. Measurements are taken at 45° incidence, and at 90° out of phase with PL. Solid lines show fits to the data. Dashed line shows the position of the $H_{22}$ transition. Individual spectra have been offset by factors of $2.5 \times 10^{-4}$. 
Fig. 5.11 Series of spectra of RMB1048 showing the CM moving through resonance with the ‘forbidden’ $H_{21}$ transition. Experimental data are shown as dots. Measurements are taken at $25^\circ$ incidence, and at $90^\circ$ out of phase with PL. Solid lines show fits to the data. Dashed line shows the position of the $H_{21}$ transition. Individual spectra have been offset by factors of $2.5 \times 10^4$. 
Fig. 5.11 shows six PR spectra of the CM feature moving through resonance with the $H_{21}$ transition. These data come from the set of spectra taken at an incident angle, $\theta_i = 25^\circ$, and are taken across an energy range of $\sim 1.25$ eV to 1.30 eV. The solid lines show the fits to the data using the VCSEL-PR model described in Section 5.2.2, appropriate to the CM interacting with a ‘forbidden’ QW transition, and consequently uses eqns. (2.15), (5.2a, b), and (5.7a, b). The mean values of the parameters derived from this modelling are given in Table 5.4, and labelled “VCSEL-PR model”. The dashed line shows the derived position of the QW transition $H_{21}$.

There is an obvious difference between these two sets of spectra. In Fig. 5.10, which shows the CM moving through resonance with the ‘allowed’ $H_{22}$ transition, the combined lineshape is seen to change from a negative feature to a positive feature as the CM moves to greater energies and passes through the $H_{22}$ transition. However, in Fig. 5.11, showing the CM moving through resonance with the ‘forbidden’ $H_{22}$ transition, the overall lineshape remains as a negative feature, even when the CM moves to greater energies than the $H_{21}$ transition. This phenomenon is simply an effect of the different lineshapes of $\Delta \varepsilon$ for an ‘allowed’ and ‘forbidden’ transition. For an ‘allowed’ transition the main contribution to $\Delta \varepsilon$ is from energy and linewidth derivatives due to changes in the energy of the transition (Miller, 1984), whereas for a ‘forbidden’ transition, the main contribution is from an intensity derivative due to changes in the oscillator strength (Tang, 1991) (see Section 2.2.4).

Comparing the values obtained from the modelling of these spectra, with those obtained from the lineshape of the $\Delta \varepsilon_2$ spectrum for RMB1048, shows that there is an excellent agreement for the energies for both the transitions, $H_{21}$ and $H_{22}$. In addition, identical linewidths are derived using both the methods, with $\Gamma_{qw} = 11$ meV, for the $H_{22}$ transition, and $\Gamma_{qw} = 4$ meV for the $H_{21}$ transition. For the fitting of the $H_{22}$ transition, the first derivative mixing parameter, $\theta$, was determined to be zero, as is the case with the “$\Delta \varepsilon_2$ spectrum” results. This indicates that the lineshape is made up of purely the first derivative of a complex Lorentzian with respect to $E_{qw}$.

For the CM resonances with both the $H_{22}$ and $H_{21}$ transitions, the fitting parameter $\beta_0$ was found to be an order of magnitude larger than that of $\alpha_0$. This is in agreement
with the earlier studies made on the CM interaction with the ground-state QW transition, \( H_{11} \), derived in Section 5.3.2. For the CM interaction with both these higher order transitions, the PR lineshape is enhanced by a factor of \(-10\) at resonance.

### 5.5 Investigating the QW Layer of RMB1048 by Removing the Top DBR Stack

In order to confirm the somewhat indirect results for the QW transitions acquired from the lineshape fitting of the \( \Delta \epsilon_2 \) spectrum of RMB1048, and the modelling of the full VCSEL PR spectrum, it is desirable to make a conventional PR measurement of the bare QW layer in this sample so that the effects of the VCSEL cavity are unambiguously removed. This is achieved by physically removing the top DBR stack of the structure by a wet etching.

#### 5.5.1 Experimental Details

The etching reagent used to remove the top DBR stack layers of structure RMB1048 was a 1:1:1 mixture of \( \text{KCr}_2\text{O}_7 \) (14.7g / 100ml), \( \text{CH}_3\text{COOH} \), and \( \text{HBr} \). This has an etch rate of \( 2 - 4 \mu\text{m} / \text{min} \). Prior to any optical measurements, the sample was first cleaned in methanol, then dipped in a 1:1 mix of \( \text{HCl} : \text{H}_2\text{O} \) for 20 secs. The sample was then etched in 5-second steps, with a PR spectrum being taken in-between each etch step. It required a total of nine steps, or \(- 45\) seconds etching time to remove the upper DBR stack layers.

The He-Ne laser was chopped at a frequency of 333 Hz and attenuated to \(- 0.8\) mW. The phase of the lock-in amplifier was set at 90\(^\circ\) out of phase with the PL. The measurement was performed at an angle of incidence, \( \theta_i = 45^\circ \), over an energy range of 1.13 eV to 1.55 eV using the apparatus shown in Fig. 2.4a. The spectrometer slit measured 2 mm \( \times \) 400 \( \mu\text{m} \), giving an instrumental resolution of 1.9 meV (FWHM) across this energy range.
5.5.2 Results

The lower plot in Fig. 5.12 shows the PR spectrum of the etched section of RMB1048. This will be referred to as the “ETCH-PR” spectrum. The spectrum has been magnified by a factor of 20. In the same figure, the $\Delta e_2$ spectrum of RMB1048 of Fig. 5.6b has also been included for comparison. The solid lines show the fits to the data. For the etched sample the fitting was performed over an energy range of 1.16 eV to 1.35 eV, and assumed that there are five confined-state QW transitions across this energy region. From the theoretical modelling of this structure, described in Section 5.6, it is known that three of these transitions, $H_{11}$, $H_{13}$, and $H_{22}$, are ‘allowed’ and these were consequently modelled using eqns. (2.15) and (5.6a, b) with the derivative mixing parameter, $\theta$, in eqn. (5.6a, b) set to zero. As this is a conventional PR spectrum and thus free from any cavity effects, the Seraphin coefficients in eqn. (2.15) can be assumed to be energy independent. The remaining two transitions, which are the ‘forbidden’ transitions $H_{12}$ and $H_{21}$, are modelled using eqns. (2.15) and (5.7a, b). The values of the parameters $E_{q_w}$ and $\Gamma_{q_w}$, are given in Table 5.4, and are labelled “ETCH-PR”. The energies of the transitions, as determined by the fitting, are indicated on Fig. 5.12 by the arrows.

As can be seen from Table 5.4, the energies of the transitions, as determined by the fitting of eqns. (2.15) and (5.6a, b), and, (2.15) and (5.7a, b), to the ETCH-PR spectrum, are in excellent agreement with those determined by the fitting of the $\Delta e_2$ spectrum. The linewidths, $\Gamma_{q_w}$, of the transitions in the etch-PR spectrum range from 6 - 16 meV, and are slightly greater than those observed in the $\Delta e_2$ spectrum, which range from 3 - 11 meV.
Fig. 5.12 PR spectrum of RMB1048 after top DBR stack has been removed (lower spectrum) shown as dots. Solid line shows the fit to data. The energies of QW transitions, as determined by lineshape fitting, are given by the arrows. Also shown on the graph is the $\Delta\varepsilon_2$ spectrum of RMB1048 (upper spectrum) as given in Fig. 5.8. Sections of both spectra are scaled by numbers in parentheses. $\Delta\varepsilon_2$ spectrum has been offset by $1 \times 10^3$. 
An important difference between the two spectra of RMB1048 is the relative strengths of the transitions, in particular the ratio of intensities of the \( H_{11} \) and \( H_{22} \) transitions. In the ETCH-PR spectrum, the intensity of the \( H_{22} \) transition is about half that of the \( H_{11} \) transition. However, with the \( \Delta \varepsilon_2 \) spectrum, even though the \( H_{11} \) transition is only partially present in the \( \Delta \varepsilon_2 \) spectrum, the fitting performed in Section 5.4.3 allows its intensity to be determined to a certain degree, and it is found to be around five times stronger than the \( H_{22} \) transition. In Section 5.4.3, it was stated that \( \beta_{\text{max}} \) in eqn. (5.9) does not change significantly across this section of the sample. Although this statement is true in that the change in \( \beta_{\text{max}} \) does not affect the derivation of the \( \Delta \varepsilon_2 \) spectrum, it does in fact change significantly enough to affect the ratio of intensities of the \( H_{11} \) and \( H_{22} \) transitions. Nearer the edge of the wafer, the individual layer thicknesses deviate away from their nominal values, causing \( \Gamma_{\text{cm}} \) to increase. This has been confirmed by measurements of \( \Delta \) spectra, which show \( \Gamma_{\text{cm}} \) at the centre of the wafer is approximately twice that at the edge of the wafer. Consequently, \( \beta_{\text{max}} \) in eqn. (5.10) is effectively twice as large at the edge of the wafer than it is in the centre. This leads to the \( H_{22} \) transition appearing to be far weaker that the \( H_{11} \) transition in the \( \Delta \varepsilon_2 \) spectrum, than it does in the etched-PR spectrum.

5.6 Theoretical Modelling of QW Layers in RMB627 and RMB1048

This section uses a theoretical model to predict the energies of the confined-state QW transitions for both RMB627 and RMB1048. These are then matched as closely as possible to the values derived from the various experimental spectra of the structures, and used to determine the true composition and width of the QW layers within each sample.

5.6.1 Theoretical Model
The theoretical model used to calculate confined-state transition energies within the QW layers uses an effective mass formalism (Andreani, 1987) with the bulk valence band described by a three band $k \cdot p$ Hamiltonian (O'Reilly, 1989). A list of the binary compound parameters used is given in Table 3.5, and the ternary compound parameters used in the model are interpolated from their constituent binary compound values using the formulae described by Krijn (Krijn, 1991). Band alignments at the QW interfaces are calculated using model solid theory (Van de Walle, 1989). Adjustments are made to the flat-band model to account for the presence of an electric field within the QW layers (quantum confined Stark effect) (Miller, 1984), and to account for exciton binding energies.

The magnitudes of the electric fields present in the QW layers of both samples were calculated from the graphical analysis of FKO's present in the PR spectra, as described in Section 3.2.2 (Shen, 1995; Hughes, 1995). For structure RMB627, this was calculated to be 13.5 ± 0.9 kV/cm. The upper theoretical limit of the internal field for RMB627 was determined to be 24.8 kV/cm, assuming a potential drop of 1.42 eV across an intrinsic cavity region of 5729 Å. The built-in electric field of sample RMB1048 has already been determined by the graphical analysis of FKO's in Section 4.2.2 and was found to be 18.0 ± 0.8 kV/cm. The resulting shifts of the theoretically predicted transition energies due to the presence of electric fields were found to be negligible for both structures, with the largest being for the $H_{11}$ transition: + 0.5 meV in RMB627, and + 0.7 meV in RMB1048.

Exciton binding energies were calculated for the $H_{11}$ transition using the fractional dimensionality approach described in Section 1.3.3 (Mathieu, 1992a; Mathieu, 1992b). The exciton binding energy shifts were found to be + 9 meV for both samples.

5.6.2 Results of Modelling

For RMB627, only the energies of the $H_{11}$ and $H_{12}$ transitions were known from experiment, with the energy of the $H_{12}$ transition being less certain than that of $H_{11}$.
From a comparison of these with the theoretical predictions (Table 5.4), the compositions and widths of the three QWs in structure RMB627 were determined to be close to the nominal values, with the layers having an indium composition of 22% and widths of 85 Å.

For RMB1048, the energies of a greater number of transitions were known from experimental measurements, giving greater validity to conclusions from a comparison with the theoretical calculations (Table 5.4). The width of the single QW in this sample was found to be close to its nominal value of 85 Å. However, the indium composition deviated somewhat from the nominal value of 23% and was determined to be 28%. This conclusion is in agreement with other studies on this sample (Sale, 1995) and explains why, at room temperature, the energy of the ground-state QW transition is some 20 meV lower than that of the cavity mode.

Owing to the strain-splitting of the valence band, there are no confined light-hole states in either of the structures. The values of the conduction band and heavy-hole valence band well depths, along with the associated $Q_c$ values, as given by eqn. (1.3), calculated for both structures, are given in Table 5.3.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>RMB627</th>
<th>RMB1048</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB well depth (meV)</td>
<td>129.3</td>
<td>156.7</td>
</tr>
<tr>
<td>HH valence band well depth (meV)</td>
<td>75.4</td>
<td>96.5</td>
</tr>
<tr>
<td>CB offset $Q_c$ (%)</td>
<td>63.2</td>
<td>61.9</td>
</tr>
</tbody>
</table>

Table 5.3 Values of the conduction band and heavy-hole valence band well depths, along with the conduction band offset for structures RMB627 and RMB1048 as determined from theoretical model.
The theoretically predicted transition energies are given in Table 5.4. Also given are the energies, linewidths and derivative-mixing parameters, as derived from the modelling of experimental spectra using one of the three methods described earlier: fitting the experimentally derived $\Delta e_2$ spectrum (labelled as "$\Delta e_2$ spectrum"); fitting of the actual VCSEL PR spectra with the CM near to resonance with a confined-state QW transition, using the model defined in Section 5.2.2 (labelled as "VCSEL-PR model"); fitting of a conventional PR spectrum after the top DBR was removed (labelled as "ETCH-PR").

![Table 5.4](image)

Table 5.4 Comparison of experimentally determined and theoretically predicted confined-state QW transition energies for sample RMB1048 and RMB627.

5.7 Summary
In Chapter 4, the energy of the CM feature in both the PR and R spectrum of a VCSEL was shown to have a dependence upon the experimental angle of incidence. Here, because of variation of the cavity length owing to growth irregularities across the wafer, the energy of the CM also depends upon the position on the sample, and this has been used to tune the CM feature through resonance with the ground-state QW transition in sample RMB627. The PR spectrum shows a great enhancement of the lineshape when the two features are in resonance, by a factor of \( \sim 40 \).

A new model has been developed to describe the PR lineshape of a VCSEL when the CM is close to resonance with a QW transition. The model is based on the discovery that the Séraphin coefficients of the QW layers in a VCSEL are no longer constant but are energy dependent. By numerical differentiation of \( R \), calculated by the transfer matrix method outlined in Chapter 4, the Séraphin coefficients have been calculated for both structures RMB627 and RMB1048. The Séraphin coefficients were then approximated in the model by the real and imaginary parts of a complex Lorentzian. Suitable lineshapes based on first differentials of a complex Lorentzian were used to describe the modulated changes in the complex dielectric function of the QW layers.

The VCSEL PR model was used to fit sets of PR spectra in which the CM moves through resonance with the ground-state QW transition, where each set was taken at a different angle of incidence. In all cases, the majority of the PR signal was found to come from the product of the Séraphin coefficient \( \beta \) and \( \Delta \varepsilon_2 \). In addition, the majority of the lineshape describing the modulated change in the complex dielectric function of the QW layers was found to come from the energy derivative of a complex Lorentzian. For some of the spectra in the series taken at \( 60^\circ \) incidence, the model has been extended to allow for the CM feature interacting with more than one confined-state QW transition.

A novel feature of the new VCSEL PR model made it possible to use the measured PR spectra to derive spectrum of the modulated change in the imaginary part of the dielectric function of the QW layers, \( \Delta \varepsilon_2 \), free from any effects of the cavity. The experiment required multiple PR and R spectrum pairs to be taken, with each single point in the \( \Delta \varepsilon_2 \) spectrum being derived from a separate PR and R spectrum pair. This
was done for both samples RMB627 and RMB1048. In the case of RMB1048 it was possible to do this across a large energy range revealing four additional higher-order QW transitions. The new VCSEL PR model was also used to fit the PR spectra where the CM is in resonance with higher-order QW transitions. A conventional PR spectrum was also taken of the exposed QW showing the full manifold of QW transitions in RMB1048, after removal of the top DBR stack by etching.

The confined-state QW transition energies derived from these various experimental methods have been compared with those predicted by a theoretical model based on an effective mass formalism. This comparison showed that the composition and width of the QW layers in RMB627 are close to those nominally intended, with the indium composition being 22% and the well width being 85 Å. However, although the width of the QW layer in RMB1048 was close to the intended 85 Å, the indium composition was found to depart significantly from the nominal 23% and was found to be 28%. 

5.8 References

Aspnes D E 1973 Surface Science 37 418
Fischer J E and Seraphin B O 1967 Solid State Commun. 5 973
Glembocki O J and Shanabrook B V 1992 The Spectroscopy of Semiconductors,
Semiconductors and Semimetals (New York: Academic Press) 36 221
Semicond. Sci. Technol. 10 1568
Krijn M C P 1991 Semicond. Sci. Technol. 6 27
Miller D A B, Chemla D S, Damen T C, Gossard A S, Weigmann W, Wood T H and
O'Reilly E P 1991 Semicond. Sci. Technol. 4 121
Qiang H, Pollak F H, Sotomayor Torres C M, Leitch W, Kean A H, Stroscio M A,
Seraphin B O and Bottka N, 1966 Phys. Rev. 145 628
Shen H and Dutta M 1995 J. Appl. Phys. 78 2151
Tang Y S 1991 J. Appl. Phys. 69 8298
3042
54 608
CHAPTER 6

Photomodulated Reflectance Studies of Self-Assembled InAs/GaAs Quantum Dot Structures

6.1 Introduction

This chapter uses photomodulated reflectance (PR) to examine material systems based on so-called 0-dimensional structures. Such low-dimensional structures are often referred to as quantum dots (QD), and the particular type of QD investigated in this chapter is the self-formed, or self-assembled type, fabricated using the InAs/GaAs material system. This work studies a number of self-formed QD structures, one containing just a single layer of QDs, and two containing two layers of QDs. PR studies are made on each of these samples at both room temperature and 80K.

The remainder of this chapter is organised as follows. The process by which self-assembled QDs are formed is described, and is followed by a review of the literature on such systems. A description of the samples used in this work is then given, followed by an examination of the PR studies. In addition, the effects of rapid thermal annealing (RTA) on self-assembled QD structures are investigated. Finally a series of measurements are made to investigate the temperature dependence of the energy and linewidth of the lowest energy QD transition.
6.1.1 Self-Assembled Quantum Dots and the Stranksi-Krastanow Growth Mode

A brief introduction to lower dimensional systems is given in Chapter 1, Section 1.5. The interest in creating QDs using semiconductor materials was initiated by the proposal that using such a system for the active component of a semiconductor laser would have a beneficial effect on the laser’s performance (Arakawa, 1982). Such lasers have since been realised and do indeed exhibit the properties originally predicted such as low threshold currents (Bimberg, 1996). Furthermore, other uses of QD structures have been proposed since their advent. For example, InAs/GaAs self-assembled QDs, such as those studied in this work, have recently been used to fabricate memory devices for use in optical computers (New Scientist, 1999; New Scientist, 1998). For a general review of QD systems and the effects of 0-dimensional confinement, the reader is referred to Johnson and Yoffe (Johnson, 1995; Yoffe, 1993).

Early attempts to fabricate QDs were made using lithographic techniques. However, with such techniques it is difficult to produce structures of a sufficiently small size to exhibit 0-dimensional confinement effects. Progress was made after the discovery that dot structures would form by themselves under certain epitaxial growth conditions – i.e. self-assembly. This occurs if one attempts to grow a layer of one material on another when there is a sufficiently large lattice mismatch between the two materials. In such a situation, 3-dimensional islands are formed by the relaxation of the highly strained epitaxial layer. This is described as the Stranski-Krastanow (SK) growth mode (Stranski, 1939; Stranski, 1981; Tiller, 1991), which is an intermediate growth regime lying between the 2-dimensional layer-by-layer growth and full 3-dimensional Volmer-Weber growth. SK growth is characterised by island nucleation and high diffusivity of surface adatoms.

The SK growth of dislocation-free islands was first demonstrated in 1990 using Ge grown on Si(110) (Eaglesham, 1990), and then in the following year for III-V semiconductors with InGaAs islands grown on GaAs (Snyder, 1991). However, 3-
Chapters: Photomodulated Reflectance Studies of Self-Assembled InAs/GaAs Quantum Dot Structures

dimensional growth and the formation of islands was noticed as early as 1985 in InAs/GaAs strained layer superlattices (Goldstein, 1985). Since then, the interest in such growth techniques has increased rapidly. Many different material systems have now been used to fabricate self-formed QD systems, with most of the work being carried out on the InAs/GaAs system (Leonard, 1993; Moisson, 1994; Madhukar, 1994; Grundmann, 1995; Yu, 1996). Other material systems that have been studied include InAs/InP (Houdré, 1993; Lamber, 1998), InP/InGaP (Kurlenbach, 1996), InAs/AlInAs (Fafard, 1996), and GaAs/GaAlAs (Qiang, 1994). Self-formed QDs have also been grown on crystallographic planes other than the conventional (001) orientation (Nishi, 1996; González-Borrero, 1996). For a review on the growth of self-assembled QD structures, the reader is referred to Nötzel (Nötzel, 1996).

An extensive amount of research has been performed investigating the shape and size of self-formed QDs, as well as their electronic structure. Structural characterisations have included using atomic force microscopy (AFM) (Moisson, 1994; Garcia, 1997), transmission electron microscopy (TEM) (Ruvimov, 1996), scanning transmission electron microscopy (STEM) (Lian, 1998; Sivers, 1999), reflection high energy electron diffraction (RHEED) (Lee, 1998), reflectance anisotropy spectrometry (RAS) (Steimetz, 1996), and spectroscopic ellipsometry (SE) (Steimetz, 1997). Various spectroscopic techniques have been employed to determine the energy levels within QDs, such as photoluminescence (PL) (Fafard, 1995; Saitoh, 1996; Raymond, 1996; Adler, 1998), PL excitation (Fafard, 1994; Heitz, 1996; Steer, 1996), photocurrent (Murray, 1999), capacitance (Schmidt, 1996), and resonant tunnelling techniques (Nahiro, 1997; Thornton, 1997). Until recently, modulation spectroscopy had only been used to a limited extent in the examination of the electronic structure of QDs with the contactless-electroreflectance (CER) study of InAs/GaAs material system (Aigouy, 1997). However, PR has since been used to examine confined states within such QDs at 80K (Sun, 1998), and at both 80K and room temperature (Rowland, 1998).

6.1.2 The InAs on GaAs (001) Material System
By far the most extensively researched material system from which self-formed QDs can be fabricated is that of InAs grown on GaAs(001). There is ~ 7.2% lattice mismatch between InAs and GaAs. Consequently, an epilayer of InAs on GaAs grows under extreme biaxial compressive strain, and when this layer exceeds a certain critical thickness its growth moves into the SK growth regime and islands of InAs begin to form. For the InAs/GaAs material system this critical thickness is ~ 1.7 monolayers (ML) (Moisson, 1994). The resultant InAs islands have a typical base size ~ 10-25 nm and a height ~ 2-10 nm (Moisson, 1994; Leonard, 1994), with the actual size being dependent to some extent upon the growth conditions. In fact, studies performed by Solomon et al. show that the size of the islands formed depends upon the temperature of the substrate during growth (Solomon, 1995a). Typically the temperature of the substrate ranges from 390-540°C. The density of island formation has been shown to be dependent upon three factors: growth rate, V/III growth flux ratio, and monolayer coverage (Solomon, 1995b). A decrease in the first two factors and an increase in the third all result in an increase in the island density. For a 2 ML coverage of InAs, assuming the island size is approximately 180 Å, the in-plane island density is ~ 30% of the ideal close packed density. When initially formed, the dots take the shape of four-sided pyramids with faces in the (136) planes (Lee, 1998). However, after the GaAs overgrowth on top of the formed dots, there is some degree of interdiffusion of the island material with the surrounding GaAs layer, so the final shape and composition of the dots are uncertain (Garcia, 1997).

To date, a number of alternative models have been proposed predicting the electronic structure within self-assembled QDs. These will be discussed only briefly here as no theoretical modelling of the QD transitions has been carried out in this work. Aside from knowing what final shape the actual dots take after the GaAs overgrowth, the biggest problem to overcome in producing a model of the electronic states is knowing the strain profiles through a QD. Different methods have been used to do this, such as by using calculations based on molecular dynamics (Jiang, 1997) or on a finite element method (Grundmann, 1995a). The first theoretical studies of the confined states within a QD used a single band effective mass model (Marzin, 1994) and
assumed that the strain within the dots is constant. The single band theory was then applied to pyramidal shaped dots (Grundmann, 1995a). However, this model still neglected details such as mixing between the light- and heavy-hole valence bands, and changes in the effective mass due to strain. These factors are accounted for in the subsequent model proposed by Cusack (Cusack, 1996).

### 6.1.3 InAs/GaAs QD Samples

The samples used in this work were grown by solid source molecular beam epitaxy, and were supplied by Dr. R. Murray\(^7\). Three samples were investigated, denoted U6036 which has a single layer of InAs QDs in GaAs, and U7120 and U7121 which have two layers of QDs. In sample U7120 the two QD layers are separated by 50 Å of GaAs, and in sample U7121 by 100 Å of GaAs. The samples were fabricated as follows: a 0.4 μm undoped GaAs buffer layer was first grown on a GaAs substrate at a temperature of 580\(^{0}\)C. The substrate temperature was then reduced to 520\(^{0}\)C and a further 200 Å of GaAs was deposited. Following this, 2 MLs of InAs were then deposited. For sample U6036, this was the only deposition of InAs, but for U7120, and U7121, this was followed by the deposition of 50 Å, and 100 Å, respectively, of GaAs, followed by another 2 ML of InAs. All three samples then received another 200 Å of GaAs at 520\(^{0}\)C, followed by 300 Å of GaAs at 580\(^{0}\)C. The InAs coverage was grown at 0.25 μm h\(^{-1}\). In much of the literature this InAs coverage is assumed to remain as a thin layer 1-2 ML thick, and is referred to as the wetting layer. However, as is discussed in this work, it is more likely that this layer has diffused somewhat into the overlying GaAs layer and has formed a 3-dimensional InGaAs layer surrounding the QDs. Hence, in this work, such layers will be referred to as the confining layer (CL). STEM studies on these samples showed the dots have a lateral dimension of ~40 nm, a height of ~11.5 nm, an average lateral separation of ~60 nm, and a density of 3 ×10\(^{10}\) cm\(^{-2}\) (Siverns, 1998).

\(^7\) Centre for Electronic Materials and Devices, Imperial College, London SW6 2BZ.
6.2 Photomodulated Reflectance Measurements

This section examines the PR measurements made on samples U7120 and U7121 at both room temperature and ~80K, and compares the results with PL measurements performed at 13K. Although PR measurements were performed at both temperatures for sample U6036, only the 80K measurements were successful in observing any clear spectra from the QDs. Consequently, the bulk of the discussion will focus on the results from samples U7120 and U7121.

6.2.1 Experimental Details

Room temperature measurements were performed on all three samples using the experimental apparatus described in Section 2.2 and shown in Fig. 2.4a. The 2 mW HeNe laser was chopped at a frequency of 333 Hz. Measurements were performed at an incident angle of 45° over an energy range of 0.98 - 1.46 eV using a spectrometer slit of 2 mm x 800 μm. This gave an instrumental resolution of 3.0 meV (FWHM) across the energy range studied. Owing to the weak signal from the QDs it was necessary to use scan times of up to 24 hours to achieve an adequate signal to noise ratio. The room temperature measurements were taken with the lock-in set to be in phase with the PL from the samples.

The ~80K measurements were performed on all three samples using the experimental apparatus described in Section 2.2 and shown in Fig. 2.4a. The sample was housed in a cold-finger liquid nitrogen cryostat. Measurements were performed at an experimental angle of incidence of 23°. The sample was again modulated at 333 Hz,
using an attenuated laser power of 0.02 mW. Measurements were performed over an energy range of 1.09 - 1.55 eV, using a spectrometer slit of 2 mm × 800 μm, giving an instrumental resolution of 3.2 meV (FWHM) over this energy range. The 80K measurements were taken 90° out of phase with the PL, as it was found that at this temperature such a phase setting gave a better signal to noise ratio.

The PL measurements shown in this chapter were performed elsewhere.

6.2.2 PR Measurements of U7120 and U7121

Fig. 6.1 shows an example of a PR spectrum obtained for one of the double layered samples, U7120, at room temperature across the whole energy range. The spectrum is of one of the double layered samples, U7120. A feature can be seen at ~ 1.42 eV which is due to the GaAs layers within the sample. Also present in the spectrum at energies above this, is structure due to the Franz-Keldysh oscillations (FKO) within the GaAs layers. At energies of ~1.33 eV and ~1.37 eV two features can be seen which are due to confined-state transitions within the InGaAs CL. At energies below the CL transitions, there are a number of smaller features arising from transitions within the QDs. These can only be seen in the inset on a more sensitive scale. Indeed such features can be seen to have intensities of ~ 1×10⁶. This highlights the difficulty in obtaining an adequate signal to noise ratio in the PR spectra of QD structures. Graphical analysis of the FKO's present in the room temperature PR spectra were used to determine the built-in electric field within each sample using the methods outlined in Chapter 3, Section 3.2.2 (Shen, 1995; Hughes, 1995). The built-in fields were found to be: 21 ± 7 kV/cm for U6036, 11 ± 7 kV/cm for U7120, and 9 ± 7 kV/cm for U7121.
Fig. 6.1 PR spectrum of QD sample U7120 (two layers, 50 Å GaAs separation) taken at room temperature and in phase with the PL. Shown on the figure is structure due to Franz-Keldysh oscillations (FKO), GaAs layers, and confining layers. Inset graph shows confined-state transitions within the QDs.

Figs. 6.2a, and 6.2b, show the room temperature PR spectra for samples U7120, and U7121, respectively, across the energy range of the QD transitions. The experimental data are shown as dots and the solid lines show the lineshape fits to the data. Both spectra have been fitted with a number of third differential functional forms (TDFF) (Aspnes, 1973) defined by eqn. (2.31), using an exponent of \( n = 2 \), suitable for excitonic confined states. In each spectrum, five such TDFFs have been used corresponding to the five observed confined-state transitions within the QDs, denoted as QD1-QD5. A vertical and horizontal line are used to represent each fitted TDFF, with the position and length of the vertical line indicating the energy, \( E_g \), and intensity, \( C/T^3 \), respectively, of the fitted TDFF. The length of horizontal line represents the half width at half maximum of the TDFF. There is a sloping background present in the spectra of both U7120 and U7121, the cause of which is unknown but which may be due to the residual tail of near by CL and GaAs features. Consequently, it was necessary to include a sloping linear background to fit these spectra.
Figs. 6.2a (top), and 6.2b (bottom), Room temperature PR spectra of QD samples U7120, and U7121, respectively, taken in phase with the PL. The experimental data are shown as dots, with the solid line showing the fit. The positions and lengths of the vertical lines indicate the energies, $E_g$, and intensities, $C/\Gamma$, respectively, of the TDDs fitted to the QD transitions. The lengths of the horizontal lines represent the half widths at half maximum.
Figs. 6.3a (top), and 6.3b (bottom). Room temperature PR spectra of QD samples U7120, and U7121, respectively, taken in phase with the PL. The experimental data are shown as dots, with the solid line showing the fit to the data. The positions and lengths of the vertical lines indicate the energies, $E_p$, and intensities, $C/I^3$, respectively, of the TDFFs fitted to the CL transitions. The lengths of the horizontal lines represent the half widths at half maximum. In Fig. 6.3b a section of the spectrum has been scaled by the factor in parentheses.
The fitted energies and half widths at half maximum (HWHM) of the QD transitions are given in Table 6.1 (see end of this Section).

Figs. 6.3a, and 6.3b, show the room temperature PR spectra for samples U7120, and U7121, respectively, across the energy range of the CL and GaAs transitions. Two CL transitions were identified in each spectrum and were fitted with TDFFs, eqn. (2.31) with $n = 2$. These have been denoted as CL1 and CL2. Again, the position and length of the vertical lines, and the length of the horizontal lines in the figure represent the $E_g$, $C/T^3$, and HWHM, respectively, of these TDFFs. The bulk GaAs feature in each spectrum was fitted using two TDFFs, $n = 2.5$. The energies and HWHM of the two CL transitions are given in Table 6.1.

Figs. 6.4a, and 6.5a, show the PR spectra of samples U7120, and U7121, respectively, taken at ~ 80K. Again, both the spectra were fitted using a number of TDFFs, eqn. (2.31) with $n = 2$. The fits to the data are shown as the solid lines. A total of seven TDFFs were used to fit both spectra, five corresponding to confined-state transitions within the dots, and two corresponding to transitions within the CLs. All the fitted TDFFs have been represented by a horizontal and vertical line. The corresponding energies and HWHM are given in Table 6.1. It should be noted that at 80K the intensities of the QD transitions are of the same order of magnitude as the CL transitions. This was not the case for the room temperature measurements where the PR signal from the QDs was several orders of magnitude weaker than that from the CLs.

Figs. 6.4b, and 6.5b, show the modulus of PR spectra, $|\text{PRI}|$, for samples U7120, and U7121, respectively. The purpose and application of a $|\text{PRI}|$ spectrum is described in Chapter 3, Section 3.2.3 (Hosea, 1995). The energies of the QD transitions, as defined by the positions of the peaks in the $|\text{PRI}|$ spectra, are in good agreement with the energies of the TDFFs fitted to the PR spectrum (shown by the vertical lines in Figs. 6.4a and 6.5a).
Fig. 6.4a (top) PR spectrum of QD sample U7120 taken at 80K and at 90° out of phase with the PL, shown as dots. The solid line shows the fit to the data. The positions and lengths of the vertical lines indicate the energies, $E_p$, and intensities, $C/F^2$, respectively, of the TDFs fitted to the QD and CL transitions. The lengths of the horizontal lines represent the half widths at half maximum. A section of the spectrum has been scaled by the factor in parentheses.

Fig. 6.4b (middle) Modulus of PR spectrum of QD sample U7120, calculated from the PR spectrum shown in Fig. 6.4a.

Fig. 6.4c (bottom) PL spectrum of QD sample U7120 taken at 13K, shown as dots. Solid line shows the fit to the data using five Gaussians. The grey lines show the individual Gaussians used in the fit.
Chapter 6: Photomodulated Reflectance Studies of Self-Assembled InAs/GaAs Quantum Dot Structures

Fig. 6.5a (top) PR spectrum of QD sample U7121 taken at ~ 80K and at 90° out of phase with the PL, shown as dots. The solid line shows the fit to the data. The positions and lengths of the vertical lines indicate the energies, $E_p$, and intensities, $C/T^3$, respectively, of the TDFs fitted to the QD and CL transitions. The lengths of the horizontal lines represent the half widths at half maximum. A section of the spectrum has been scaled by the factor in parentheses.

Fig. 6.5b (middle) Modulus of PR spectrum of QD sample U7121, calculated from the PR spectrum shown in Fig. 6.5a.

Fig. 6.5c (bottom) PL spectrum of QD sample U7121 taken at 13K, shown as dots. Solid line shows the fit to the data using five Gaussians. The grey lines show the individual Gaussians used in the fit.
Figs. 6.4c, and 6.5c, show PL spectra of samples U7120, and U7121, respectively, taken at 13K. In both figures, the data are shown as dots with the fit to the data shown as a solid line. The fit comprises five Gaussian lineshapes, with each individual Gaussian being shown by a grey line. The energies and HWHM of the fitted Gaussians are given in Table 6.1.

All six figures of 6.4a-c and 6.5a-c have been graphed on the same energy scale. This is to allow a direct comparison between the PR and IPRI measurements performed at 80K, and the PL measurements performed at 13K. Using Varshni's law (see Section 1.2.2) (Varshni, 1967), the maximum shift in the bandgap for bulk InGaAs, between 80K and 13K is only of the order of 10 meV. Therefore it is reasonable to compare directly the 80K measurements with those taken at 13K.

The PR spectra of samples U7120 and U7121 show that there are five confined-state transitions within the QDs. These transitions are roughly equally spaced, by $54 \pm 5$ meV at room temperature, and by $54 \pm 10$ meV at 80K. Up to five confined state transitions have been observed experimentally within similar QD structures (Raymond, 1996). Equally spaced transitions are consistent with a roughly parabolic confining potential within the QDs (Drexler, 1994; Gumbs, 1994). Assuming the conduction-band/valence-band offset ratio is the same in these QDs as it is for an InGaAs/GaAs QW, i.e. 65:35 (Hosea, 1996), then the electron confining potential is $-225$ meV. Thus if one assumes an electron confinement energy of 45 meV (Drexler, 1994), then this would indeed indicate that there are up to five confined electron states within the QD. Until recently there was some debate over the number of confined electron states within the type of QD examined here. It has been shown theoretically that the number of confined electron-states depends upon not only the size of the dot, but also its shape (Kim, 1998). Only one confined electron-state is predicted for pyramidal shaped dots (Grundmann, 1995a), whilst at least two are predicted for cone shaped dots (Marzin, 1994). Recently, this matter has been clarified experimentally by Itskevich et al. (Itskevich, 1999). They showed, using the quenching of PL emissions under high pressure, that the transitions in these types of QDs are in fact between...
electron- and hole-states with the same quantum number, in agreement with the interpretation of Schmidt et al. (Schmidt, 1996).

In the PR spectra of U7120 and U7121, at both room temperature and 80K, (Figs. 6.3a, 6.3b, 6.4a, and 6.5a) there are two features which are attributed to transitions within the CLs. Similar features are seen in the CER study by Aigouy et al. (Aigouy, 1997). They describe these features as being due to ground-state heavy-hole and light-hole transitions within a superlattice formed by multiple InAs wetting layers. However there are no superlattices in the samples examined here, and owing to the large built-in strain of the CL, there should be no confined light-hole states. It is possible that the two thin InAs layers within the double layered samples act as a coupled QW system. In such a case both of the transitions would be due to the $H_{11}$ transition. However, STEM measurements made on these samples (Siverns, 1998) show that the capping of QDs causes In to migrate out of the InAs wetting layer into the overlying GaAs layer forming a three-dimensional $\text{In}_x\text{Ga}_{1-x}\text{As}$ CL, with $x = 0.07$ and a thickness of $\sim 65 \text{ Å}$. Such a layer would still be expected to have no confined light-hole states, and the energy separation of the two transitions observed in the spectra are too small for one of them to be a higher-order heavy-hole confined state. It may be possible that the presence of the QDs within the CLs perturbs the confined-states making transitions with light-hole valence band possible. It would seem that a simple examination of a similar sample, which contains only a single QD layer, would clarify the matter. Such an examination could have two possible outcomes:

(a) The presence of only one CL transition in the PR spectrum which would indicate that in the double layered samples, the two transitions observed are due to the two thin InAs WLs acting as a coupled QW system, or

(b) the presence of two CL transitions in the PR spectrum of a single layered sample which would confirm that the layer is in fact a diffuse three-dimensional CL.

In a similar PR study of a single layered QD sample, Sun et al. (Sun, 1998) observed only one CL transition. However, as can be seen in Fig. 6.7, PR measurements made on U6036 indicate the presence of two CL transitions in this single layered sample. Hence the question remains unresolved. It may be possible to use some form of
polarisation-dependant experiment to determine if the CL transitions in U7120 and U7121 arise from both heavy- and light-hole confined-states or whether they are both due to the $H_{11}$ transition.

Comparing the room temperature measurements with those taken at 80K for both samples reveals additional information about the QDs themselves. For sample U7120, the whole set of QD transitions shift in energy by $\sim 110$ meV between room temperature and 80K. For sample U7121 the shift is $\sim 90$ meV. This shift is too large for the dots to be composed only of InAs, as the calculated shift in direct bandgap for bulk InAs is only $\sim 55$ meV between room temperature and 80K. This suggests that the QDs are in fact some form of InGaAs composite. This shift in energy of the QD transitions is in fact larger than the shift of the bandgap of bulk GaAs, which is calculated to be $\sim 83$ meV between room temperature and 80K. There are other factors, therefore, influencing the shift in the QD transition energies between these two temperatures, such as changes in the strain within the QDs. STEM studies on these samples (Siverns, 1998) have determined the composition of these QDs to be $\text{In}_x\text{Ga}_{1-x}\text{As}$, where $x = 0.31$.

Another point of significant interest is the effect that the change in temperature has on the linewidth of some of the QD transitions. Conventionally, lowering the temperature from room temperature to 80K in a PR experiment has the effect of narrowing the linewidths of features observed in the spectrum (Pollak, 1993). However, for the QD samples U7120 and U7121 studied here, lowering the temperature from room temperature to 80K has the effect of increasing the linewidths of some of the confined-state transitions within the dots. This can be seen by comparing Figs. 6.2a, and 6.2b, with Figs. 6.4a, and 6.5a, respectively, or by comparing the linewidths (HWHM) of the fitted TDFFs given in Table 6.1. For example, the HWHM of the QD transition, QD1, in sample U7120 at room temperature is only 19 meV, whilst at 80K it has increased to 40 meV. The cause of this phenomenon can be explained as follows. The actual linewidth of a confined-state transition within a single QD is in fact very narrow, due to the $\delta$-function-like density of states. Grundmann et al. have
reported ultranarrow cathodoluminescence lines (<0.15 meV) originating from single InGaAs/GaAs QDs (Grundmann, 1995b). The broadness of the QD transitions observed in the PR and PL spectra of the samples studied here is due to the inhomogenous broadening caused by the distribution of dot sizes.

As the sample is cooled, it is possible that there is a deepening in the confining potential within the dot. The cause of the deepening is most likely to be a change in the strain profile within the dots. For a given distribution of dot sizes, an increase in the confining potential within the dots will result in an increase in the distribution of transition energies, effectively increasing the observed linewidth. However, owing to the parabolic shape of the confining potential, this effect will be greatest for the lowest lying QD transition, and confined-states lying nearer the top of the confining potential will be affected less. This can be seen by examining the linewidths of QD transitions QD1-QD5 for samples U7120 and U7121. There is an increase in linewidth for transitions QD1-QD2 in sample U7120, and for transitions QD1-QD4 in sample U7121 when there is a change from room temperature to 80K. But for the same temperature change, there is a decrease in the linewidth of the higher lying confined transitions; QD3-QD5 for sample U7120, and QD5 for sample U7121. Other explanations have been offered for this phenomenon, which are described in Section 6.4, where the broadening of QD1 transition with reduced temperature is explored in more detail.

The samples U7120 and U7121 both contain two layers of QDs, with a separation of 50 Å in U7120, and 100 Å in sample U7121. Owing to these relatively close spacings, it is reasonable to anticipate some degree of coupling between the confined-states within the dots of the two layers. It has been shown that during growth, interacting strain fields, induced by the presence of islands in one layer, force self-organised growth in a vertical direction (Xie, 1995; Mukhametzhanov, 1998). That is to say that islands in a second layer will tend to nucleate directly above a QD in the first layer. Owing to the parabolic-like nature of the confining potential, the lower lying confined
states are not expected to couple so strongly to confined-states within the second layer of dots, unlike the higher lying confined-states.

![Diagram of Vertically Aligned QDs](image)

Fig. 6.6 Schematic of the confining potentials of two vertically aligned QDs. In situation (a) QDs are separated. In situation (b), the higher confined-states of the QDs are coupled.

This is demonstrated in Fig. 6.6, which shows the schematic of the confining potentials of two vertically aligned QDs. In situation (a), the separation between the dots is such that the confined-states within each dot remain separate. However, in situation (b) where there is less separation in the vertical direction, the higher lying states within each QD are now coupled.

This effect is evident when comparing the QD transition energies derived from the 80K PR measurements of sample U7120 with U7121. For transitions QD1-QD3, there is little difference in the energy of the transitions between the two samples. However, the transitions QD4 and QD5 have a greater energy in sample U7120 than they do in sample U7121. As the separation between the two layers in sample U7120 is only 50
Å, the situation is analogous to that shown in Fig. 6.6 (b), and the higher lying states are coupled. This causes a blueshift of QD4 and QD5 in sample U7120, relative to sample U7121.

6.2.3 PR Measurements of U6036

The studies of the sample with a single QD layer, U6036, provided less information than did the double layered samples, U7120 and U7121. It was not possible to observe any structure from confined-state transitions within the QDs at room temperature using PR, although the CL transitions were present. In addition, no 13K PL measurements were available for this sample. However, the 80K PR measurements were successful in determining the energies of the QD transitions QD1-QD5, as well as several CL transitions.

![PR spectrum of QD sample U6036 taken at room temperature and in phase with the PL, shown as dots. The solid line shows the fit. The positions and lengths of the vertical lines indicate the energies, $E_p$, and intensities, $C/T^3$, respectively, of the TDFFs fitted to the CL transitions. The lengths of the horizontal lines represent the half widths at half maximum. The section of the spectrum corresponding to the bulk GaAs feature has been scaled by the factor in parentheses.](image)
Fig. 6.7 shows the room temperature PR measurements of U6036, as the series of dots. The solid line shows the fit to the data using TDFFs, eqn. (2.31) with $n = 2$. The energies of the two CL transitions are again marked by the position of the vertical lines, with their lengths representing the intensities, $C/F^3$, of the TDFFs. The horizontal lines represent the HWHMs. The energies and HWHM of the two CL transitions are given in Table 6.1.

Fig. 6.8a shows the PR spectrum of sample U6036 taken at ~80K. The section of the spectrum above 1.46 eV is shown as the thin solid line and has been scaled by a factor of 0.06. Seven TDFFs, eqn. (2.31) with $n = 2$ were used to fit the data, with the fit being shown as the solid line. Again, as with the double layer samples, U7120 and U7121, five QD transitions were detected and the energies of these are labelled in the figure as QD1 - QD5. The two confining layer transitions are labelled CL1 and CL2. The energies and HWHM of the fitted TDFFs are given in Table 6.1.

Fig. 6.8b shows the corresponding modulus of PR spectrum, |PR|, for sample U6036 at 80K. This spectrum confirms the positions of the two CL transitions and also suggests that there are at least four QD transitions present, corresponding to the positions of QD1, QD3, QD4, and QD5 in Fig. 6.8a.

The PR spectrum at 80K (Fig. 6.8a) indicates that there are five equally spaced QD transitions present in the single layered sample, with an average separation of 51 ± 2 meV. The two confining layer transitions observed at both room temperature and 80K have less energy separation than in the case of the double layered samples. The fact that there are two such transitions in only a single layered sample does suggest that the CL is a diffuse 3-dimensional InGaAs layer, and that the presence of the QDs within this layer perturb the confined valence-band states, enabling transitions with the light hole valence band.
There are two significant differences between the QD transitions in the single layered sample, U6036, and in the double layered samples, U7120 and U7121. The first is that in U6036, the transitions are shifted to slightly higher energies than in the double layered samples: the energy of QD1 in U6036 is 1.212 eV, some 50 meV higher than in samples U7120 or U7121. Other workers have reported such a shift in the energy of QD1 (~80 meV) for similar material systems (Solomon, 1996; Wang, 1997; Heitz, 1998). The second difference between the single layered sample (U6036) and the double layered samples (U7120 and U7121) is that the linewidth of QD1 is reduced in the double layered samples. The cause of both of these effects is as follows: in the
double layered sample, self-organised growth also occurs in the vertical direction, with QDs in the second layer having a tendency to nucleate above a QD in the first layer. Owing to the presence of the underlying QD, the dot in the second layer experiences a reduced strain field, which improves the island shape and size uniformity. The reduction in the distribution of dot sizes and shapes reduces the linewidth of QD1, whilst the reduced strain field in the dots, red shifts its energy (Solomon, 1996; Heitz, 1998).

<table>
<thead>
<tr>
<th>Transition</th>
<th>PR (300K)</th>
<th>PR (80K)</th>
<th>PL (13K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_g$ (eV)</td>
<td>HWHM (meV)</td>
<td>$E_g$ (eV)</td>
</tr>
<tr>
<td>U7120 (Two QD Layers, 50 Å Separation)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QD1</td>
<td>1.053</td>
<td>19</td>
<td>1.162</td>
</tr>
<tr>
<td>QD2</td>
<td>1.105</td>
<td>22</td>
<td>1.214</td>
</tr>
<tr>
<td>QD3</td>
<td>1.160</td>
<td>36</td>
<td>1.269</td>
</tr>
<tr>
<td>QD4</td>
<td>1.224</td>
<td>25</td>
<td>1.344</td>
</tr>
<tr>
<td>QD5</td>
<td>1.277</td>
<td>33</td>
<td>1.385</td>
</tr>
<tr>
<td>CL1</td>
<td>1.329</td>
<td>16</td>
<td>1.421</td>
</tr>
<tr>
<td>CL2</td>
<td>1.365</td>
<td>13</td>
<td>1.483</td>
</tr>
<tr>
<td>U7121 (Two QD Layers, 100 Å Separation)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QD1</td>
<td>1.074</td>
<td>24</td>
<td>1.162</td>
</tr>
<tr>
<td>QD2</td>
<td>1.126</td>
<td>26</td>
<td>1.213</td>
</tr>
<tr>
<td>QD3</td>
<td>1.182</td>
<td>22</td>
<td>1.264</td>
</tr>
<tr>
<td>QD4</td>
<td>1.228</td>
<td>26</td>
<td>1.325</td>
</tr>
<tr>
<td>QD5</td>
<td>1.278</td>
<td>24</td>
<td>1.374</td>
</tr>
<tr>
<td>CL1</td>
<td>1.347</td>
<td>19</td>
<td>1.416</td>
</tr>
<tr>
<td>CL2</td>
<td>1.386</td>
<td>9</td>
<td>1.458</td>
</tr>
<tr>
<td>U6036 (Single QD Layer)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QD1</td>
<td>-</td>
<td>-</td>
<td>1.212</td>
</tr>
<tr>
<td>QD2</td>
<td>-</td>
<td>-</td>
<td>1.262</td>
</tr>
<tr>
<td>QD3</td>
<td>-</td>
<td>-</td>
<td>1.312</td>
</tr>
<tr>
<td>QD4</td>
<td>-</td>
<td>-</td>
<td>1.362</td>
</tr>
<tr>
<td>QD5</td>
<td>-</td>
<td>-</td>
<td>1.414</td>
</tr>
<tr>
<td>CL1</td>
<td>1.365</td>
<td>19</td>
<td>1.436</td>
</tr>
<tr>
<td>CL2</td>
<td>1.384</td>
<td>13</td>
<td>1.451</td>
</tr>
</tbody>
</table>

Table 6.1  Gives the energies and half width at half maximum (HWHM) of all QD and CL transitions observed in the QD samples U7120, U7121, and U6036. Values given are derived from room temperature PR measurements, 80K PR measurements, and 13 K PL measurements.
6.3 The Effects of Rapid Thermal Annealing

In this section, one of the double layered QD samples, U7121, which was subjected to rapid thermal annealing (RTA), is examined by PR to investigate the effects of this heat treatment on the electronic and structural properties of the QDs. Such RTA treatment of InAs/GaAs QD samples is reported to cause a blue shift in the QD transition energies and a narrowing of the associated linewidths (Lean, 1996; Kosogov, 1996; Malik, 1997; Xu, 1998).

6.3.1 Experimental Details

The RTA, which was performed elsewhere\textsuperscript{7}, involved capping a section of sample U7121 with 1000 Å of SiO\textsubscript{2}. This was then annealed for 120 seconds at a temperature of 850°C, after which the SiO\textsubscript{2} cap was removed. Room temperature and 80K PR measurements were then performed on the sample using conditions identical to those described in Section 6.2.1. The 13K PL measurements shown for the annealed section of U7121 were performed elsewhere\textsuperscript{7}.

6.3.2 PR Measurements

Fig. 6.9 shows the room temperature spectrum of the annealed section of sample U7121. The data are shown as dots, with the section of spectrum above the energy of 1.36 eV scaled by a factor of 0.03. The solid lines show the fits to the data using four
TDFFs, eqn. (2.3) with $n = 2$. Of the QD transitions, only the lowest energy one, QD1, has been fitted, and the energy, intensity, and linewidth of this are again indicated by the vertical and horizontal lines. Furthermore, only one CL transition was detected, also fitted with a single TDFF. The remaining two TDFFs were used to fit the bulk GaAs feature. The QD1 transition was found to have blue shifted in energy by $\sim 270$ meV to $\sim 1.330$ eV, as a result of the RTA treatment. Furthermore, the linewidth of this transition was found to decrease from 24 meV to 6 meV (HWHM). Although only one QD transition has been fitted with a TDFF in the room temperature spectrum, there is an indication of a second QD transition, QD2, at an energy of $\sim 1.350$ eV (marked on the figure by an arrow). The CL transition was found to have an energy of 1.462 eV, having undergone a smaller blue shift because of the RTA, of $\sim 38$ meV. The energies and HWHM of the fitted TDFFs are given in Table 6.2.

![Fig. 6.9 PR spectrum of QD sample U7121 after RTA at 850°C for 120 seconds, taken at room temperature and in phase with the PL. The data are shown by the dots and the solid lines show the fits to the data. The positions and lengths of the vertical lines indicate the energies, $E_p$, and intensities, $C/T^3$, respectively, of the TDFFs fitted to the QD1 and CL1 transitions. The lengths of the horizontal lines represent the half widths at half maximum. Also indicated by an arrow is the presence of the second confined-state QD transition, QD2. A section of the spectrum has been scaled by the factor in parentheses.](image)

---

7 Centre for Electronic Materials and Devices, Imperial College, London SW6 2BZ.
Chapter 6: Photomodulated Reflectance Studies of Self-Assembled InAs/GaAs Quantum Dot Structures

Fig. 6.10a (top) PR spectrum of QD sample U7121 after RTA at 850°C for 120 seconds, taken at 80K and 90° out of phase with the PL. Data are shown as dots and the thick solid line shows the fit. The positions and lengths of the vertical lines indicate the energies, $E_g$, and intensities, $C/T^3$, respectively, of the TDFFs fitted to the QD and CL transitions. The lengths of the horizontal lines represent the half widths at half maximum. A section of the spectrum has been scaled by the factor in parentheses and is shown as the thin solid line.

Fig. 6.10b (middle) IPRI spectrum of QD sample U7121 after RTA at 850°C for 120 seconds. Calculated from the PR spectrum shown in Fig. 6.10a.

Fig. 6.10c (bottom) PL spectrum of QD sample U7121 after RTA at 850°C for 120 seconds, taken at 13K. Data are shown as dots and solid line shows the fit to the data using three Gaussians. Each Gaussian in the fit is shown by a grey line.
Chapter 6: Photomodulated Reflectance Studies of Self-Assembled InAs/GaAs Quantum Dot Structures

Fig. 6.10a shows the PR spectrum taken at ~ 80K for sample U7121 after RTA. The data are shown as the series of dots, with the spectrum above 1.495 eV shown as the thin solid line and scaled by a factor of 0.05. The thick solid line shows the fit to the data. Three QD transitions and one CL transition are present in the spectrum and the energies and HWHM of these are given in Table 6.2.

Fig. 6.10b shows the |PRI| spectrum calculated from the PR spectrum shown in Fig. 6.10a. This spectrum again confirms the usefulness of calculating such a spectrum, as the energy positions of the fitted TDFFs in the ΔR/ΔT spectrum agree well with the positions of the peaks in the |PRI| spectrum.

Fig. 6.10c shows the 13K PL spectrum of the annealed section of U7121. The solid line indicates the fit to the data using three Gaussians. The individual Gaussians used in the fit are shown as the grey lines. The energies and HWHM of the fitted Gaussians are given in Table 6.2. Again there is an excellent agreement between the results of the two techniques.

<table>
<thead>
<tr>
<th>Transition</th>
<th>PR (300K)</th>
<th>PR (80K)</th>
<th>PL (13K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eg (eV)</td>
<td>HWHM (meV)</td>
<td>Eg (eV)</td>
</tr>
<tr>
<td>QD1</td>
<td>1.330</td>
<td>6</td>
<td>1.410</td>
</tr>
<tr>
<td>QD2</td>
<td>(1.350)</td>
<td>-</td>
<td>1.424</td>
</tr>
<tr>
<td>QD3</td>
<td>-</td>
<td>-</td>
<td>1.442</td>
</tr>
<tr>
<td>CL1</td>
<td>1.385</td>
<td>10</td>
<td>1.462</td>
</tr>
</tbody>
</table>

Table 6.2 gives the energies and half width at half maximum (HWHM) of all QD and CL transitions observed in the QD sample U7121 after RTA at 850°C for 120 seconds. Values given are derived from room temperature PR measurements, 80K PR measurements, and 13K PL measurements.
After the RTA, the position of QD1 in the 80K PR measurements is blue shifted by ~250 meV. Similar results were observed by Xu et al. (Xu, 1998) who observed a blue shift of the QD emission energy of ~260 meV for an annealing temperature of 850°C. They also showed that the greater the annealing temperature, the greater the shift of the transition energy. The annealing process also narrows the linewidths of the transitions, with the HWHM of QD1 narrowing from 39 meV to 11 meV. Similar effects are described by Leon et al. (Leon, 1996) who showed that a 30 second anneal at 850°C was sufficient to cause a similar decrease in the linewidth. Only one CL transition was detected in the 80K PR spectrum, and this experienced less of a blue shift than the QD transitions, of ~46 meV.

As a result of the RTA, the three QD transitions observed in both the PR (80K) and PL (13K) measurements are more closely spaced with only ~16 ± 2 meV between each transition. We can conclude from this that the size of the QDs has increased, and this leads to an explanation of both the blue shift and narrowing of the transition energies. Xu et al. (Xu, 1998) claim that annealing at a temperature of 850°C is enough to destroy the QDs. However, the QDs are clearly not destroyed in the sample investigated here. Malik et al. (Malik, 1997) suggest that an anneal such as the one performed here causes the QD to roughly double in diameter, which would cause the transition energies to experience a red shift. However, this increase in size also causes a dilution of the In concentration within the QDs, and this dilution effect would be proportional to the increase in the volume of the QD. Thus, as the diameter of the dot doubles, the volume increases by a factor of 8, consequently the In concentration is reduced by a factor of 8, causing a blue shift in the transition energy. It is believed that this latter effect dominates, resulting in an overall blue shift of the observed transition energies. The increase in size of all the QDs also reduces the relative distribution of dot sizes. This would explain the observed reduction in the linewidths of the transition energies. There is also a small shoulder observed in the PR spectrum (Fig. 6.10a) at ~20 meV below QD1. This feature is not present in the PL spectra even at low excitation power. Its cause is unknown and requires further investigation.
6.4 Temperature Dependence of the Linewidth of QD1

In Section 6.2.2 it was noted that the linewidths of confined-state QD transitions, observed in the PR spectra, did not undergo the usual narrowing as the temperature was lowered from room temperature to 80K. Instead, the linewidths of some of the QD features appeared to increase. This section investigates this behaviour further, in sample U7121, by studying the lowest energy QD transition, QD1, over a range of temperatures from 80K to room temperature.

Such a decrease in the QD1 transition linewidth with increasing temperature has been reported by Lubyshev et al. (Lubyshev, 1996) and has been attributed to carrier transfer between the dots. In other cases, first a decrease in linewidth, and then an increase, is observed with increasing temperature (Lee, 1997). Dai et al. have reported that the amount of monolayer coverage used to form the dots influences whether an increase or a decrease in PL linewidth is observed with increasing temperature (Dai, 1997). The behaviour of the linewidth in such PL experiments is explained by two thermally activated PL quenching processes (Brusaferri, 1996). Above a certain temperature, excitons begin to dissociate and the carriers escape from the dots. This process will begin with the smallest dots, effectively reducing the distribution of dot sizes. In addition, carriers can now transfer between the QDs via the CL. The carriers will naturally migrate to the lowest energy states and therefore the effect will be to concentrate the carriers in the dots with the deepest confining potential thus reducing the distribution of transition energies. However, an alternative explanation is feasible (see Section 6.2.2): that a reduction in temperature causes an increase in the strain profile within the dots, increasing the distribution of QD1 energies for a given distribution of dot sizes. This would explain the increased linewidths of QD1 observed (Rowland, 1998).

---

8 It should be noted that such processes only explain the observed behaviour of the linewidth in PL measurements. The same explanation is not valid in the case of PR measurements.
Chapter 6: Photomodulated Reflectance Studies of Self-Assembled InAs/GaAs Quantum Dot Structures

6.4.1 Experimental Details

Sample U7121 was used to test the behaviour of QD1 across the range of temperatures. The experiments were conducted at normal incidence using the apparatus depicted in Fig. 2.4b. The sample was placed inside a nitrogen exchange gas cryostat and the temperature of the sample was measured using a thermocouple temperature sensor. The HeNe modulation source was chopped at a frequency of 333 Hz and attenuated to various powers ranging from 0.03 mW - 2 mW depending on the requirement of each particular spectrum. Spectra were taken across a number of different energy ranges: from 1.040 to 1.215 eV; to, 1.080 to 1.265 eV. The spectrometer slit measured 2 mm x 800 μm, giving an instrumental resolution of 2.9 meV (FWHM) across the energy range studied. Starting at the lowest temperature achievable using this cryostat, PR spectra were taken 90° out of phase with the PL, over the region of the QD1 transition. The temperature was increased in steps of ~10K with subsequent PR spectra taken at each step.

6.4.2 Results

Nine PR spectra were recorded between the temperatures of ~90K to 160K. Each individual PR spectrum was fitted with a single TDFF, eqn. (2.31) with \( n = 2 \).

The results of the fitting are shown in Fig. 6.11a and 6.11b. Fig. 6.11b gives the energy of QD1 versus temperature.
Fig. 6.11a (top) Shows the HWHM of the confined-state QD transition, QD1, in sample U7121 as a function of temperature, as derived from PR measurements. Dashed line shows simple linear regression through the data points.

Fig. 6.11b (bottom) Shows the energy of the confined-state QD transition, QD1, in sample U7121 as a function of temperature, as derived from PR measurements. Dashed line shows the expected behaviour of bulk InGaAs, calculated from eqn. (1.2)

The dashed line in Fig. 6.11b shows the behaviour of the bandgap of a strained (001) In$_{0.2}$Ga$_{0.8}$As QW, calculated using Varshni's equation (Varshni, 1967), eqn. (1.2), with $E_g(0) = 1.312$ eV, $\alpha = 4.8 \times 10^{-4}$ eV/K, and $\beta = 140$ K (Huang, 1991). It was
necessary to offset this line by \( \sim 140 \) meV. It is clear from this figure that the energy of QD1 does follow the expected behaviour with temperature.

Fig. 6.11a shows the HWHM of QD1 versus temperature. The dashed line shows a simple linear regression through the lower set of data points (not including the values at 300K). If this linear regression is extrapolated to room temperature, it passes through the HWHM value at room temperature (see Table 6.1).

This suggests that for these samples there is a gradual decrease in HWHM of the lowest energy transition with increasing temperature. This may be due to a carrier tunnelling processes suggested by Lubyshev et al. (Lubyshev, 1996), or it may be an effect caused by changes in the confining potential of the dots as described in Section 6.2.2, brought on by strain variations with temperature.

### 6.5 Summary

This chapter has demonstrated that PR can be used to probe confined-state transitions within QDs. This has been achieved at both room temperature and ~ 80K. In all the samples investigated, five evenly spaced transitions (with \( \sim 54 \) meV between each transition) were observed originating from the QDs, confirming the parabolic-like nature of the confining potential within the dots. In addition to the five QD transitions, two further transitions were observed in the PR spectra of all the samples studied. These were identified as originating in the three-dimensional confining layer which surrounds the QDs.
Although it was not possible to observe the QD transitions in the PR spectrum at room temperature for the sample with only one layer of QDs, the 80K PR measurements revealed some obvious differences between the sample with only a single layer of QDs and the two with two layers: the QD transitions in the samples with two QD layers were found to be lower in energy and have a slightly reduced linewidth as compared to the sample with only a single QD layer. This is a consequence of the second layer of dots in the double layered samples having more uniform sizes and reduced strains fields.

The two samples with two layers of QDs were used to determine the degree of coupling between the electronic-states within the dots of the two layers. The results indicate that there is some degree of coupling between the confined-states responsible for transitions QD4 and QD5, but none between the confined states responsible for the lower energy transitions, QD1-QD3.

The effects were investigated of a rapid thermal annealing of one of the samples for 120 seconds, at 850°C. This was found to blue shift the energies of the QD transitions by ~250 meV. It also had the effect of narrowing the transition linewidths and reducing the energy spacing between them.

Unlike the usual narrowing of linewidths which is observed in PR measurements when the experimental temperature is reduced, the linewidth of the ground-state QD1 transition in these samples was found to increase on cooling. This phenomenon was investigated further by studying the linewidths of QD1 across a range of temperatures. It was found that QD1 showed a gradual increase in linewidth with decreasing temperature.

There is still some considerable scope for further work. The exact nature of the CL transitions is still unclear, and it would be useful to perform some form of polarisation sensitive PR experiment to ascertain from which valence band, light-hole or heavy-
hole, each transition originates. Finally, it would be useful to perform micro-PR experiments, where possible, to probe the confined-state transitions within individual QDs.
6.6 References

Adler F, Geiger M, Bauknecht, A, Haase D, Ernst P, Dornen A, Scholz F and
Schwiezer H 1998 J. Appl. Phys. 83 1631

Aigouy L, Holden T, Pollak F H, Lendentsov N N, Ustinov W M, Kop'ev P S and
Bimberg D 1997 Appl. Phys. Lett. 70 3329

Arakawa Y and Sakaki H 1982 Appl. Phys. Lett. 40 939

Aspnes D E 1973 Surface Science 37 418

Bimberg D, Lendentsov N N, Grundmann M, Kirstaedter N, Schmidt O G, Mao M H,
Ustinov V M, Egorov A Yu, Zhukov A E, Kop'ev P S, Alferov Zh I, Ruvimov

Brusaferri L, Sanguinetti S, Grilli F, Guzzi M, Bignazzi A, Bogani F, Carraresi L,
3354


4489

Lett. 73 16


Phys. Lett. 68 1996


1099

González-Borrero P P, Lubyshev D I, Marega E, Jr., Petitprez E and Basmaji P 1996
J. Cryst. Growth 169 424


Grundmann M, Christen J, Lendentsov N N, Böhrer J, Bimberg D, Ruvimov S S,
Huang Y S et al. 1991 J. Appl. Phys. 70 7537
Chapter 6: Photomodulated Reflectance Studies of Self-Assembled InAs/GaAs Quantum Dot Structures


Madhuker A, Xie Q, Chen P and Konkar A 1994 *Appl. Phys. Lett.* **64** 2727


*New Scientist*, 29th August 1998 p.22

*New Scientist*, 27th February 1999 p.13


Pollak F H, Shen H 1993 *Materials Science and Engineering* **R10** 275

Qiang H and Pollack F H 1994 *Appl. Phys. Lett.* **64** 2830


Shen H and Dutta M 1995 *J. Appl. Phys.* **78** 2151


Chapter 6: Photomodulated Reflectance Studies of Self-Assembled InAs/GaAs Quantum Dot Structures

Stranski I N 1981 Zeitschrift fur Kristallographie 156 167
Varshni Y P 1967 Physica 34 149
Yoffe A D 1993 Advances in Physics 42 173
This thesis has shown photomodulated reflectance (PR) to be a simple, powerful, and non-destructive tool, suitable for the optical characterisation of a wide range of semiconductor systems. In this work, PR is used along with a number of complementary techniques to characterise both the structural and optical properties of a variety of material systems used in the fabrication of semiconductor lasers and related opto-electronic devices. The additional techniques used include photoluminescence (PL), reflectance (R), and double crystal x-ray diffraction (DCXRD). The systems investigated are those of strained quantum well (QW) structures, vertical cavity surface emitting lasers (VCSEL), and quantum dot (QD) structures.

In the studies performed on the series of tensilely strained QW structures, PR was used to derive the energies of all the confined-state transitions within the QWs, along with the magnitude of the built-in electric field within each structure. This demonstrates the superiority of PR over related techniques such as PL. For such systems, PL is usually only able to probe the ground-state transition within the QWs, whereas PR gives information on all the confined-states within the well as well as the barrier. Whilst PR measurements were used to derive the optical properties of the strained QWs, complementary DCXRD measurements gave structural information about the layers within each sample. Together, the two techniques were used, along with a theoretical model, to derive the strains, compositions and layer thicknesses
within each structure, as well as to determine the behaviour of the ground-state QW transitions with increasing tensile strain. For this material system, the ground-state QW transitions, $H_{11}$ and $L_{11}$, are predicted to become degenerate for a tensile strain of $\sim 0.36\%$.

PR was used, along with normalised reflectance measurements, to investigate VCSEL structures. VCSELS intrinsically have distinct reflectance responses because of the nature of their design. Theoretically modelling the R spectrum of a VCSEL allowed error in the growth fluxes for each structure to be derived. PR measurements proved to be particularly useful for characterising VCSELS, as information on both the ground-state QW transition and the optical mode of the cavity could be gained from a single spectrum. For a VCSEL to operate correctly, it is essential that these two coincide in energy. The lineshape observed in a PR spectrum of a VCSEL, where the cavity mode (CM) is close to resonance with a confined-state QW transition, displays unusual behaviour, and this prompted the development of a new PR lineshape model for such a situation. One consequence of the model developed was that it showed how the imaginary part of the dielectric function of the QW layers within a VCSEL structure can be probed without any influence from the surrounding cavity.

PR has also been shown to be successful in probing confined-state transitions within self-formed QD systems. Transitions arising from both within the QD structures as well as from the surrounding confining layer material were observed in PR measurements performed at both $\sim 80K$ and room temperature. At the time of writing, these are the only measurements to be performed successfully on such structures using PR at both of $80K$ and room temperature. The range of PR results were used to gain an insight into the nature of the QDs, as well determining certain properties such as the degree of coupling between the electronic states of the dots in different layers. The effects of rapid thermal annealing on the properties of these QD structures was also studied, and was found to both increase the size of the QDs as well as diluting their Indium content.

The VCSEL and QD technologies have recently been combined and used to fabricate laser devices (Optics and Photonics News, 1998). In such cases, layers of self-assembled QDs are used in place of the conventional QW layers within a VCSEL-like
micro cavity. Such lasers have been fabricated using QDs formed from a InGaAs/GaAs material system (Nishioka, 1996; Lott, 1997).

There are opportunities for further work that may be developed from some of the work in this thesis. In particular, the work on the QD systems leads to a number of questions on points such as the nature of the confining potential within the dots as well as the true nature of the confining layers. Such ideas are discussed in the summary of Chapter 6, Section 6.5. There is also the possibility of studying more recently developed QD structures, similar to those studied in Chapter 6 but with emission wavelengths nearer 1.3 μm (Murray, 1999). Furthermore, there is a need for a theoretical study of both the strain profiles within the QDs, as well as their electronic properties. A comparison of the results of the experimental optical measurements performed here with a suitable theoretical model would lead to a better understanding of the true nature of the QDs.

There is still some scope for further developments to the actual PR experiment itself. During the course of this work, the possibility of adapting the current experimental arrangement, to allow micro-PR experiments to be performed, was investigated. Such techniques, which are used extensively in PL studies (Kasai, 1995), can easily be adapted to PR experiments (Aigouy, 1997) by replacing the optics, delivering the probe beam to the sample, with a microscope objective. Some trial PR measurements were successfully performed with such an arrangement. Experiments were performed at normal incidence with both the probe beam light and the modulating laser being delivered to the sample via the same optics. Once developed fully, such an arrangement would allow PR measurements to be performed on individual VCSEL devices, already fabricated as part of a large array. Furthermore, the greatly reduced probe image would enable PR measurements to be performed on single QDs.
7.1 References

Optics and Photonics News, January 1998 p.30