Photomodulation spectroscopy
and characterisation of both near and
mid-infrared semiconductor
materials and devices

by

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Abstract

In this thesis we report on a range of studies of both near and mid-infrared semiconductor materials and devices. We have used photomodulated reflectance (PR) to investigate the gain-cavity de-tuning in the wafer of a high-finesse vertical-cavity surface-emitting laser (VCSEL), designed to operate at 760 nm as a high temperature oxygen gas sensor. From this study we were able to determine that the VCSEL cavity mode (CM) is tuned to the quantum well (QW) ground state transition energy at a temperature of ∼ 115 °C, when λ_CM ≈ 760 nm.

We have also developed a new VCSEL PR model, able to describe the PR of high finesse samples such as the one studied here. This was developed through analysis of calculated VCSEL reflectance (R) and Seraphin coefficient data, a study which revealed that the Seraphin coefficients were Kramers-Kronig pairs in the vicinity of the VCSEL CM. This study also revealed that the broadening of a VCSEL CM may be proportional to the absorption in the cavity due to the QWs in the sample. This provided evidence for the CM broadening effect which we observed in VCSEL reflectance measurements conducted here.

We have also conducted temperature and pressure dependent studies of the threshold current of two 760 nm edge-emitting lasers with similar active regions to the VCSEL studied. These studies have revealed that the devices suffer from thermally activated carrier leakage of electrons into the X-minima of the barrier/cladding layers, which reduces their efficiency and stability at elevated temperatures.

Finally we have developed a mid-infrared PR system for investigating narrow gap semiconductors, enabling studies of the fundamental band gap and the spin-orbit splitting energy (Δ₀) in a series of InAsSb and GaInAsPSb samples. From these we measure the bowing of Δ₀ in InAsSb to be ∼ −165 meV at low temperature (∼ 10 K), in line with theoretical predictions of other authors, but quite different to the only previously reported experimental value of +1170 meV.
Acknowledgements
Firstly I would like to thank my PhD supervisor, Jeff Hosea, for all his support during my time at Surrey. From my first day, when he battled “the powers that be” to ensure that I got a car parking permit, I knew that we would get on! Since that day Jeff has been a source of invaluable guidance, enabling me to overcome experimental, analytical, and theoretical problems on numerous occasions.

I also thank Martin Merrick, with whom I worked to develop the mid-infrared PR setup. With his knowledge and experience of working in the invisible world of the mid-infrared, Martin was able to impart a great deal of useful knowledge to me. For their assistance with my device studies I would also like to thank Darren Lock and Daniel McConville – for a spectroscopist routinely studying sensibly sized samples I would have found working with those tiny edge-emitting lasers very difficult without their help! I also thank Gary Strudwick who was able to repair, fix and stitch just about anything in the lab, getting me up and running on a number of occasions.

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I would also like to thank those most dear to me. Mum and Dad, over the years you have been a constant support to me, both financially and emotionally. This was especially so during my time at Southampton, where I obtained my first degree – an achievement which I owe to you both. I also thank my two brothers, Scott and Ashley, for their support. I apologise to them too since having a physics geek for an older brother probably did nothing for their street cred! I thank Jane’s family too, who have supported both Jane and me during our relationship together.

Finally I want to thank Jane, who, right from the start supported, my decision to undertake this PhD. Jane, you have been there for me throughout,
whether I am putting you through the millionth iteration of a draft conference presentation, or telling you that I have to work in the lab over the weekend, you have always understood. For me, the completion of this work represents the opportunity of spending more precious time with you, and the beginning of a new chapter in our lives together.
Publications


- S.A. Cripps, T.J.C. Hosea, A. Krier, V. Smirnov, P.J. Batty, Q.D. Zhuang, H.H. Lin, Po-Wei Liu, and G. Tsai “Midinfrared photoreflectance study of InAs-rich InAsSb and GaInAsPSb indicating negligible bowing for the spin orbit splitting energy” *Appl. Phys. Lett.* 90 172106 (2007)


Conference Presentations


## Glossary

The following is a list of abbreviations used throughout this work:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>CIISII</td>
<td>Conduction, heavy-hole, spin split-off hole, heavy-hole (Auger recombination process)</td>
</tr>
<tr>
<td>CM</td>
<td>Cavity-mode</td>
</tr>
<tr>
<td>DBR</td>
<td>Distributed Bragg reflector</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>$e_{1hh_1}$</td>
<td>Electron to heavy-hole ground-state quantum well transition</td>
</tr>
<tr>
<td>$e_{1lh_1}$</td>
<td>Electron to light-hole ground-state quantum well transition</td>
</tr>
<tr>
<td>EEL</td>
<td>Edge-emitting laser</td>
</tr>
<tr>
<td>ER</td>
<td>Electroreflectance</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-width at half-maximum</td>
</tr>
<tr>
<td>FKO</td>
<td>Franz Keldysh oscillation</td>
</tr>
<tr>
<td>HWHM</td>
<td>Half-width at half-maximum</td>
</tr>
<tr>
<td>JDOS</td>
<td>Joint density of states</td>
</tr>
<tr>
<td>LPE</td>
<td>Liquid Phase Epitaxy</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>MIR</td>
<td>Mid-Infrared</td>
</tr>
<tr>
<td>ND</td>
<td>Neutral density (filter)</td>
</tr>
<tr>
<td>OPD</td>
<td>Optical path difference</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PR</td>
<td>Photomodulated reflectance</td>
</tr>
<tr>
<td>QTH</td>
<td>Quartz Tungsten Halogen (light source)</td>
</tr>
<tr>
<td>QW</td>
<td>Quantum well</td>
</tr>
<tr>
<td>R</td>
<td>Reflectance</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>VCA</td>
<td>Virtual Crystal Approximation</td>
</tr>
<tr>
<td>VCSEL</td>
<td>Vertical-cavity surface-emitting laser</td>
</tr>
</tbody>
</table>
"Whiteness and all grey Colours between white and black, may be compounded of Colours, and the whiteness of the Sun's Light is compounded of all the primary Colours mix'd in a due Proportion."

Sir Isaac Newton (1642–1727), from Opticks (1704)
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1 Introduction

1.1 Motivation

The unique optoelectronic properties of semiconductor materials have ensured that they have received a high level of both scientific and commercial interest over the years since lasing was first reported in GaAs in 1962. [1] Figure 1.1 shows the annual global sales of the semiconductor industry since 1975. As can be seen from this there has been a continued growth throughout the period, equating to a compounded annual growth rate (CAGR) of 15%. Much of this growth is driven by the computer industry and presently around 85% of sales in the total semiconductor industry is related to integrated circuit production. [2] The second largest sector within the industry relates to the sale of optoelectronic devices and sensors, which together account for ~10% of the industry. [2] Telecommunications has been a key driver for the growth of the optoelectronics industry, where semiconductor lasers emitting at 1.3 μm and 1.55 μm are routinely used in worldwide communication networks based on silica optical fibers. At these wavelengths silica fibers exhibit
1. Introduction

zero dispersion (@ 1.3 \( \mu m \)) and an attenuation minimum (@ 1.55 \( \mu m \)) \cite{3} and semiconductor lasers operating at either of these wavelengths are able to exploit these properties and thus make global fiber telecommunication systems a viable commercial reality.

The operating wavelengths of commercial optoelectronic devices are not limited to the near infrared telecommunication wavelengths of 1.3 \( \mu m \) and 1.55 \( \mu m \). Indeed, there are other communication systems which operate at different wavelengths. These are based on plastic optical fibre networks and they employ semiconductors emitting at around 650 nm, where the plastic fibres exhibit an attenuation minimum. \cite{4}

Another application using semiconductor lasers is data storage solutions, where the density of information that can be stored is limited by the spot size of the focussed laser beam. Thus the possibility of providing greater amounts of data storage has focussed a great deal of attention of developing short wavelength semiconductor lasers. This is demonstrated by the developments in optical storage media: The first such medium, the compact disc (CD), is read by a laser operating at 780 nm and can store \( \sim 700 \) MB, while 'second generation' DVDs, which use 650 nm red lasers, can store approximately 5 GB. More recent progress on lasers outputting blue light at 405 nm has lead to the development of so-called blue-ray DVDs, which can store up to 25 GB – over 35 times more information than a conventional CD.

Data storage applications have clearly generated a great deal of effort in developing efficient, scalable material systems which are able to operate at short wavelengths. However, there are other commercial applications which call for the use of so called narrow gap semiconductors, which emit light at longer wavelengths, into the mid-infrared (2–10 \( \mu m \)). An example of one such application involves the military who use optoelectronic devices in ordnance guidance and countermeasure systems. \cite{5} Due to the optical window in the Earth’s atmosphere between 3–5 \( \mu m \) there is also interest in developing so called free space optical communication systems. Such line of sight systems are economically attractive since they rely only on a detector and transmitter and no other infrastructure such as underground fiber networks. Another important application that uses mid-infrared semiconductors is gas sensing.
Many gaseous compounds exhibit strong absorption lines in this wavelength region (CO₂ for example, at 4.25 μm [6]) and these can be probed by semiconductor lasers operating at the appropriate wavelengths.

Unfortunately, due to their narrow band gaps, mid-infrared semiconductors suffer from non-radiative recombination process which can limit their effectiveness as commercial optoelectronic devices. Despite this, the range of potential applications in the mid-infrared means there is a great deal of research into developing efficient material systems. In this work we shall focus primarily on characterising near-infrared (~760 nm), and mid-infrared (~3–5 μm) narrow gap semiconductors. It is our aim to develop on the understanding of these semiconductor materials so that the knowledge may be used to aid the development of new, more efficient optoelectronic devices.

Our studies of near-infrared ~760 nm semiconductors are heavily focussed on the devices fabricated from the materials: In chapter 4 we study the wafer of a ~760 nm vertical-cavity surface-emitting laser, and in chapter 3 we study ~760 nm edge-emitting lasers. In the next section we describe some of the basic properties of these semiconductor lasers.

1.2 Semiconductor lasers

Since much of this thesis concentrates on the studies of semiconductor lasers and the materials from which they are made we give a brief introductory background to these devices here. The aim of this is to give a reader unfamiliar with semiconductor lasers a basic introduction so that the results in the latter chapters may be put into some meaningful context.

Figure 1.2 illustrates the basic design of an edge-emitting laser (EEL). Based on a p-n junction, carriers are injected into the active region of the device through electrical contacts on the top and bottom of the laser. In modern EELs the active region, responsible for providing the material gain, contains quantum wells (QWs) which act to confine the carriers, helping to increase the efficiency of the device. The QWs also reduce the number of dimensions in which the carriers can move freely and this reduces the density of states in the active region. This in turn reduces the threshold current.
Figure 1.2: Basic design of an edge-emitting semiconductor laser.

of the laser, further increasing the efficiency. [7] Since QWs are very thin (〜10 nm is typical) they are unable to confine an optical field. Therefore, EELs are often designed with a separate optical confinement region, in which the QWs are located and the lasing mode is guided. This optical confinement is achieved by ensuring the outer layers have lower refractive indices than the confinement region. The Fabry-Pérot cavity of the laser is defined by the cleaved facets at either end of the laser chip. These facets are mirror-like since the cleaves are made along crystal planes and they are typically 〜30% reflective. Since the optical mode travels perpendicularly to the direction in which the device was grown (see Fig. 1.2) the mode travels in the plane of the QWs between the two facets. This distance is relatively large (a typical cavity length is 〜500 µm) giving a large interaction between the material gain and optical field. Therefore, the modest reflectivities of the cleaved facets are high enough to achieve lasing in many lasers. In some cases the facets are coated in order to improve the reflectance characteristics in order to reduce to cavity losses. [8]

Once the separation between the quasi Fermi levels of the valence and conduction band (the levels that define a 50% probability of a state being populated in either band) is greater than the energy separation of the electron and hole confined ground states in the QWs it is possible for a device to start lasing. [9] When their separations are equal the material is transparent at
that energy. The stimulated emission exits from the laser facet with a highly divergent, asymmetric profile resulting from diffraction out of the narrow width of the waveguide from which the light emerges. This laser design has proved to be very successful and many such devices have been produced, operating across a wide range of wavelengths.

Despite the many successes of EELs they do have some weaknesses, which for certain applications can prove disadvantageous. One such weakness is the tendency for EELs to mode-hop – a process whereby a device suddenly changes its lasing wavelength. [10] This is caused by changes in the gain spectrum of a laser with say temperature and it is possible in EELs due to the relatively long length of the optical cavity (\( \sim 500 \, \mu m \)), which results in a small wavelength separation between the allowed cavity modes. Mode-hopping can result in noise in the laser output power, reduce the thermal stability of a device, and furthermore the changes in operating wavelength can also be unacceptable in certain applications. Distributed feedback gratings can be etched into the waveguides of such lasers to promote the propagation of only certain modes. This is commonplace in EELs, where it is used routinely to produce single-mode devices. However, it does have the disadvantage of requiring the additional etching process. Another solution to the problem is to greatly reduce the length of the optical cavity so that the separation between the optical modes becomes very large. This is realised in a design known as a vertical-cavity surface-emitting laser (VCSEL). [11] Such a structure is illustrated in figure 1.3. In a VCSEL the Fabry-Pérot cavity typically has an optical thickness equal to, or a few multiples of, the desired operating wavelength of the device. The optical thickness is equal to the refractive index multiplied by the physical thickness of the cavity. A cavity of optical thickness equal to the lasing wavelength, \( \lambda \), is depicted in the central section in Fig. 1.3, surrounded by two layers of material with lower refractive index than the cavity layer. The material gain of the laser is provided by QWs, located at the centre of the cavity, where the optical field (represented by the sinusoidal curve in Fig. 1.3) is strongest. This ensures that the optical mode overlaps fully with the material gain of the QWs.

As can be seen from Fig. 1.3 the optical mode travels vertically through
1. Introduction

The device, in the direction of the growth of the structure. This means that for each round trip an individual photon will have very little interaction with the gain medium in the active region since the QWs are only a few nanometres thick. This is unlike in EELs, where the optical mode travels in the plane of the QWs, resulting in a high interaction between photons and the material gain medium. Since the overlap between the optical field and the gain medium in a VCSEL is greatly reduced due to the design geometry it is necessary to have highly reflective cavity boundaries of ~ 100% in order to have multiple passes through the QWs. This is achieved in VCSELs by using distributed Bragg reflectors (DBRs) grown either side of the central cavity. These DBR mirrors consist of layers of materials having alternating high and low refractive indices and optical thickness of 1/4 of the desired lasing

Figure 1.3: Basic design of a vertical-cavity surface-emitting semiconductor laser.
1. Introduction

wavelength. The higher the contrast between the two refractive indexes, the fewer layers are required to achieve the high reflectivities desired. In many VCSELs the DBR layers, like the cavity, are made from semiconductors. This allows them to also fulfil the role of being the p and n-doped sides of a p-n junction required to inject carriers into the active region within the cavity. Because the refractive index contrasts which can be achieved using III-V semiconductors are not large (~ 20% is typical using AlGaAs), each DBR mirror will often require between 30–40 layers. Therefore, the resulting structures are often complicated, having ~ 100 layers.

Due to the geometry of a VCSEL the emission profile is much improved compared to that of an EEL. [11] This is principally due to the fact that light is not emitted from such a small aperture as in an EEL, so the diffraction of the beam is greatly reduced – overcoming one of the main problems associated with EELs. The aperture of a VCSEL can be made circular by creating a ring shaped electrical contact, this creates a spherical beam profile which can be easily coupled into a fibre. This geometry also makes it possible for arrays of VCSELs to be constructed on a single wafer, which is attractive for a number of applications such as multiplexing in communication networks. [12]

VCSELs exhibit complex reflectance spectra as a result of their structure and an example of such a spectrum is shown in figure 1.4. The DBR mirrors create a high reflectance stop band, extending for several tens of nanometers. In this stop band the reflectance can reach values of ≥ 99.9%. [13] The Fabry-Pérot cavity in the centre of the two DBR mirrors creates a sharp 'dip-like' feature at the cavity mode wavelength, λ_{CM}. If the VCSEL is designed correctly this feature will lie in the centre of the high reflectance stop band. The value of λ_{CM} defines the wavelength at which the VCSEL will lase since it is at a wavelength of an optical mode supported by the cavity. Other wavelengths which do not meet the criteria of being a Fabry-Pérot cavity mode cannot propagate and optical gain cannot be realised. It is this property that means that VCSELs do not suffer from mode-hopping in the same way that EELs do, since with such a small cavity the free spectral range of a VCSEL is too large to allow this phenomenon. Therefore, for applications in which such mode-hopping would be detrimental, VCSELs provide a good
1. Introduction

1.0 VCSEL

Alternative to conventional EELs. Also, since the lasing wavelength is defined by $\lambda_{CM}$, which tends to be less temperature sensitive than the peak in the material gain curve, VCSELs tend to exhibit higher thermal stabilities of the lasing wavelength than EELs. Since an operational device must have the peak in its material gain curve aligned to the cavity mode wavelength in order to lase efficiently, the amount of gain-cavity de-tuning (if any is present) is a crucial aspect in VCSELs. In chapter 3 of this work we shall be studying this property in detail for a particular VCSEL sample.

In the next chapter we shall discuss the theoretical background of the work in this thesis. Following this, in chapter 3 we discuss our photomodulated reflectance results of a high-finesse 760 nm VCSEL, designed to be a high-temperature oxygen gas sensor in order to parameterise the gain-cavity de-tuning in the sample. In chapter 4 we then study the carrier recombination mechanisms in edge-emitting lasers with similar active regions to this VCSEL in order to investigate the suitability of the material system for use in high-temperature 760 nm optoelectronic devices. In chapter 5 we look
1. Introduction

in detail at simulated VCSEL reflectance and photomodulated reflectance results in order to develop an understanding in this area. From this we develop a new photomodulated reflectance lineshape model for high-finesse VCSELs and we use it to successfully describe the measurements made in chapter 3. In chapter 6 (the final results chapter in this thesis) we discuss our newly developed mid-infrared photomodulated reflectance setup and we present results for the fundamental band gap and spin-orbit splitting energies in InAsSb and GaInAsPSb. The diversity of the samples studied in this thesis sees us measuring photomodulated reflectance features at wavelengths ranging from 730 nm to 4.25 μm. Despite this wide spectral range we have been able to exploit the powerful properties of modulation spectroscopy to learn much about the materials and devices investigated.

References


1. Introduction


2. Theoretical Background

In this section we give a short introduction to the background theory and techniques used in this work. Throughout the course of this thesis we make reference to the material in this chapter.

2.1 Band structure of Semiconductors

Here we discuss the band structure of both bulk and quantum confined semiconductors since these define many of the parameters we study in this thesis. We restrict our discussion to elemental and III-V semiconductor compounds since our investigations are restricted to these materials.

2.1.1 Bulk semiconductors

Silicon is an example of an elemental semiconductor and we use it here to describe how the energy band gap is formed in such a material. A silicon atom has the electronic configuration \([\text{Ne}]3s^23p^2\). The outer \(n = 3\) (principal quantum number) level is relatively weakly bound to the atom and so these electrons may be involved in chemical reactions and bonding with other atoms. The s subshell \((l = 0\), where \(l\) is the angular momentum quantum number\) of the atom is full with two electrons. However, the p subshell \((l = 1\)\) has four empty states. As we bring two silicon atoms together the outer orbital electron wavefunctions of each atom combine into so-called \(sp^3\) hybridised orbitals (having four outer electrons in this configuration is energetically more favourable than having two s and two p electron states). [1] The wavefunctions of the hybrid orbitals for the two atoms then combine either symmetrically (bonding) or anti-symmetrically (anti-bonding). A bonding orbital concentrates the electronic density between the atoms, whereas an anti-bonding orbital has zero electronic density here. In the case of bonding orbitals, as the separation between the two atoms is reduced the energy of the system is initially reduced as the two atomic cores are attracted by the electronic density between them. However, at small separations the repulsion of the two positively charged atomic cores becomes important and as a result
there is an equilibrium point in the atomic separation which yields the lowest total energy for the system. Anti-bonding orbitals do not exhibit an energy minimum versus separation since there is no electronic density between the atoms. Due to the repulsive effects between the positively charged atomic centres the energies in this system increase as the separation is reduced.

Figure 2.1 shows a schematic illustration of the process described above, but for a large number (N) of silicon atoms. [2] As the interatomic spacing between the atoms decreases (x-axis) the discrete p and s energy levels begin to interact and overlap. As the separation decreases further the levels again split to form two distinct energy bands (dark grey shaded area). Bands are formed since the energy differences between the individual levels are so small when a large number of atoms are brought together that they merge into an indistinguishable continuum of allowed energy states. [2] The lower energy band can accommodate 4N states and is completely full at a temperature of 0 K. This is the valence band and electrons in these states will contribute to the binding of the crystal (covalent bonding). These are the symmetrically combined wavefunctions and the minimum in the energy of this band can be seen in Fig. 2.1. The upper band, which can also contain 4N states is empty. This is known as the conduction band, so called because electrons excited into
this band are able to contribute to electrical conduction within the material. The wavefunctions in this band are combined anti-symmetrically.

On the x-axis the lattice constant of silicon is marked, $a_0 = 5.43 \, \text{"AA}$. At this separation the conduction and valence bands are illustrated in the left hand side of figure 2.1. The edge of the valence and conduction bands are denoted $E_v$ and $E_c$ respectively and there is a forbidden energy gap $E_g$ between the two bands. Within this gap no electron states may exist – electrons with energy $E_v$ must receive energy equal to or greater than $E_g$ to traverse the gap and be excited into the conduction band.

The energy bands in compound semiconductors such as GaAs are formed in the same way. However, due to the differing elements involved the wavefunctions are not shared equally between each atom. Therefore, these materials tend to be slightly ionic, whereas a pure silicon crystal will be fully covalent. In this work we study III-V semiconductors, so called because the elements in the materials either contain three or five outer valence electrons. Taking GaAs as an example, gallium has the electronic configuration [Ar]4s²4p (three valence electrons) and arsenic has [Ar]4s²4p³ (five valence electrons). Compound semiconductors, especially those containing more than two elements are of great interest since by mixing different proportions of elements together different band gap energies can be obtained. Therefore, materials can be designed for specific opto-electronic applications. We report results in this thesis on binary (containing two elements), ternary (three elements) and pentenary (five elements) semiconductors.

After discussing the band gap in semiconductors the next important consideration is the band structure of these materials. This is essentially the dispersion relation of the bands, i.e. how the energy varies with momentum. The dispersion relation for a free electron is given by the relation between its kinetic energy and momentum, $p$, given by $E = \hbar^2 k^2/2m$, where $m$ is the free electron mass, $\hbar$ is the reduced Planck's constant and $k = p/\hbar$ is the electron wavevector. Therefore, for a free electron the energy increases with the square of its wavevector. As a first approximation this relationship can be used for the electrons in the conduction band of a semiconductor.

Within a real material even conduction band electrons are not truly free
since they will be influenced by the periodic potential from the ionic cores of the atoms in the crystal and so the band structure is dependent on the crystal structure. [4] An example of a real band structure is shown in Fig. 2.2 for GaAs. [5] This is theoretically calculated data. However, it gives a good representation of the complexity of a semiconductor’s band structure. The area shaded in grey represents the energies of the forbidden energy gap.

Here the energy of the bands is plotted as a function of the wavevector, referred to as the crystal momentum. The marks along the $x$-axis refer to points of significant interest in the Brillouin zone of the crystal structure. For a III-V semiconductor such as GaAs the crystal lattice is a zinc-blende configuration and this has a Brillouin zone in reciprocal space such as the one shown in figure 2.3. [3] The $\Gamma$ point occurs at the centre of the Brillouin zone, where the crystal momentum is zero. In III-V semiconductors the valence band edge (highest point of the band) always occurs at this point. However, only in direct semiconductors such as GaAs does the conduction band minimum also occur here. This minimum in the band gap can be seen.
at the $\Gamma$ point in Fig. 2.2 for GaAs and this band gap is referred to as the fundamental band gap ($E_0 = \Gamma_6 - \Gamma_8$) of the semiconductor. Most optoelectronic processes occur at this point and as such much interest is focussed on this part of the band structure.

There are other points of interest in the Brillouin zone (BZ) which should also be mentioned. For example, the $X$-point, which has a crystal momentum of $(2\pi/a_0) <100>$, appears at the edge of the BZ, in the centre of the square faces. There are six equivalent $X$-points in the BZ, each being electronically identical due to the symmetry of the crystal. As can be see in the band structure of GaAs (Fig. 2.2) the dispersions of the conduction and valence bands are both zero at the $X$-point and there is a local minimum in the band gap here ($X_6 - X_7$). These are known as the $X$-minima since there are six equivalent minima, one for each of the $X$ points in the first BZ. Another point of interest in the BZ shown in Fig. 2.3 is the $L$-point. There are eight equivalent $L$-points in the BZ, each occurring at the centres of the hexagonal shapes at the edge of the BZ, with momentum $(2\pi/a_0) <111>$. Again from the band structure in Fig. 2.2 we see that at the $L$-point the dispersion of the
2. Theoretical Background

conduction and valence bands goes to zero and there is another local band gap minimum at this point (eight within the first BZ). In chapter 4 when we look at carrier leakage in edge-emitting lasers we discuss how electrons may 'escape' from the conduction band minimum at the Γ-point and become located at these X and L minima. Such leakage processes can play important roles in limiting the efficiencies of opto-electronic devices and so knowledge of the energy separation between the conduction band edge and the X and L minima in the conduction band can be of great significance.

The region near the Γ-point is magnified in Fig. 2.2 so that the detail of the band structure here can be discussed. It can be seen that the conduction band (CB) is nearly parabolic as in the case of a free electron. The valence band is more complex however, and there are actually three separate bands, each having a different curvature (dispersion). If we consider quasi-particles in these bands (i.e. electrons under the influence of the crystal potential) we can talk of an effective mass of the particles in these bands. For the free electron we said that $E = \frac{\hbar^2 k^2}{2m}$ and using this we can describe a generalised relationship between the dispersion of an energy band and the effective mass of a particle within the band:

$$m_{\text{eff}} = \frac{\hbar^2}{\left( \frac{\partial^2 E}{\partial k^2} \right)^{-1}}$$

(2.1)

The units of this mass are dimensionless – expressed as a fraction of the free electron mass. From Eq. 2.1 we see that a band of high curvature corresponds to a particle of low effective mass.

In the next section we shall discuss how electrons in the valence band may be excited into the conduction band. For now we mention that when this process occurs, a hole is left in the valence band in place of the missing valence electron. It is more convenient to talk of a near empty valence band containing one hole than a near full band missing an electron. The properties of such a hole allow us to treat it as a quasi-particle in the same way as we treat the electrons within the conduction band. Therefore, when we look at the curvatures of the three valence bands in the magnified region of Fig. 2.2 we can talk of bands relating to holes of differing effective masses.
At the $\Gamma$ point two of the valence bands are degenerate in a bulk, unstrained semiconductor. However, for finite wavevectors they split due to the different curvatures (effective masses) of the bands. The uppermost of these bands is known as the heavy-hole (HHH) band since its curvature is less than that of the light-hole (LII) band.

For a particular band in a semiconductor the deviation from parabolic behaviour is due largely to the interactions with the other bands of similar electronic configuration in the material and the influence of the crystal potential. The size of the effect from the other bands is stronger for bands lying closer to the band in question due to the perturbative nature of the interaction. [6] The heavy-hole band, with secondary total angular momentum quantum number $m_j = \pm \frac{3}{2}$, is influenced by bands separated from it by a large energy and thus it is not greatly affected by this perturbative interaction. The light-hole band on the other hand has $m_j = \pm \frac{1}{2}$ and is heavily influenced by the much closer conduction band, which also has $m_j = \pm \frac{1}{2}$. Therefore, this band has a strong curvature and light effective mass, as does the conduction band.

The third band in the magnified region of Fig. 2.2 has a curvature similar to that of the LH band since it also has $m_j = \pm \frac{1}{2}$. However, it is split off from the valence band edge by an energy $\Delta_0$ at the $\Gamma$-point. $\Delta_0$ is known as the spin-orbit splitting energy since the band is split as a result of the spin-orbit interaction on the electron energy levels in the material. [4] The magnitude of $\Delta_0$ is important, especially in narrow-gap semiconductors, since it can influence non-radiative carrier recombination processes such as Auger-recombination. [7] In chapter 6 we investigate this splitting energy in our mid-infrared photomodulated reflectance studies of InAsSb and GaInAsPSb semiconductor alloys.

2.1.2 Carriers within the bands

As we mentioned in the previous section at a temperature of 0 K the valence bands are full of electrons and the conduction band is empty. At higher temperatures electrons may be thermally excited into the conduction band
leaving holes in the valence band. The concentration of thermally excited electrons in the conduction band is governed by Fermi-Dirac statistics and is given by

\[ n = \int_{E_c}^{\infty} f(E)g(E)dE \]  

(2.2)

where \( f(E) \) is the Fermi-Dirac distribution function given by Eq. 2.3 and \( g(E) \) is the density of states (DOS) in the conduction band. \( E_c \) is the conduction band edge: the lowest point in the band.

\[ f(E) = \frac{1}{\exp\left(\frac{(E - E_F)}{k_B T}\right) + 1} \]  

(2.3)

In Eq. 2.3 \( E_F \) is the Fermi energy and when \( E = E_F \), \( f(E) = 0.5 \), meaning a state at this energy has a 50% chance of being occupied. For a bulk semiconductor, using the approximation that the band is parabolic, \( g(E) \) is given by Eq. 2.4.

\[ g(E)dE = \frac{1}{4\pi^2} \left( \frac{2m_{eff}}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2} dE \]  

(2.4)

It can be seen from this relationship that the DOS depends on the effective mass (curvature) of the conduction band raised to the power 3/2. It is also dependent on the square root of the energy above the band edge. Figure 2.4 shows how the DOS given by Eq. 2.4 varies with energy above the conduction band edge.

When considering optical processes in semiconductors (e.g. photon absorption creating a hole in the valence band and an electron in the conduction band) it is necessary to consider the density of states of both bands in what is known as the joint density of states (JDOS). This is given here by equation 2.5, where \( dS \) is an area element on a surface of constant energy:

\[ \text{JDOS} \propto \int_S \frac{1}{4\pi^2 |\nabla_k (E_c - E_v)|_{E_c - E_v = \hbar \omega} dS } \]  

(2.5)

The JDOS is a rapidly varying function of \( k \) where \( \nabla_k (E_c - E_v) = 0 \) and this condition occurs at the critical points in the semiconductor band structure.
2. Theoretical Background

Figure 2.4: Schematic illustration of the density of states (DOS) near the conduction band edge energy, \( E_c \), in a bulk semiconductor with an idealised, parabolic band edge given by Eq. 2.4. The DOS above \( E_c \) displays a square root energy dependence and below this it is zero.

where the dispersions of the bands are either equal or both zero (Fig. 2.2). The most important critical point occurs at the highly symmetric \( \Gamma \)-point of the Brillouin zone in direct gap semiconductors where both the valence and conduction band dispersions are zero. Therefore, the crystal structure, which defines the dispersion relations of the band structure of a semiconductor also heavily influences the density of states. As we discuss in section 2.1.4 the JDOS is directly related to the optical properties of a semiconductor and as such plays an important role in the performance of opto-electronic devices.

2.1.3 Quantum confined semiconductors

By growing semiconductor materials of differing band gaps in layers (heterostructures) it is possible to confine electrons and holes in the resulting potential wells which are formed. This is illustrated schematically in figure 2.5, where the \( \Gamma \)-point band lineups are shown for the conduction band (CB) and valence band (VB). For simplicity we have only considered one valence band in this picture. The well material has a lower fundamental band gap of \( E^w_0 \) and the wider gap barrier material has a band gap of \( E^b_0 \).
The relative positions of the bands is determined by the electron affinities of the materials and can be estimated using the model solid theory of Van de Walle. [8] For many materials a well of the type in Fig. 2.5 is formed, with a potential well of depth $\Delta E_c$ in the CB, and $\Delta E_v$ in the VB, where $E_0 - E_0 = \Delta E_c + \Delta E_v$. If the physical width of the well is of the order of or less than the de Broglie wavelength of the carriers in the material ($L \leq 500$ Å) then quantum confinement effects will occur. Within the wells (where the confinement potential is zero) the electrons and holes will have symmetric or anti-symmetric oscillatory wavefunctions. However, within the barriers the wavefunctions will exponentially decay to zero if the carrier energies are less than the potential barrier height. Therefore, by matching the amplitudes and gradients of the wavefunctions at the barrier-well interfaces it is possible to calculate the eigenstates (energies) of the allowed confined states. In Fig. 2.5 we show schematically the electron and hole confined ground states (the lowest energy states allowed in the wells), having energy $e_1$ and $h_1$ respectively. Processes such as absorption within this quantum well (QW) will involve these states rather than the CB and VB edges of the bulk material and thus the absorption edge of the well material is shifted.
in energy by \((e_1 + h_1)\) meV. In fact the shift is smaller than this due to the binding energy (Coulomb attraction) of the excitons which form prior to the electrons and holes recombining. An exciton is simply an electron and hole in orbit about one another and is analogous to a hydrogen atom. In three dimensional bulk materials it is possible to express the exciton binding energy as: [1]

\[ E_B = -R_\infty \frac{\mu}{m} \frac{1}{\varepsilon_r^2} \]  

(2.6)

where \(R_\infty = 13.6\) eV is the Rydberg constant (binding energy of a hydrogen atom), \(\mu\) is the reduced mass of the exciton, and \(\varepsilon_r\) is the dielectric constant of the semiconductor in question. Using appropriate parameters we find that \(E_B \approx 4\) meV for GaAs. In two dimensions the binding energy is increased by a factor of four, [9] thus making excitons far more stable in quantum wells than in bulk semiconductors. Therefore, excitonic effects in optical spectra can be seen at room temperature in QWs. [10]

QWs are used routinely in modern devices since they bring a number of benefits to their performance. Firstly it is possible to tailor the desired operating wavelength of a device by growing QWs of specific thicknesses since the confinement energies of the electrons and holes are dependent on the well width. Also the simple physical confinement of the carriers means that they are unable to escape easily from the active region of a device before recombining. Another advantage is the step-like density of states which occurs in QWs which leads to improved performances in QW semiconductor lasers over conventional heterojunction devices. [11] Strain too can be incorporated into the wells by mismatching their lattice size with that of the substrate material. In compressively strained QWs, the heavy-hole band lies above the light-hole band at the \(\Gamma\)-point with the effective mass of the heavy-hole band reduced in the plane of the well. This causes a reduction in the density of states and an improved performance in lasers containing such wells follows. [12, 13, 14] For each of these reasons QWs are now integral parts in many devices such as semiconductor lasers or light-emitting diodes.

Although calculating the confinement energies within a well using a single wavefunction (such as described in this section) gives a reasonable approxi-
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mation of the energies it is more accurate to consider the multiple bands in the semiconductor since these bands are coupled by the interactions between them. In appendix A we discuss the multi-band envelope function approximation technique used in this work to calculate the confined states in the QWs studied in this work. This gives greater accuracy than the standard single band approach discussed here.

2.1.4 Optical properties of semiconductors

The optical properties of semiconductor materials are closely related to their electronic band structures. The ability to tailor the band structure in these materials gives us the control over their optical properties and this has been a principal reason for the large interest in semiconductors over the last 50 or so years. In this work we primarily use optical characterisation techniques to study semiconductors and we discuss here what governs the interactions between light and matter in these materials.

The dispersion and absorption of a plane wave in a semiconductor can be described by the material's complex refractive index \( N = n + i\kappa \), where both the real and imaginary components are functions of wavelength. The complex refractive index is related to the complex dielectric function of a material by the relation \( \varepsilon = \varepsilon_1 + i\varepsilon_2 = N^2 \), giving

\[
\varepsilon_1 = n^2 - \kappa^2 \text{ and } \varepsilon_2 = 2n\kappa
\]

(2.7)

The dielectric function of a material essentially describes how it responds to an applied electric field – in particular, it tells us how displaced the atoms within it become, and the level of polarisation within the material under an electric field. In this work we refer to the dimensionless relative dielectric function, \( \varepsilon = \varepsilon_m/\varepsilon_0 \), where \( \varepsilon_0 = 8.8532 \times 10^{-12} \text{ Fm}^{-1} \) is the permittivity of free space, and \( \varepsilon_m \) is the actual permittivity of the material.

Through causality, the real and imaginary parts of the dielectric function are related by the Kramers-Kronig dispersion relations below, where \( P \)
denotes the Cauchy principle value of the integral: [15]

\[ \varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega \varepsilon_2(\omega')}{\omega^2 - \omega'^2} d\omega' \quad \text{and} \quad \varepsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^{\infty} \frac{\varepsilon_1(\omega')}{\omega^2 - \omega'^2} d\omega' \]  

(2.8)

where \( \omega \) is the angular frequency of the electromagnetic wave and is related to the wavelength by \( \omega = c k_0 \), where \( k_0 = 2\pi/\lambda_0 \) is the free space wavevector.

A consequence of the dispersion relations is that if the behaviour of the real (imaginary) part of the dielectric function is known over all wavelengths then the imaginary (real) part can be calculated at any specific wavelength value.

The real and imaginary parts of any linear response system can be related by similar expressions so long as the system obeys causality.

We discuss later on in chapter 5 an interesting relationship between the Seraphin coefficients of a VCSEL and the Kramers-Kronig (KK) dispersion relations. The KK relations can also be used to analyse modulation spectroscopy data as explained later in this chapter. As a result they are important in the field of modulation spectroscopy and so we call upon the relations often in this work.

The dielectric function of a material plays a key role in the interactions between light and matter and the imaginary part of the dielectric function \( \varepsilon_2 \) is closely related to the joint density of states of a semiconductor. In the case of direct, interband transitions this relation is given by equation 2.9, where \( M_{vc} \) is the matrix element, which depends on the wave functions of the initial and final states (i.e. of the electron state in the valence band and conduction band). For a given initial and final state, \( M_{vc} \) essentially defines the probability of an electronic transition occurring between the states, induced by an incident electromagnetic wave of energy \( \hbar \omega \). The surface integral (excluding the matrix element) represents the joint density of states as discussed in section 2.1.2

\[ \varepsilon_2 = \frac{8\hbar^2 \pi e^2}{\varepsilon_0 m \omega^2} \int_S 4\pi^2 |\nabla_k (E_c - E_v)|_{E_c - E_v = \hbar \omega} dS \]  

(2.9)

In this relation \( E_c \) and \( E_v \) are the conduction and valence band edges; \( m \) is the free electron mass and \( e \) is the electronic charge. Wherever \( \nabla_k (E_c - E_v) \to 0 \) the joint density of states becomes a rapidly varying function of \( k \). This
condition can occur at so called critical points in the semiconductor band structure. The most important critical point occurs at the highly symmetric Γ-point of the Brillouin zone in direct gap semiconductors where both the valence and conduction band dispersions are zero. It is at this point where the majority of radiative carrier recombination occurs since this is the smallest band gap in III-V direct semiconductors such as GaAs.

The absorption coefficient ($\alpha_{\text{abs}}$) of a material is a measure of the intensity attenuation per unit length of a plane wave travelling through the medium and is related to the imaginary part of the dielectric function. The common expression for $\alpha_{\text{abs}}$ is written in terms of the extinction coefficient $\kappa$ and the free-space wavelength $\lambda_0$:

$$\alpha_{\text{abs}} = \frac{4\pi \kappa}{\lambda_0}$$

(2.10)

The absorption, like $\varepsilon_2$, is closely related to the joint density of states of a material. For an ideal semiconductor photons of energy below that of the band gap will be unable to excite valence electrons into the conduction band and at such energies $\alpha_{\text{abs}} = 0$. Above the band gap $\alpha_{\text{abs}}$ increases roughly in line with the joint density of states (Fig. 2.4). It is possible to measure $\alpha_{\text{abs}}$ directly in semiconductors. However, due to the presence of free-carriers near the band edges (i.e. from intentional doping or thermal excitation effects) and defect states lying within the band gap it is not always possible to ascertain accurate values of the band gap from such measurements. As an example of this, figure 2.6 shows the absorption of GaAs near the band edge for a range of different doping concentrations. [16] It is clear that determining $E_0$ from each of these spectra is not a simple case of inspection, especially for higher levels of doping concentration. Therefore, in order to study the band structure of semiconductors it is often necessary to turn to techniques with greater sensitivity.
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2.2 Modulation spectroscopy of semiconductors

2.2.1 Fundamentals of modulation spectroscopy

As mentioned above it is often not possible to accurately study the band structure of a semiconductor using conventional optical characterisation techniques such as absorption spectroscopy or reflectance and transmission spectroscopy. One family of techniques that offers a higher accuracy and sensitivity is modulation spectroscopy, a powerful optical characterisation technique that plays an important role in developing the understanding of both semiconductor materials and devices. Throughout this work we exploit the powerful properties of this technique and so here we aim to give a brief background into modulation spectroscopy.

Modulation spectroscopy essentially involves periodically perturbing the optical properties of a sample in some way and measuring the resulting changes in say the reflectance, transmission or absorption spectrum. The advantage of modulation spectroscopy over conventional optical techniques such as measuring the reflectance is that critical points in the band structure appear as sharp, well defined features, with the slowly varying background reflectivity removed. This is due to the differential nature of the technique and is illustrated in figure 2.7, where both the reflectance and modulated reflectance spectra for GaAs at room temperature are displayed. [17] The form
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Figure 2.7: Reflectance ($R$) and modulated reflectance ($\Delta R/R$) of GaAs at room temperature over a large energy range, covering a number of critical points in the band structure. [17]

of the reflectance ($R$), although showing some weak features at the marked critical point energies ($E_0$, $E_1+\Delta_1$ and $E_0'$ for example), is not strongly dependent on the band structure. This makes it difficult to determine the various energies of interest from $R$. In contrast, the modulated reflectance spectrum ($\Delta R/R$) exhibits sharp derivative-like features at six discrete critical points in the band structure—each clearly discernable, allowing the energies of the features to be determined with great accuracy.

There are two different types of modulation spectroscopy, classified in terms of whether the perturbation is applied externally or internally. [17] Internal perturbation methods involve changes to the measurement conditions: for example, the measuring wavelength could be modulated. External perturbation methods involve changing the sample’s properties in some way by applying say an electric field, stress or heat. In this work the focus is on photomodulation spectroscopy ($PR$), a contactless form of electromodulated reflectance ($ER$). In this technique, a sample's internal electric field or carrier concentration is modulated by illuminating it with mechanically-chopped laser light. This in turn alters the sample’s dielectric function by
some small amount $\Delta \varepsilon = \Delta \varepsilon_1 + i\Delta \varepsilon_2$, where, due to causality $\Delta \varepsilon_1$ and $\Delta \varepsilon_2$ are Kramers-Kronig pairs, related by Eq. 2.8 on page 23. It is possible to measure the resulting differential change in the intensity of the reflection $\Delta R = R_{\text{laser on}} - R_{\text{laser off}}$ that arises from this change in the dielectric function and the $PR$ signal is defined as:

$$\frac{\Delta R}{R} = \frac{1}{R} \left( \frac{\partial R}{\partial \varepsilon_1} \right) \Delta \varepsilon_1 + \frac{1}{R} \left( \frac{\partial R}{\partial \varepsilon_2} \right) \Delta \varepsilon_2 = \alpha \Delta \varepsilon_1 + \beta \Delta \varepsilon_2$$  (2.11)

where $\alpha$ and $\beta$ are the Seraphin coefficients. [18] For bulk, single layer systems the Seraphin coefficients are typically slowly varying functions of wavelength and their effect on the lineshape of the $PR$ can then be essentially ignored so that the experimental measurement is primarily representative of $\Delta \varepsilon$.

The form that $\Delta \varepsilon$ takes is influenced by the size of the perturbing electric field induced in the material by the modulation laser. There are three regimes in which $\Delta \varepsilon$ assumes different forms of lineshape and these depend on the perturbation and system energies for both interband and intraband carrier acceleration mechanisms. [19] In this work we are primarily concerned with the so called low-field regime where, for interband mechanisms the carrier energy gained from acceleration due to the perturbing electric field across the unit cell is small compared to the band gap energy. For intraband mechanisms the low-field regime occurs when the average carrier energy gained from the acceleration is small compared to the lifetime broadening $\Gamma$ of the carrier states. In this low-field regime $\Delta \varepsilon$ can be shown to be related to the third-derivative of the unperturbed dielectric function after Aspnes, [19] which as we shall show later has a relatively simple form.

$$\Delta \varepsilon \propto \frac{\partial^3}{\partial E^3} \left( E^2 \varepsilon(E, \Gamma) \right)$$  (2.12)

Aspnes states that the reason for this relation is due to the fact that applying an electric field alters the symmetry within a crystal meaning that the crystal momentum is no longer a good quantum number. This alters which transitions may occur near the band edges, and thus, the profile of the modulated dielectric function and results in a behaviour described by
2. Theoretical Background

Eq. 2.12. [19] Other modulation spectroscopy techniques which do not alter the crystal symmetry (for example temperature modulation spectroscopy) exhibit first derivative lineshapes for $\Delta \varepsilon$. [20, 21] In such techniques the dielectric function is typically shifted in energy, rather than having its profile altered and so the $\Delta \varepsilon$ lineshapes are simpler to those seen in $ER$ and $PR$ measurements. The trade-off however is that the techniques which yield first derivative lineshapes are usually more difficult to perform compared to $ER$ and $PR$ experiments.

If the internal electric field of a sample being modulated is greater than in the low-field regime (and the associated electo-optic energy of the field is comparable to the energy broadening of the critical point in question [19]) the $PR$ spectrum may exhibit so called Franz-Keldysh oscillations (FKOs). [22] In this intermediate to high-field regime the $PR$ spectra are notably more complex and as a result, more difficult to interpret. Figure 2.8 shows an example of a measured $PR$ spectrum exhibiting FKO's. [23] This displays the trademark decaying oscillations at energies above the band gap (1.42 eV in this case) and an exponential decay below the band gap. As we shall see in the next section, this is rather more complex than a typical low-field $PR$ or $ER$ spectrum.

Fortunately the samples we study in this work tend to lie in the low-field
regime and we do not need to discuss in detail the process for analysing measurements such as the one in Fig. 2.8. However, we mention the existence of both the intermediate-field regime and FKOs here since in chapter 6 some of the samples investigated exhibit slightly complicated PR spectra, not describable by a standard low-field regime model. It is therefore useful to have some knowledge of the intermediate-field regime in order to understand our spectra and to ensure they are analysed in an appropriate manner.

2.2.2 Analysis of modulation spectroscopy lineshapes

To derive an analytical form for Eq. 2.12 it is necessary to develop the relationship for $\Delta \varepsilon_2$ in equation 2.9. This way a model for the low-field PR can be determined and used to parameterise measured data. In reference [17] it is shown that the complex dielectric function for differing parabolic critical points can be expressed using the following simple form:

$$\varepsilon (E, \Gamma) = C e^{i\theta} (E - E_0 + i\Gamma)^{-m}$$  \hspace{1cm} (2.13)

where $C$ is an amplitude, $\Gamma$ a broadening parameter, $\theta$ a phase parameter, $E_0$ the energy of a critical point, and $m$ an exponent. The value of $m$ depends on the type of critical point with which the dielectric function is associated: for 1D critical points the exponent is 1/2; for 2D it becomes 0; and for 3D critical points $m = -1/2$. Discrete excitons can be modelled by setting the exponent to a value of 1. As a first approximation this is suitable for describing the dielectric functions of excitons in QWs, which have a Lorentzian profile. Although this approximation is adequate for most of the work in this thesis, in section 5.2.1 we introduce a more detailed description of the dielectric function of excitons in QWs. In that chapter the extra detail is required to fully account for the effects of the QWs on the optical properties of a particular sample.

When the exponent $m$ is set to $-1/2$ equation 2.13 yields the square root behaviour for $\varepsilon_2$ with energy as depicted in figure 2.4 for bulk semiconductors near the fundamental band gap $E_0$. It should be noted that the form of equation 2.13 is suitable only for taking the derivative of (as in Eq. 2.12)
2. Theoretical Background

as it does not include any additional constant background terms required to give the full dielectric function value of a material. Therefore it is a suitable starting point for deriving a low-field PR model, but not for use as a stand alone dielectric function model.

Combining Eqs. 2.11–2.13 gives the so called third-derivative functional form (TDFF) for a low-field PR lineshape developed by Aspnes [19]:

\[ \frac{\Delta R}{R} = \text{Re} \left[ (\alpha - i\beta)(\Delta \varepsilon_1 + i\Delta \varepsilon_2) \right] = \text{Re} \left[ Ce^{i\theta} (E - E_0 + i\Gamma)^{-n} \right] \]  \hspace{1cm} (2.14)

Since taking the third derivative increases (negative sign included in power term) the magnitude of the exponent \( m \) in Eq. 2.13 by three, it follows that a 3D critical point will have \( n = -1/2 + 3 = 2.5 \) in a TDFF. The TDFF equation is valid only if the Seraphin coefficients are slowly varying enough that \( \alpha - i\beta \) can be considered a constant, so that its effect can be incorporated into the TDFF by suitably redefining the amplitude \( C \) and the phase factor \( \theta \). It is also only truly valid for parabolic, ideal semiconductors. Successfully fitting a TDFF lineshape to measured PR data allows the energy and broadening of a critical point to be accurately determined, making it a very useful fitting function. In this work we use a least squares fitting routine using the Levenberg-Marquardt algorithm [24] written by Hosea [25] to analyse our measured PR spectra.

For PR of QW samples the lineshapes are not described using a third derivative relationship such as Eq. 2.12. They are in fact derived using a first derivative relationship since this is more appropriate for the effects of a perturbing electric field on excitons confined in QWs. [26, 27] Fortunately we can still use the general TDFF equation in order to describe QW PR lineshapes. However now \( n = m + 1 \) since only the first derivative is taken. Therefore we can use Eq. 2.14 with \( n = 2 \) to describe the PR lineshapes seen for QW samples. We often refer to QW PR features in this work as being fitted with the TDFF equation in Eq. 2.14 although strictly speaking, when used in this way it is not a TDFF, but a first-derivative functional form.

For some samples fitting the measured PR with a lineshape model can be troublesome for a number of different reasons. Fortunately there is a simple
and quick way of estimating the energies of critical points by calculating the modulus of a PR spectrum. This can be done using the relationship in Eq. 2.15. [31, 28]

\[
\text{Mod} \left\{ \frac{\Delta R}{R} \right\} = \sqrt{\left( \frac{\Delta R}{R} \right)^2 + \left( \text{KK} \left\{ \frac{\Delta R}{R} \right\} \right)^2}
\]  

(2.15)

Here the PR and the Kramers-Kronig (KK) transformed PR are added in quadrature, where the KK transform is related to the modulation induced change in phase of the reflectance and is given by Eq. 2.16:

\[
\text{KK} \left\{ \frac{\Delta R}{R} \right\} = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\Delta R(\omega')}{R(\omega')} \frac{\omega'}{\omega^2 - \omega'^2} d\omega'
\]

(2.16)

Although the integral in Eq. 2.16 extends from zero to infinite energy it is possible to truncate the range to cover those energies for which the measured PR spectrum is non-zero. Therefore calculating the KK transform is straightforward and we do it here using Simpson’s rule for the integration. [29]

The modulus spectrum is simpler than the PR spectrum since the phase information is removed and the modulus appears as a simple peak centred at the critical point energy. This is demonstrated by Eq. 2.17, the modulus lineshape of a TDFF (Eq. 2.14), derived using Eq. 2.15:

\[
\text{Mod} \left\{ \frac{\Delta R}{R} \right\} = \frac{C}{[(E - E_0)^2 + \Gamma^2]^{n/2}}
\]

(2.17)

Therefore it is possible to simply read the energy from the peak in the spectrum. This is highlighted by the solid curves shown in figure 2.9 (a) and (b). In Fig. (a) the solid curve represents a computed TDFF lineshape (Eq. 2.14), generated using the parameters stated in the figure. The HWHM of the lineshape is \( \Gamma = 40 \text{ meV} \). The solid curve in Fig. 2.9(b) shows the modulus of the TDFF, calculated using Eqs. 2.15 and 2.16. As can be seen this is a symmetric, Lorentzian-like shape with a peak at the critical point energy \( E_0 = 1.3 \text{ eV} \). The HWHM of the modulus lineshape is \( \Gamma = 40 \text{ meV} \), equal to that of the TDFF in (a). It is clear that the modulus graph is easier
2. Theoretical Background

Figure 2.9: (a) Simulated photomodulated reflectance lineshape using Eq. 2.14 (p. 30) for a standard feature (solid curve) and a feature with an energy dependent broadening (dashed curve). The amplitudes of the two functions are equal at $C = 11.7$. (b) Calculated modulus $PR$ spectra of the two lineshapes in (a) using Eq. 2.15 on page 31.

to interpret than the TDFF in (a) and we use the technique routinely in this work alongside least squares fitting with the TDFF function to analyse our $PR$ data.

As well as being a simple and quick way of interpreting $PR$ spectra, the modulus technique also provides a reliable way of estimating critical point energies of spectra which for some reason cannot be fitted with a model such as the TDFF equation. We demonstrate this here by plotting a TDFF in Fig. 2.9(a) (dashed curve) with the same parameters as the previous one, except now the HWHM is a function of energy, varying linearly between 40 $\leq \Gamma \leq$ 90 meV over the energy range displayed. This has the effect of spoiling the lineshape so that it cannot be described by a standard TDFF. It has been
suggested previously that such an energy dependent broadening could be used as an empirical way of modelling PR spectra which are complicated by effects such as strain or non-uniform electric field distributions. [30] The calculated modulus of this lineshape is plotted in Fig. 2.9(b) (dashed curve). It can be seen that this modulus feature is not perfectly symmetric (especially when compared to the modulus spectrum of the standard TDFF shown by the solid curve) and this is due to the energy dependence of \( \Gamma \) here. However, despite this non-symmetric profile we see that the modulus still peaks at 1.3 eV, the value of \( E_0 \). This indicates that the modulus technique is able to reveal \( E_0 \) for this lineshape when the conventional TDFF model is unable to.

Although the modulus technique is a very useful one for estimating critical point energies we must mention that its accuracy is not always as high as in the demonstration in Fig. 2.9. This is especially so for PR spectra which consist of several closely spaced transition features, separated by energies less, or comparable to their HWHMs. [31] The most desirable situation is to be able to obtain high quality fits with a model such as that of Eq. 2.14.

2.2.3 Experimental technique of photomodulated reflectance

Figure 2.10 shows the experimental set-up used for the visible and near-infrared reflectance and PR experiments carried out in this work. White light from a tungsten filament bulb is monochromated by a grating spectrometer and the output light is focussed onto the surface of the sample using quartz glass lenses. The sample can be heated or placed in a cryostat to be cooled so that thermal effects on the band structure can be investigated. The sample on its mount can also be rotated so that the reflectance (or PR) can be measured as a function of angle of incidence. This is particularly useful when studying VCSELs, as explained later. For such measurements it is necessary for the sample to lie directly on the axis of rotation so that the optical alignment is not spoilt by changing angles.

The photo-induced modulation of the dielectric function of the sample is achieved by shining a mechanically-chopped laser onto its surface so that the laser beam spot overlaps the probe light from the spectrometer. This is
2. Theoretical Background

![Experimental setup](image)

**Figure 2.10:** Experimental setup used in this work to conduct visible and near-infrared reflectance and photomodulated reflectance measurements on semiconductor materials and devices.

illustrated in the face-on view of the sample in Fig. 2.10. Here the monochromated light produces a focussed image of the rectangular exit slit of the spectrometer on the surface of the sample. The modulation is achieved here using a $\sim 2$ mW HeNe laser, and the power densities required to achieve acceptable PR signals are typically low enough that it is not necessary to focus the laser onto the sample surface. The laser-generated carriers which cause the perturbation to the sample's internal electric field are believed to be captured in traps which have lifetimes of the order of milliseconds. Therefore it is important that the modulation frequency should be low enough to allow the carriers to be released from the traps so that the modulated signals can be detected. If the modulation frequency is too high it is possible for the size of the measured signal to be compromised. [32] In our visible and near-infrared experiments we used a modulation frequency of 333 Hz.

It is desirable that the detector and amplifier used are able to register both ac and dc signals so that both the reflectance $R$ and the difference signal ($\Delta R = R_{\text{Laser on}} - R_{\text{Laser off}}$) can be measured. A dc coupled volt meter can then be used to channel the reflectance signal to a computer while a lock-
in amplifier can be used to detect $\Delta R$. Once both spectra have been recorded they can be divided to give the PR signal $\Delta R/R$ defined in equation 2.11. An advantage of this division process is that any arbitrary system response effects are cancelled out. If one desires a measurement of the true reflectivity of the sample, i.e. without system response effects, it is necessary in our set-up to measure the system response in a separate experiment without the sample in the optical path. The reflectance can then be divided through by this measurement to give the normalised reflectance values.

2.2.4 Photomodulated reflectance of VCSELs

As discussed in section 1.2 the operational efficiency of a VCSEL is heavily dependent on the amount of de-tuning between the cavity mode energy ($E_{CM}$) and the peak in the material gain curve, which will be close to the ground state transition energy of the quantum wells in the device ($E_{QW}$). Therefore, characterising this property is a very useful way of determining if a sample has been grown correctly before processing it into a functioning device. While determining $E_{CM}$ is relatively simple since it can be found from the reflectance spectrum (see Fig. 1.4 on page 8 for example) determining $E_{QW}$ is more complicated due to the high reflectance stop-band caused by the DBR layers. This means that conventional PL spectroscopy cannot be used to measure the emission from the QWs since the luminescence is internally reflected by the DBRs, and can only escape at $E_{CM}$. It is possible to remove the upper DBR of a VCSEL by etching it, leaving the cavity and lower DBR intact. The PL may then be measured to reveal the value for $E_{QW}$. [33] The main issue with this process is that it is destructive to the sample and therefore non-ideal.

It was shown in 1996 by Berger et al. that despite the strongly reflecting DBRs in a VCSEL it is possible to observe PR features from both the CM and QWs, allowing a non-destructive measurement of the de-tuning between the two. [34] Since then a great deal of work has been done to develop PR as a non-destructive technique for characterising VCSEL wafers. It is now known that the PR feature arising from the CM of a VCSEL is caused by a
photo-induced modulation of the cavity refractive index and/or absorption. In the current understanding this alters the position and depth of the CM feature, as illustrated in figure 2.11. [35] Here we have shown the modulation in terms of changes to the dielectric function of the cavity since the Seraphin coefficients are defined as functions of $\varepsilon_1$ and $\varepsilon_2$. As can be seen from the figure, a modulation in the real part of the dielectric function ($\delta\varepsilon_1$) causes the optical thickness of the cavity to increase and so $E_{CM}$ decreases. Therefore, the CM dip in $R$ moves to a lower energy. The $\alpha$ Seraphin coefficient will take the approximate form given by $R(\varepsilon_1 + \delta\varepsilon_1) - R(\varepsilon_1)$, which can be seen from Fig. 2.11 to be anti-symmetric and centred about $E_{CM}$. A modulation in $\delta\varepsilon_2$ of the cavity is believed to alter the depth of the CM dip in $R$ and this results in a symmetric lineshape for the $\beta$ coefficient, also centred about $E_{CM}$. [36] These modulations to the cavity absorption and optical thickness are believed to be due principally to a modulation of the QWs, which, lying within the cavity region contribute to the overall cavity absorption and optical thickness. A VCSEL PR signal is a multiple of the QW modulated dielectric function and the Seraphin coefficients of the cavity shown in Fig. 2.11.
2. Theoretical Background

Δε of the QW can often be suitably described using a TDFF function given by Eq. 2.14 on page 30. It has also been verified that the form of the Seraphin coefficients shown in Fig. 2.11 can be represented by simple Lorentzian lineshapes. This leads to a VCSEL PR lineshape model which can be used to fit measured PR spectra: [36]

\[
\frac{\Delta R}{R} = \text{Re} \left\{ \left[ \frac{I_\alpha \Delta_{CM}}{\Delta_{CM}^2 + \Gamma_{CM}^2} - i \frac{I_\beta \Gamma_{CM}}{\Delta_{CM}^2 + \Gamma_{CM}^2} \right] \left[ \frac{e^{i\theta}}{(\Delta_{QW} + i\Gamma_{QW})^n} \right] \right\} \quad (2.18)
\]

Here Δ_{CM} = E_{CM} - E and Δ_{QW} = E_{QW} - E, Γ_{CM} and Γ_{QW} are the half-width at half-maximum of the CM and QW features respectively. I_{\alpha,\beta} are the respective amplitudes of the two Seraphin coefficient lineshapes. The remaining QW parameters in the TDFF part of the equation are explained on page 29.

Eq. 2.18 gives a fitting model with eight variable parameters (including the exponent n of the TDFF) which can be used to describe measured PR spectra and to quantify the results. Despite the relatively complex form of the relationship it is often possible to achieve good fits to measured data, especially when PR features for both the CM and QW are observable—this enables one to make good estimates of the initial parameter values in Eq. 2.18 for the fitting routine. This lineshape formula has been successfully used a number of times previously to fit measured PR lineshapes of a range of VCSELS and related structures. [36, 39, 37, 38]

A correctly grown VCSEL will actually be de-tuned at room temperature, with E_{QW} a few meV higher than E_{CM}. This allows the QW gain peak to come into resonance with the CM as the active region heats up during laser operation. Therefore, when studying VCSEL wafers using PR it is useful to vary the de-tuning between the CM and QW so that the conditions for which E_{CM} = E_{QW} can be determined. One way of doing this is to vary the temperature of a sample by mounting it on a heater, or in a cryostat. As the temperature increases the band gap of a QW will be reduced, causing E_{QW} to decrease. E_{CM} also reduces as the temperature increases, but at a slower rate, [39] allowing E_{QW} to be tuned through E_{CM} so long as the initial de-tuning is not so large that the required temperatures can be applied without
damaging the sample. The CM energy changes due to thermal effects on
the refractive index of the cavity medium, which causes the optical thickness
to increase. The physical thickness of the cavity is also increased due to
thermal expansion. However, this effect is considerably less significant than
the change in refractive index. [40]

Another method for varying the de-tuning is to mount the sample on a
turntable and record the PR at different angles of incidence. [41] In this type
of experiment the QW energy levels are unaffected and the CM can be tuned
(blue-shifted) through the transition energies, so long as the initial conditions
are favourable. This technique is discussed further in section 3.4.1 where we
look specifically at the angle dependent PR of a 760 nm VCSEL wafer.

There are other methods available for tuning the QW and CM in a VCSEL
wafer; it is possible to do so for example by applying hydrostatic pressure
to a sample. [42] However, in this work we limit our studies to investigating
angle and temperature dependent PR .

During previous PR studies of VCSELS and related structures some key
findings have been made which give us very useful tools for determining from
the PR spectra when a VCSEL is tuned with $E_{CM} = E_{QW}$. These tools are
particularly useful if the spectra are too troublesome to fit with the lineshape
model of Eq. 2.18, or if the QW PR feature is too weak to be discerned so
that its energy cannot be determined.

The first of these findings is that when $E_{CM} = E_{QW}$ the amplitude of the
PR becomes maximum. [38, 43] This amplitude resonance effect is known to
occur in VCSELS that have $\Gamma_{CM} \approx \Gamma_{QW}$ and is caused by the multiplicative
effect between the CM Seraphin coefficients and the QW modulated dielectric
function, which is largest when $E_{CM} = E_{QW}$. [35] Therefore, if one wishes
to determine when a VCSEL is tuned it may be possible to simply look
for the condition in which the measured PR signal is a maximum. Such
a convenient technique makes it straightforward to interpret the PR of a
VCSEL. However, as we illustrate later in our studies on a 760 nm VCSEL,
an amplitude resonance can occur when $\Gamma_{CM}$ is not approximately equal
to $\Gamma_{QW}$ but this is not necessarily an indication that a VCSEL is tuned.
Therefore, caution needs to be exercised when interpreting such a resonance.
There is another technique for determining when a VCSEL is tuned by simply studying the appearance of the measured \( PR \). This method involves the symmetry of the lineshape and is applicable to VCSELs in which \( \Gamma_{CM} \ll \Gamma_{QW} \). In such VCSELs it has been observed that the measured \( PR \) becomes anti-symmetric when \( E_{CM} = E_{QW} \). [44, 45] In VCSELs with \( \Gamma_{CM} \ll \Gamma_{QW} \) the \( PR \) lineshape is dominated by the form of the Seraphin coefficients in the vicinity of the CM as illustrated in figure 2.12. The upper plots in this figure show the sharp Seraphin coefficients of width \( \Gamma_{CM} \) at the CM energy. Below these are a representation of the modulated dielectric function of the QWs at \( E_{QW} = E_{CM} \), having \( \Gamma_{QW} \gg \Gamma_{CM} \). These are plotted with

![Figure 2.12: Schematic illustration of the Seraphin coefficients of a VCSEL (upper plots) and the modulated dielectric functions of the quantum wells within the cavity (middle plots). In this example the quantum well feature is significantly more broad than the cavity mode (\( \Gamma_{QW} \gg \Gamma_{CM} \)) and the resulting multiples of the Seraphin coefficients and dielectric functions are seen to be anti-symmetric when \( E_{QW} = E_{CM} \) (lower plots).](image-url)
2. Theoretical Background

$\Delta \varepsilon_2$ having a dispersive profile since the modulation process is believed to slightly shift the QW absorption edge (a change in the magnitude of the quantum confined Stark effect [46]) as the electric field across the wells is altered. The two components of the $PR$ signal (i.e. the multiples $\alpha \Delta \varepsilon_1$ and $\beta \Delta \varepsilon_2$) are shown in the bottom two plots. Looking at $\alpha \Delta \varepsilon_1$ we see that the lineshape is anti-symmetric since it is governed principally by the shape of $\alpha$, with $\Delta \varepsilon_1$ being slowly varying over the energy region of the CM feature. Therefore this element of the $PR$ gives rise to an anti-symmetric lineshape when $E_{CM} = E_{QW}$. The other component of the $PR$, $\beta \Delta \varepsilon_2$, is very weak due to the fact that $\Delta \varepsilon_2$ goes through zero at the CM energy causing an anti-resonance in the amplitude of this component. Therefore, the overall $PR$ signal is dominated by the anti-symmetric $\alpha \Delta \varepsilon_1$ component and this is the reason why in VCSELs with $\Gamma_{CM} \ll \Gamma_{QW}$ the $PR$ becomes anti-symmetric when $E_{CM} = E_{QW}$. This gives another powerful method for determining when a VCSEL is tuned and can be realised by simply monitoring the phase of the measured $PR$ lineshapes.

The amplitude resonance effect and the anti-symmetry effect are both very useful methods for determining when a VCSEL is tuned. However, in order to use either, the relative widths of the CM and QW features must be known. We show in chapter 3 that it is possible to get misleading amplitude resonances occurring when $E_{CM} \neq E_{QW}$ in a VCSEL with $\Gamma_{CM} \ll \Gamma_{QW}$. Since we knew the relative widths of the two features in this case we were able to discount the amplitude resonance. However, if we were unable to compare the widths for some reason we may have mistaken the effect as being a sign that the VCSEL was tuned. Therefore, care must be taken when interpreting VCSEL $PR$ spectra, especially if the relative linewidths of the CM and QW features are unknown.

2.3 Calculating the optical properties of stratified dielectric layers

As discussed in the introduction and previous section the reflectance and photomodulated reflectance lineshapes of VCSEL structures are particularly
detailed due to the complicated nature of their design. In this section we shall discuss the method we use in this work to calculate the reflectivities of VCSELs, enabling us to gain insight into how both the design of a sample, and the materials used contribute to give such detailed optical spectra.

The reflectance (or transmittance) of an interface between two different materials is dependent on the refractive index contrast between the two. The refractive index of a material is related to the dielectric function via Eq. 2.7 on page 22. Therefore, through this and Eq. 2.9 on page 23 we see that the reflectance and transmittance at the interface between two semiconductors are influenced by the band structures of the materials. By applying the appropriate boundary conditions for an electromagnetic wave travelling across an interface between a material and some other medium of incidence it is possible to calculate these optical properties. This situation is depicted in Figure 2.13, where the interface between the two materials (1 and 2) is denoted by the \(x, y\) plane. The plane of incidence contains the normal to this plane and the unit vector \(s^{(i)}\), which represents the direction of travel for the incident plane wave. In this figure, the electromagnetic wave is represented by a simple ray diagram. \(A\) is the complex amplitude of the electric field vector for the incident plane wave. The field may be resolved into two components, one parallel to (transverse magnetic (TM)), and the other perpendicular to
2. Theoretical Background

(Transverse electric (TE)) the plane of incidence. These components are denoted by \( A_{||} \) and \( A_{\perp} \) respectively. It can be seen that the incident plane wave splits into two waves at the boundary, one being reflected and the other refracted. These two separate components are labelled \( r \) and \( t \) respectively. By considering the time variation of the electric fields across the boundary it can be shown that the angle at which the reflected wave makes with a unit vector along the \( z \) axis is given by \( \theta_r = \pi - \theta_i \), where \( \theta_i \) is the angle of incidence. This treatment also leads to Snell's law of refraction, which relates the angles of incidence and refraction with the refractive indices of the two layers:

\[
N_1 \sin(\theta_i) = N_2 \sin(\theta_t)
\]

(2.19)

In Ref. [47] the following Fresnel formulae are derived for the amplitudes of \( r \) and \( t \) for both TM and TE polarisations:

\[
t_{||} = \frac{2N_1 \cos(\theta_i)}{N_2 \cos(\theta_i) + N_1 \cos(\theta_t)} A_{||}
\]

(2.20)

\[
t_{\perp} = \frac{2N_1 \cos(\theta_i)}{N_1 \cos(\theta_i) + N_2 \cos(\theta_t)} A_{\perp}
\]

(2.21)

\[
r_{||} = \frac{N_2 \cos(\theta_i) - N_1 \cos(\theta_t)}{N_2 \cos(\theta_i) + N_1 \cos(\theta_t)} A_{||}
\]

(2.22)

\[
r_{\perp} = \frac{N_1 \cos(\theta_i) - N_2 \cos(\theta_t)}{N_1 \cos(\theta_i) + N_2 \cos(\theta_t)} A_{\perp}
\]

(2.23)

These amplitudes may possibly be complex and the actual reflectivity and transmissivity values that are measurable by experimentation are based on light intensity values rather than the complex electric field amplitudes. It can be shown that these intensity values relate to the amplitude values via the following relationships:

\[
R = \frac{|r|^2}{|A|^2} \quad \text{and} \quad T = \frac{N_2 \cos(\theta_i)|t|^2}{N_1 \cos(\theta_i)|A|^2}
\]

(2.24)

For normal incidence, the reflectivity of a single interface between two semi-infinite, non-absorbing materials becomes independent of polarisation and
simplifies to the familiar expression:

\[ R = \left( \frac{n_2 - n_1}{n_2 + n_1} \right)^2 \quad (2.25) \]

In order to calculate the reflectivity or transmissivity of a more complex, multi-layered structure such as a VCSEL, the interference between the reflections from each interface must be taken into account. This can be achieved using transfer matrices to describe the propagation of light through stratified dielectric layers. [47] With each layer, such as the one shown in figure 2.14,

![Figure 2.14: Propagation of light through a stratified, dielectric layer of thickness z and refractive index N surrounded by two semi-infinite materials.](image)

we associate a characteristic transfer matrix: [47]

\[
M(z) = \begin{bmatrix}
\cos(k_0 N z \cos(\theta)) & -\frac{i}{p} \sin(k_0 N z \cos(\theta)) \\
-i p \sin(k_0 N z \cos(\theta)) & \cos(k_0 N z \cos(\theta))
\end{bmatrix}
\quad (2.26)
\]

\[
p_{||} = \sqrt{\frac{\varepsilon}{\mu}} \cos(\theta) \quad , \quad p_{\perp} = \sqrt{\frac{\mu}{\varepsilon}} \cos(\theta)
\quad (2.27)
\]

where \( k_0 \) is the free-space wavenumber of the wave in the layer, \( 2\pi/\lambda_0 \) and \( p \) represents the optical impedance of the layer for either TM or TE polarisations. \( \theta \) is the angle of propagation through the layer, as defined in Fig. 2.14. It should be noted that the angle \( \theta \) appearing in these equations may be complex, due to the complex refractive index of the medium.

When using transfer matrices, the amplitude of the reflectivity and trans-
mission defined in equations 2.20–2.23 can be expressed using the following relations:

\[
\begin{align*}
    r &= \frac{(m_{11} + m_{12} p_L)p_1 - (m_{21} + m_{22} p_L)}{(m_{11} + m_{12} p_L)p_1 + (m_{21} + m_{22} p_L)} A \\
    t &= \frac{2p_1}{(m_{11} + m_{12} p_L)p_1 + (m_{21} + m_{22} p_L)} A
\end{align*}
\] (2.28) (2.29)

where \(p_1\) represents the optical impedance of the semi-infinite incident medium, \(p_L\) is the optical impedance of the semi-infinite final medium, and \(m_{ij}\) are the individual transfer matrix elements for the layer in question. TM or TE polarisations can be accounted for by using the correct form of the optical impedance in Eq. 2.27, and the correct incident electric field amplitude, \(A_{||}\) or \(A_{\perp}\). The intensity values for the reflectivity and transmissivity can then be calculated using Eq. 2.24.

For a multilayer structure of \(Q\) layers (such as a VCSEL) equations 2.28 and 2.29 still hold, but the transfer matrix elements \(m_{ij}\) refer to the transfer matrix for the entire stack of layers, given by the product:

\[
M = \prod_{j=1}^{Q} M_j
\] (2.30)

Using this technique the reflectance and transmission of complicated structures such as VCSELs can be calculated so long as the thicknesses, and the complex refractive indexes (which are functions of wavelength), are known for each layer. We use this technique extensively in chapter 5 in order to further our knowledge of both the reflectance and photomodulated reflectance of VCSEL structures, ultimately enabling us to develop a new lineshape model for VCSEL PR.

2.4 References

2. Theoretical Background


2. Theoretical Background


2. Theoretical Background


3 Photomodulated reflectance of a 760 nm vertical-cavity surface-emitting laser

3.1 Introduction

In this chapter we report on the reflectance ($R$), and photomodulated reflectance ($PR$) measurements used to characterise the gain-cavity de-tuning in a ~760 nm vertical-cavity surface-emitting laser (VCSEL) designed for oxygen sensing at high-temperatures.

Oxygen gas exhibits strong, near-infrared absorption at around 760 nm in the so-called 'A-band' absorption region. [1] Figure 3.1 shows the transmission spectrum of a gaseous sample of pure oxygen in this region, measured using a Fourier-Transform spectrometer. [1] The complexity of the absorption spectrum is clear, demonstrating many closely spaced lines resulting from various atomic transitions. The present VCSEL is designed to probe the absorption from these lines at operational temperatures of ~100 °C, making it suitable for use in the exhaust systems of automotive engines. Monitoring the quantity of oxygen in an engine's exhaust gas is a way of determining
if the fuel-air mixture in the cylinders is at the desired level. By using an oxygen sensor as part of a feedback system corrective measures may be taken as necessary to adjust the fuel to air ratio. An on-board computer can then be programmed to control the system so as to either maximise the efficiency, or the power output of the engine. A VCSEL can be used in such an application as part of a line of sight sensor system, where the concentration of uncombusted oxygen would be determined by the amount of absorption of the laser's emission.

VCSELs have a number of qualities which make them ideal for gas sensing applications. For example, the single mode, narrow linewidths of their emission means that high-resolution gas sensing can be achieved. This makes it possible to resolve the kind of detail seen in Fig 3.1. Another advantage is the dependence of the cavity mode (CM) wavelength on the level of current applied to a device. [2] This is a result of current induced heating in the active region, which affects the refractive index, and in turn, the CM wavelength. This dependence means that a VCSEL's emission wavelength can be swept through the positions of various absorption lines by changing the current. [3] The relationship can also be used more subtly: the highly-accurate technique of wavelength modulation spectroscopy can be performed by simply applying modulated drive currents. [4] This technique has a greater sensitivity than conventional transmission measurements, in much the same way that PR is more sensitive than conventional R measurements (in the context of semiconductor band structures). Therefore, wavelength modulation spectroscopy is very useful for detecting small 'trace gas' concentrations. Together, these qualities make VCSELs a simple, cost effective solution for a variety of gas-sensing applications. [5, 6]

We begin our characterisation of the current VCSEL by conducting preliminary R measurements on the unprocessed wafer. Then, in order to determine the energies of the important quantum well (QW) transitions at room temperature, we measure the angle dependent PR. Finally, we investigate the temperature dependent PR in order to determine the temperature at which the material gain peak and CM wavelength coincide. This property is of most interest here since the present VCSEL is designed to operate at
3. Photomodulated reflectance of a 760 nm vertical-cavity surface-emitting laser

3.2 Sample details

The structure of the present VCSEL is similar in design to the example shown in figure 1.3 on page 6. It is entirely Al$_x$Ga$_{1-x}$As based, grown on a GaAs substrate by molecular beam epitaxy. It was grown at the Optoelectronics Research Centre, part of the Tampere University of Technology in Finland. The distributed Bragg reflectors (DBRs) consist of 46.6 nm thick high-refractive index (n) layers of Al$_{0.386}$Ga$_{0.614}$As and 51.3 nm low-n layers of Al$_{0.901}$Ga$_{0.099}$As. In order to reduce the series resistance of an operational VCSEL (caused by conduction and valence band discontinuities) the DBR pair layers are separated by thin (10 nm) 'intermediate layers' of Al$_{0.67}$Ga$_{0.33}$As (not shown in figure 1.3). The upper DBR contains 36 repeats of this periodic structure and is terminated by a GaAs cap layer to prevent oxidation of the layers high in aluminium content. The lower DBR contains 46 periods. The Fabry-Perot cavity layer of the VCSEL is made from the high-n Al$_{0.386}$Ga$_{0.614}$As material and is nominally 216 nm thick. The optical thickness of the cavity, which is dependent on n, is designed to be ~760 nm at the desired operational temperature. Since the cavity is of a higher refractive index than the surrounding DBR layers the optical cavity mode must exhibit anti-nodes at the cavity interfaces. This fulfills the requirement that reflected waves must undergo a $\pi$ phase shift at the boundary when traveling from a low to a high impedance region. The cavity mode also exhibits a maximum intensity anti-node at the centre of the cavity and has $\lambda_{CM} = n d$, where $d$ is the cavity layer thickness (216 nm). Such a cavity is known as a 'Y'-cavity and the corresponding mode has an order ($m$) of two (the $m = 1$ mode exhibits a node at the cavity centre). To ensure that the material gain of the VCSEL coincides spatially with the maximum optical field intensity of the CM, the cavity contains three, 8nm Al$_{0.154}$Ga$_{0.846}$As QWs at its centre—separated by 6nm Al$_{0.386}$Ga$_{0.614}$As barriers.
3. Photomodulated reflectance of a 760 nm vertical-cavity surface-emitting laser

3.3 Normal incidence, room temperature reflectance measurements

Figure 3.2 shows the room temperature, normal incidence $R$ spectrum of the VCSEL wafer. The high-reflectance stop-band can be seen to extend for over 40 nm, from around 734 to 778 nm. A sharp feature associated with the CM can be seen at $\sim$756 nm, close to the centre of the stop-band. Figure 3.3 shows the $R$ spectrum in the region of the CM feature. In order to maintain a suitable signal to noise ratio in this measurement the slit widths of the spectrometer were set to 75 $\mu$m, which corresponds to an instrumental resolution of 0.23 nm. The disadvantage of this is that the CM feature is not quite fully resolved. It is clear from figure 3.3, however, that the CM is of a very high quality, with a measured full-width at half-maximum (FWHM)\(^1\) of just 0.3 nm. The CM wavelength, taken from where $R$ is a minimum, can be seen to be 755.75 nm. In order to determine the true, fully-resolved FWHM of the CM feature, we measure $R$ using decreasing slit widths to

\(^1\)In the case of the CM dip in $R$ the FWHM refers to the full width at half the depth, where the depth $= R_{\text{max}} - R_{\text{min}}$ (Figure 3.3)
3. Photomodulated reflectance of a 760 nm vertical-cavity surface-emitting laser

![Normalised, room temperature reflectance spectrum of the 760 nm VCSEL wafer at normal incidence in the region of the cavity mode feature.](image)

Figure 3.3: Normalised, room temperature reflectance spectrum of the 760 nm VCSEL wafer at normal incidence in the region of the cavity mode feature.

observe the effect of the instrumental resolution. Figure 3.4 shows the results of this study, clearly showing that as the slit widths are reduced and the instrumental resolution is improved, the measured CM FWHM decreases. However, for slit widths below 40 µm (instrumental resolution better than 0.12 nm) the measured FWHM remains approximately constant, indicating that the CM feature is fully resolved here. This gives us a true CM FWHM of just 0.19 nm. Although this is slightly larger than the splitting between some of the absorption lines shown in figure 3.1 (typically ~0.1 nm) it is low enough to resolve sufficient detail within the oxygen 'A-band'.

The quality of any resonator, such as the Fabry-Pérot cavity of this VCSEL, can be parameterised by a quantity known as finesse (F), since it is directly related to the temporal storage of energy within a resonator. The finesse is defined as being the free spectral range divided by the FWHM of a resonance. In terms of the $m^{th}$ order resonance in an optical cavity this can be expressed as $F = \frac{\lambda_{CM}}{m \Gamma_{CM}}$ (for $\Gamma_{CM} \ll \lambda_{CM}$), where $\lambda_{CM}$ is the CM wavelength and $\Gamma_{CM}$ is the FWHM. Both values are obtained from the $R$ measurements for our current VCSEL and as explained in section 3.2, $m$ equals two. Using our measured values, this relationship gives us $F \approx 2000$. 

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In order to compare this value to that of other types of resonators it is necessary to account for the penetration of the optical cavity mode into the DBR layers. This results from the relatively small refractive index differences between the DBR layers \((n_H - n_L)\) and the effect is included by defining an effective finesse \(F_{eff}\): [7]

\[
F_{eff} = \frac{\lambda_{CM}}{(m + \frac{n_L}{n_H-n_L})\Gamma_{CM}} \tag{3.1}
\]

Here \(n_H\) and \(n_L\) are the high and low refractive indexes of the DBR layers respectively, where the cavity material also has \(n = n_H\). Using data obtained from ellipsometry measurements on AlGaAs we find approximate values of \(n_H = 3.40\) and \(n_L = 3.11\) (at \(\sim755\) nm) for this sample. [8] Equation 3.1 then gives us a value of \(F_{eff} = 320\) (a factor of \(\sim6\) times smaller than \(F\)). This value is not particularly high when compared to certain other resonator types; for example, lead-salt based mid-infrared microcavities have demonstrated \(F_{eff} \sim 1100\). [9] Such high finesses are possible in lead-salt...
structures due to the large refractive index differences available in the DBR materials. However, in III-V VCSELs, lower $F$ values are more typical: Ref. [10] quotes a 'high' Q-factor of 460 in a 400 nm InGaN VCSEL, where the Q-factor is related to the finesse by $Q = Fm$. Since their VCSEL has a 4-$\lambda$ cavity the mode order ($m$) is eight and this gives a finesse of $\sim$60.

Although the authors do not calculate a value for $F_{\text{eff}}$, we can estimate it here by obtaining the approximate DBR material (SiO$_2$/ZrO$_2$) refractive indexes from ref. [11]. This gives a value of $F_{\text{eff}} \sim 45$, and this reportedly 'high' finesse is approximately seven times less than the value of the current 760 nm VCSEL, highlighting the superior optical quality of our sample. Our group has not previously conducted PR studies on such a high-finesse VCSEL and the effects of the CM sharpness on the PR measurements will be examined in detail later.

Although our measurements show that the present VCSEL has a very high-finesse cavity it is clear from Fig. 3.2 that the sample does not exhibit the usual flat-topped $R$ stop band. Since the sample demonstrates such a high-quality CM it is unlikely that the spoiled stop-band is caused by a poorly designed cavity layer or DBRs. Therefore, in order to understand the origin of this unusual broad dip profile we focussed on the effect of the protective GaAs cap layer which was grown on top of the upper DBR. In order to do this we simulated $R$ for the VCSEL using the technique described in section 2.3. The wavelength dependent dielectric functions of the materials in the structure required for the simulations were taken from ellipsometry measurements. [8] Figure 3.5 shows the simulated reflectance at room temperature and normal incidence, both including and excluding a GaAs cap layer. It is immediately clear from this that the GaAs cap is indeed the cause of the spoiled stop band—a comparison of the measured $R$ spectrum with the simulated $R$ spectrum (including cap layer) shows a similar broad dip profile across the stop band. To determine the mechanism by which the layer causes this effect we made adjustments to the cap layer thickness in our simulations, and this resulted in dramatic changes to the profile of the stop band. This indicates that the effect is caused by strong interference within the cap layer, which by unfortunate happenstance, has a thickness
of $\sim \lambda_{CM}/4n$. We also observe that when the absorption of the GaAs cap is artificially 'switched off' in our simulations the layer ceases to have any noticeable effect on the reflectance—indicating that the broad dip is caused by absorption of interfered light within the cap layer.

Although the cap layer has a notable effect on the stop band profile of the current VCSEL wafer our measurements show that the CM feature is relatively unaffected. Therefore, in order to protect the sample from oxidation (which would have a detrimental affect on the optical quality of the sample) we left the cap layer on during our experimental investigations.

**Figure 3.5:** Simulated normal incidence, room temperature reflectance for the current VCSEL, excluding (solid curve) and including (dashed curve) a GaAs cap layer. The measured reflectance (solid symbols) of Fig. 3.2 has been scaled vertically to fit on the displayed scale.
3.4 Room temperature, angle dependent PR measurements

3.4.1 Theoretical background

As mentioned in section 3.2 the CM wavelength of the current VCSEL is designed to be ~760 nm (1.63 eV) at the desired operational temperature of the device. This property depends on both the refractive index of the cavity (n) and the physical thickness of the cavity layer (d). When studying the reflectance of a VCSEL it is possible to blue-shift the CM wavelength (λ_{CM}) by increasing the angle of incidence (θ) away from the normal. [12] This is caused by the angular dependence of the optical path difference (OPD) taken by light reflected from the first and second interfaces of the cavity layer, as demonstrated in figure 3.6. Here we ignore the presence of the QWs and approximate the cavity in our VCSEL as being a simple Fabry-Pérot cavity with an effective refractive index of n_{eff}. The CM feature seen in the R spectrum of a VCSEL (see Fig. 3.2) is caused by the destructive interference

![Figure 3.6: A simple Fabry-Pérot structure of thickness d and refractive index n_{eff} detailing the multiple reflection that leads to the cavity mode feature in the reflectance spectrum of a VCSEL.](image-url)
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of the reflected light and occurs at wavelengths for which the \( OPD = m\lambda \), \(^2\) where \( m \), an integer, is the mode order as mentioned previously. Making the approximation that \( n_{\text{eff}} \neq n_{\text{eff}}(\lambda) \), analysis of Fig. 3.6 gives us a relationship for the angle-dependent CM wavelength, \( \lambda_{\text{CM}}(\theta) \), where \( \lambda_{\text{CM}}(0^\circ) = 2nd/m \) is the CM wavelength at normal incidence and \( m = 2 \) for the current VCSEL: [12]

\[
\lambda_{\text{CM}}(\theta) = \lambda_{\text{CM}}(0^\circ) \sqrt{1 - \frac{\sin^2(\theta)}{n_{\text{eff}}^2}}
\]

Using this angle dependence it is possible to tune the CM wavelength of a VCSEL towards that of a QW transition by increasing the angle of incidence, provided that the QW transition occurs at a shorter wavelength than the CM (by no more than \( \sim 20 \text{ nm} \) or so). This is a typical condition in VCSELs since during operation they well heat up, causing the QW transition to increase in wavelength. Therefore, it is often possible to tune the CM of a VCSEL to the QW emission by mounting it on a turntable and increasing the angle of incidence. This simple, non-destructive technique has been used previously with success for other VCSELs and related structures. [12, 13, 14]

In this work we study the PR as a function of angle of incidence as a way of determining the nature of the various observed PR features, since the CM feature will move with \( \theta \) (Eq. 3.2) while any QW transitions will remain static. This will enable us to characterise the room temperature properties of the VCSEL wafer before beginning the important temperature dependent studies.

3.4.2 Results and discussion

Figure 3.7 shows the room temperature, angle dependent PR of the VCSEL wafer for a selection of the angles measured. Here we have plotted the results as a function of energy, rather than wavelength, where \( E = hc/\lambda \) (E (eV) \( \approx 1239.84/\lambda \) (nm)). The overall range of angles studied was \( \theta = 22.5^\circ - 80^\circ \), with measurements spaced every 2.5°. They were conducted using a low

\(^2\)Destructive interference occurs when the \( OPD \) is equal to an integer number of wavelengths since one of the waves undergoes a \( \pi \) phase shift on reflection at the first interface.
instrumental resolution of \( \sim 4 \) meV (achieved with spectrometer slit widths of 500 \( \mu \)m). Although this means that we do not fully resolve the detail of the \( PR \) lineshapes in the vicinity of the sharp CM, the increased signal intensities allows us to discern any weak \( PR \) features such as those from QW transitions. Looking at the spectrum of the 25° measurement, three separate \( PR \) features are clearly visible. The largest, a symmetric peak shape at \( \sim 1.653 \) eV (750 nm), is due to the VCSEL CM. The angle dependence of the CM energy (\( E_{CM} \)) is indicated by the dashed line marked CM. The \( E_{CM} \) values are determined from the \( R \) spectra which are recorded simultaneously to the modulated reflectance \( \Delta R \) signals and these are shown in figure 3.8. These \( R \) spectra have been normalised to remove system response effects using an aluminium mirror with a known reflectance. Comparing these \( R \) spectra to the measurement in Fig. 3.2 it is clear that the CM feature has become broader and shallower as a result of the poorer instrumental resolution. Therefore it is not possible to determine these CM energies with the best possible accuracy and so in section 3.6.2 we shall look specifically at the high resolution, angle dependent \( R \) measurements in order to carry out a more detailed analysis of the CM angle dependence. For now we take \( E_{CM} \) to be where \( R \) is a minimum in Fig. 3.8. The other two \( PR \) features in the 25° spectrum of Fig. 3.7 are magnified so that their lineshapes can be viewed. The stronger of these two features near 1.675 eV is also visible in the 60° spectrum and a quick comparison indicates that it remains static as \( \theta \) is increased; an indication that the feature is due to a QW transition (which will be unaffected by changes in \( \theta \)). Magnification of the weakest feature near 1.69 eV at other angles (not shown) indicates that it too does not move with \( \theta \), and is therefore likely to be due to a higher energy QW transition.

Calculating the modulus of the 25° \( PR \) spectrum as described in section 2.2.2 gives us a quick way of estimating the energies of the two static features. From this process we make a first estimate of their energies as 1.675 \( \pm 0.001 \) eV and 1.689 \( \pm 0.005 \) eV and these energies are marked in Fig. 3.7 by vertical dashed lines. The larger uncertainty of the higher energy feature is a result of its weak signal intensity. Calculating the approximate energies expected for the confined states within the QWs of this sample us-
Figure 3.7: Example spectra of the room temperature photomodulated reflectance measured as a function of angle of incidence ($\theta$) using a low instrumental resolution. The baselines of successive spectra are vertically offset for clarity. The positions of the electron to heavy-hole ($e_{1}hh_{1}$) and electron to light-hole ($e_{1}lh_{1}$) ground state transitions are marked by dashed vertical lines. The third dashed line is a guide to the eye showing the angular dependence of the cavity mode (CM) energy.
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![Reflectance spectra](image)

**Figure 3.8:** Normalised, room temperature, low resolution reflectance spectra of the 760 nm VCSEL recorded simultaneously to the measurements of Fig. 3.7. Successive spectra are vertically offset for clarity. The cavity mode energies are marked by the dashed line.

The methods discussed in section 2.1.3 and appendix A and material parameters from the review of Vurgaftman *et al.* [15] suggests that the two features are due to electron to heavy-hole ($e_1hh_1$), and electron to light-hole ($e_1lh_1$) ground-state transitions. The lowest energy $e_1hh_1$ transition is the most important here since in an operational VCSEL lasing will occur via this transition. Therefore we are interested in the energy separation between the CM and the $e_1hh_1$ transition (i.e. the gain-cavity de-tuning), which is $\sim 22$ meV at $\theta = 25^\circ$. For simplicity we shall refer to the $e_1hh_1$ transition energy as $E_{QW}$. Note: the peak in the gain curve will actually occur at a slightly higher energy than the QW transition energy so strictly speaking the separation between the CM and the $e_1hh_1$ energy is not precisely equal to the gain-cavity de-tuning.
As $\theta$ is increased it is clear from Fig. 3.7 that the form of the PR lineshape changes as the CM is blue-shifted towards the QW transitions. At $25^\circ$ the CM feature is a simple peak shape, clearly separated from the two QW features. However, as the angle is increased and the CM is tuned towards the $e_1h_1$ transition the two PR features begin to interact and the lineshape becomes more complex as a result. When $\theta = 55^\circ$ for example, $E_{CM}$ is in between the two QW features and this yields a very complex spectrum; a result of the coupling of all three PR features. Such a lineshape is too complex for a simple analysis and the only way of determining the three energies here would be to fit the spectra with the VCSEL PR model described in section 2.2.4 (Eq. 2.18, p. 37). This was attempted for this sample. However we were unable to achieve satisfactory fits for many of the recorded spectra. One of the possible reasons for this may be that we are not fully resolving the CM feature and as a result the PR lineshapes are likely to exhibit some convoluted form, not accounted for by the fitting model. A more interesting possible reason for the failure of the model can be found by examining the form of the lineshape at $\theta = 45^\circ$ in Fig. 3.7. This spectrum exhibits a total of four lobes: such a shape, in particular the two outer side-lobes, cannot be generated with the existing PR lineshape model. This suggests that the model is not suitable for this VCSEL and requires some modification in order to reproduce such a PR lineshape. We shall return to this problem in chapter 5 where we conduct a detailed study of the simulated Seraphin coefficients of a high-quality VCSEL similar to the current sample in order to determine why the currently accepted model is unable to fit our measured spectra.

Fortunately, despite the failure of the VCSEL PR model to fit the $\theta$ dependent spectra shown in Fig. 3.7, it is still possible to infer when $E_{CM} = E_{QW}$. As explained, we can obtain $E_{CM}(\theta)$ directly from the $R$ measurements and compare its value at a given angle to the approximate position of $E_{QW}$ as determined from the PR modulus spectrum. We can see from the dashed lines in Fig. 3.7 that $E_{CM} \approx E_{QW}$ when $\theta = 45^\circ$. Figure 3.9 shows the $\theta = 45^\circ$ reflectance spectrum in the region of the CM, showing a minimum corresponding to the CM at $E_{CM} = 1.678 \pm 0.001$ eV. The approximate
$E_{QW}$ value is also shown with the associated uncertainty indicated by the horizontal error bars. From this figure the close proximity of $E_{CM}$ and $E_{QW}$ can be appreciated.

![Graph](image)

**Figure 3.9**: Normalised, room temperature reflectance of the 760 nm VCSEL wafer in the vicinity of the cavity mode energy ($E_{CM}$) at an angle of incidence of 45°. The energy of the electron to heavy-hole ground-state quantum well transition ($E_{QW}$) is also shown. Horizontal error bars indicate the uncertainties of the two quantities.

We can also attempt to utilise existing theory regarding the symmetry of VCSEL PR lineshapes to infer when the VCSEL is tuned. As the CM moves closer to the $e_1h_1$ feature in Fig. 3.7 the symmetry of the PR lineshape begins to change. Most importantly we see from the $\theta = 45^\circ$ measurement that the lineshape becomes almost perfectly anti-symmetric, centred about $E_{CM}$ regardless of the extra outer lobes mentioned earlier. It was shown by Ghosh et al. [16] (see section 2.2.4) that for VCSELs demonstrating a QW PR feature broader than the CM feature the overall PR lineshape becomes anti-symmetric when the CM and QW features are tuned to the same energy. From Fig. 3.4 we see that the present VCSEL has a fully resolved CM FWHM ($\Gamma_{CM}$) of just 0.19 nm (0.4 meV). From the magnified feature in
the 25° $PR$ spectrum of Fig. 3.7 $\Gamma_{QW}$ can be seen to be $\sim 10$ meV (5 nm). Thus $\Gamma_{CM}$ is $\sim 25$ times smaller than $\Gamma_{QW}$. Therefore, since $\Gamma_{CM} < \Gamma_{QW}$, we can be reasonably confident that the observation of an anti-symmetric $PR$ lineshape is an indication that the VCSEL is 'tuned' with $E_{CM} = E_{QW}$. A simple method for quantifying the symmetry of a $PR$ lineshape, which does not require fitting it with an appropriate lineshape function, may be obtained by defining the symmetry as $|PR_{\text{max}}| - |PR_{\text{min}}|$, which gives zero for an anti-symmetric shape. Figure 3.10 shows the evolution of this approximate symmetry parameter with $\theta$ for our measured $PR$ spectra in Fig 3.7. It can be seen from this that the symmetry crosses through zero at an angle of $\theta = 47.0 \pm 0.5^\circ$, indicating that this is the angle at which the CM is tuned to the $e_1hh_1$ transition. At this angle of incidence we estimate $E_{CM}$ to be $1.6805 \pm 0.0009$ eV (737.8 nm) by appropriate interpolation of the $R$ measurements in Fig. 3.8. Therefore, we can state that the energy of the $e_1hh_1$ transition at room temperature is $1.6805 \pm 0.0009$ eV. This, more carefully determined value is $\sim 5$ meV higher than the initial estimate of $1.675 \pm 0.001$ eV,
determined from Fig. 3.7. At higher angles the symmetry parameter crosses again through zero in Fig. 3.10, at $59 \pm 1^\circ$. Looking at the $\theta = 60^\circ$ spectrum in Fig. 3.7 this second occurrence of an approximately anti-symmetric line-shape can be seen. At this angle, we find $E_{CM} = 1.696 \pm 0.002$ eV (731 nm), which suggests that this is the energy of the $e_1 h_1$ transition. This is some $\sim 7$ meV higher than the initial estimate of $1.689 \pm 0.005$ eV determined from Fig. 3.7.

3.5 High resolution, temperature dependent $PR$ measurements at normal incidence

3.5.1 Theoretical background

As mentioned previously the current VCSEL is designed to operate at elevated temperatures, making it suitable for use in environments such as the exhaust systems of automotive combustion engines. Therefore, in order to characterise the suitability of the wafer for such an application without processing it into a working device, we study the gain-cavity de-tuning here using $PR$ as a function of temperature.

In the case of III-V semiconductor alloys such as $Al_xGa_{1-x}$As, the fundamental band gap of the material decreases as the temperature is increased. Therefore, heating a VCSEL will increase the wavelength of its QW emission. Increasing the temperature will also have an effect on the refractive index ($n$) of the materials within the structure. This is most important in the cavity layer since its optical thickness determines the CM wavelength ($\lambda_{CM} = nd$). The cavity will also expand slightly and this will also have some effect on $\lambda_{CM}$. Equation 3.3 describes the temperature dependence expected for the CM wavelength, [17] where the partial differentials are obtained from the relationship $\lambda_{CM} = nd$ (see discussion after Fig. 3.6).

$$\frac{\Delta \lambda_{CM}}{\Delta T} = \frac{\partial \lambda_{CM}}{\partial n} \frac{\Delta n}{\Delta T} + \frac{\partial \lambda_{CM}}{\partial d} \frac{\Delta d}{\Delta T}$$

(3.3)

$\Delta n/\Delta T$ is the refractive index thermal coefficient of the cavity material,
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which is $\approx 2.6 \times 10^{-4} \, ^\circ \text{C}^{-1}$ for $\text{Al}_{0.386}\text{Ga}_{0.614}\text{As}$ \cite{18} and $\Delta d/\Delta T$ is the thermal expansion coefficient of the cavity—approximately $3.4 \times 10^{-6} \, \text{nm} \, ^\circ \text{C}^{-1}$. \cite{19} Using these values here we obtain an approximate value for $(\Delta \lambda_{CM}/\Delta T)$ of $0.6 \, \text{nm} \, ^\circ \text{C}^{-1}$. The effect on $\lambda_{CM}$ caused by the thermal expansion $(\Delta d/\Delta T)$ of the cavity is much less significant than that of the thermal coefficient of the refractive index, accounting for less than $0.1\%$ of the total change. Therefore, it is acceptable to neglect it here. Since all these quantities are positive, the result is that $\lambda_{CM}$, like $\lambda_{QW}$, will increase as the temperature is increased with the rate $(\Delta \lambda_{CM}/\Delta T)$ tending to be around four times slower than $(\Delta \lambda_{QW}/\Delta T)$. VCSELs are often designed with their CM at a slightly longer wavelength (lower energy) than the QW gain peak so that the two can become tuned as the device active region heats up during operation. \cite{21}

Therefore, temperature dependent $PR$ is a very useful, non-destructive characterisation technique for analysing the gain-cavity detuning in VCSELs since it exploits this property, inherent in sample design. \cite{20} It essentially allows us to simulate the effects of a high carrier concentration in the ‘hot’ cavity of an operational device by way of heating a ‘cold’ un-pumped cavity of a VCSEL wafer.

3.5.2 Results and discussion

Here we present the normal incidence, temperature dependent $PR$ measurements of the VCSEL wafer. We mounted the sample (in air) on a simple heater using heat conductive paste, allowing us to heat it from room temperature up to $\sim 200 \, ^\circ \text{C}$. The temperature was controlled using an ice junction thermocouple sensor connected to a calibrated temperature controller. Figure 3.11 shows the $PR$ spectra for a selection of the temperatures studied. The measurements were conducted using the highest possible instrumental resolution (limited by the signal to noise ratio) so as to observe the effect of the fully resolved high-finesse CM on the lineshape of the measured $PR$. One such effect, which can be immediately seen from Fig. 3.11, is on the magnitude of the $PR$ signals. The largest $PR$ signal measured in this study is $\Delta R/R \sim 2 \times 10^{-2}$ at $95 \, ^\circ \text{C}$ and this represents a $\sim 2\%$ change in the
Figure 3.11: Normal incidence photomodulated reflectance spectra of the VCSEL wafer shown for a selection of measured temperatures. The baselines of successive spectra are vertically offset by $3 \times 10^{-2}$ units for clarity. The dashed lines are guides for the eye showing the position of the cavity mode (CM) and electron to heavy-hole ground-state quantum well transition ($e_1hh_1$) energies.
sample's reflectance, which is an exceptionally large \( PR \) signal. In comparison, the largest \( PR \) signal seen in the low-resolution, angle-dependent study (Fig. 3.7) is \( \Delta R/R \sim 2 \times 10^{-3} \) (\( \sim 0.2\% \)); an order of magnitude lower. At a first glance this increased signal intensity seems counterintuitive since the absolute magnitude of \( R \) will be reduced with increased instrumental resolution due to the reduction in the spectrometer slit widths. However, we can explain the effect in terms of the convolution of a \( PR \) lineshape near the CM caused by using a low resolution, highlighting the significance of the VCSEL Seraphin coefficients on the overall \( PR \) lineshape. Consider a sharp, simple \( PR \) feature from the CM such as that seen near 1.64 eV in Fig. 3.11 at \( T = 30^\circ C \). If such a feature is measured again, using a lower instrumental resolution, its form will change. This effect can be written mathematically as a convolution of the fully resolved lineshape with a lineshape function \( G \), which represents the throughput of the spectrometer slits:

\[
PR_{\text{low res}}(E') = PR_{\text{high res}} * G = \int PR_{\text{high res}}(E)G(E' - E)dE \quad (3.4)
\]

Here \( PR_{\text{high res}} \) is the fully resolved, sharp \( PR \) lineshape and the resulting convoluted lineshape is \( PR_{\text{low res}} \). The function \( G \), which represents the wavelength dispersion across the spectrometer slits, is of a form that returns a convoluted lineshape with the same integrated area as the fully resolved lineshape. An appropriate form for \( G \) is a standard distribution function:

\[
G = \exp\left(-\frac{1}{2}\frac{(E' - E)/\Gamma_{\text{inst.}})^2}{\sqrt{2\pi}\Gamma_{\text{inst.}}}\right) \quad (3.5)
\]

Here, \( \Gamma_{\text{inst.}} \) is related to the instrumental resolution of the spectrometer. In order to demonstrate the effect of this convolution we approximate the fully resolved \( PR \) lineshape using a Lorentzian peak since this is the form used for the \( \beta \) Seraphin coefficient in the existing \( PR \) VCSEL lineshape model (Eq. 2.18, p. 37)—this is similar to the observed \( PR \) lineshape near the CM in the measurement at room temperature and normal incidence for example (Fig. 3.11). This generated lineshape is shown by the solid curve in figure 3.12. In order to perform the convolution of the two functions we
numerically calculate the integral in Eq. 3.4 using Simpson’s rule. [22] The result of this is shown by the dashed curve in Fig. 3.12. It is clear from this that convolution has made the original feature broader by a factor of approximately five times and also around four times weaker (the integrated area is the same for both).

The disadvantage of using the high resolution (narrow spectrometer slit widths) is the associated reduced signal-to-noise level from the QW transitions and here we are only able to observe one QW PR feature—the $e_1 hh_1$ transition. The weaker $e_1 lh_1$ transition seen in Fig. 3.7 is not detected and we presume it is lost in the noise. The PR feature from this transition may also be weakened due to the normal incidence of the probe light (i.e. rays travelling along the growth direction of the VCSEL, $z$). This is because light-hole states are predominantly $z$-like in character [23] and an electromagnetic wave
only has electric field components perpendicular to its direction of travel. The $e_1 hh_1$ feature has been magnified at temperatures where it is well separated from the CM so that it can be clearly seen in figure 3.11.

The temperature variation of the CM energy is marked by one of the dashed lines in Fig. 3.11 with the values taken from the simultaneously measured $R$ spectra, which are shown in figure 3.13. Focusing on these spec-

![Figure 3.13: Temperature dependence of the normal incidence reflectance of the 760 nm VCSEL wafer in the region of the cavity mode energy. Successive spectra are vertically offset for clarity. The dashed lines are guides to the eye indicating the approximate positions of the cavity mode energy ($E_{CM}$) and quantum well energy ($E_{QW}$). The corresponding $PR$ spectra are shown in Fig. 3.11.](image)

tra for a moment we notice that near the CM the form of $R$ changes with temperature; in particular the CM feature clearly broadens with increasing temperature. We shall look at this effect in detail in section 3.6.

The second dashed line in Fig. 3.11 marks the approximate variation of the $e_1 hh_1$ energy, $E_{QW}$. (Note, the sudden apparent changes in the gradi-
ent of this line are a result of the different temperature steps between the displayed spectra, which are successively vertically offset). Figure 3.14 details the temperature variation of these two features. For this, $E_{QW}$ was obtained by calculating the modulus of the $PR$ spectra as explained in section 2.2.2 (Eq. 2.15, p. 31). This method is only useful when the CM and QW features are well separated so that a discernible peak at $E_{QW}$ can be seen in the modulus spectrum. Consequently, there are no values for $E_{QW}$ in Fig. 3.14 for $75 \leq T \leq 160$ °C because in this temperature region the $e_1hh_1$ transition energy is too close to the CM for the modulus method to be reliable. However, we can interpolate between this region in Fig. 3.14 in order to find when $E_{QW} \approx E_{CM}$ because in this temperature region $E_{QW}$ appears to vary linearly: the main process for this is the reduction of the band gap of the QW material with temperature, as mentioned previously. Such a behaviour can be modelled by the

![Figure 3.14: Temperature variation of the cavity mode (CM) energy of the VCSEL wafer, determined from reflectance spectra (Fig. 3.13), and the electron to heavy-hole ground-state ($e_1hh_1$) quantum well transition energy, obtained from the modulus of the measured $PR$ spectra of Fig. 3.11. The linear fits to the data show that the two energies become equal at $1.631 \pm 0.002$ eV, when $T = 111 \pm 5$ °C.](image-url)
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Varshni [24] or Bose-Einstein [25] relationships, both of which tend to a \( \sim \) linear regime above room temperature. Linearly interpolating both the CM and QW energies in Fig. 3.14, we find that the two features cross at a temperature of \( T = 111 \pm 5^\circ C \), when \( E_{QW} = E_{CM} = 1.631 \pm 0.002 \) eV. The interpolation also shows that the \( e_1 hh_1 \) QW feature moves nearly five times faster than the CM, with \( \Delta E_{CM}/\Delta T = -0.11 \pm 0.01 \) meV °C\(^{-1} \) and \( \Delta E_{QW}/\Delta T = -0.50 \pm 0.01 \) meV °C\(^{-1} \). A calculation of the expected value for \( (\Delta E_{QW}/\Delta T) \) using the Varshni coefficients for \( \text{Al}_{0.386}\text{Ga}_{0.614}\text{As} \) [15] gives the range \(-0.46 \) meV °C\(^{-1} \) to \(-0.52 \) meV °C\(^{-1} \) for the temperature region studied here. The average of this value, \(-0.49 \) meV °C\(^{-1} \), is equal to (within error) the above measured value of \(-0.50 \) meV °C\(^{-1} \). We find a similar close agreement for our measured value of \( \Delta E_{CM}/\Delta T = -0.11 \pm 0.01 \) meV °C\(^{-1} \): the earlier estimate of \( \Delta \lambda_{CM}/\Delta T = 0.6 \) nm °C\(^{-1} \) using Eq. 3.3 is equivalent to \(-0.13 \) meV °C\(^{-1} \).

Returning to Fig. 3.11 we can see the effect on the measured PR lineshape as the QW red-shifts at the faster rate than that of the CM. At low temperatures (\( T < 70 \) °C) the \( e_1 hh_1 \) transition is de-tuned enough from the CM feature that the CM PR feature appears as a simple, symmetric peak at \( E_{CM} \). However, the spectrum at 70 °C shows the beginning of some interaction between the two features, even though they are still separated by \(~15 \) meV. The next spectrum shown in Fig. 3.11 at 85 °C shows a completely different lineshape, indicating that an extensive interaction between the two features occurs between 70 and 85 °C. Figure 3.15 shows the PR spectra for all the temperatures measured in the range 70 – 90 °C. The CM energy is marked by the dashed line, but the QW energy ranges from 1.651 – 1.641 eV in this temperature region (Fig. 3.14), outside the energy scale of the figure. The figure shows how the lineshape evolves smoothly, completely changing form over this relatively small temperature range. Such a rapid change in lineshape is believed to be due to the sharpness of the CM feature in this VCSEL.

As the temperature is increased beyond 90 °C and the QW is tuned closer towards \( E_{CM} \) the lineshape continues to evolve and from Fig. 3.11 it can be seen to become \(~\) anti-symmetric when \( T = 115 \) °C. This is close to the
Figure 3.15: Normal incidence PR spectra of the VCSEL wafer for the 70 – 90°C temperature range. The baselines of successive spectra are vertically offset for clarity. The dashed line indicates the position of the cavity mode (CM). The QW ground state transition lies beyond 1.64 eV in this temperature range.

temperature at which the linear interpolation shown in Fig. 3.14 indicates that $E_{CM} \approx E_{QW}$ ($111 \pm 5$ °C). This agreement again suggests that the lineshape becomes anti-symmetric when the VCSEL is tuned, as predicted by theory. [16] As $T$ increases above 115 °C the symmetry of the lineshape evolves further still as the QW is tuned to lower energies than the CM. Eventually, the QW PR feature can again be observed separately from the CM feature and this is shown, magnified in the 160 °C spectrum of Fig. 3.11.
In order to determine the precise temperature at which the \( PR \) becomes perfectly anti-symmetric it is necessary to quantify the symmetry as was done for the \( \theta \) dependent measurements (Fig. 3.10). For these more precise, well-resolved measurements, we study the symmetry by fitting the spectra with a suitable empirical function containing a phase parameter. The existing VCSEL \( PR \) lineshape model (Eq. 2.18, p. 37) would be ideal since this also yields values for \( E_{CM} \) and \( E_{QW} \) as well as the widths \( \Gamma_{CM} \) and \( \Gamma_{QW} \). Although we were unable to fit this model to the low resolution, \( \theta \) dependent \( PR \) of this sample we attempted to fit the high resolution spectra in Fig. 3.11 in the hope that the reason for the model's failure was solely the convolution of the \( PR \) caused by the low resolution (see for example the convoluted lineshape in Fig. 3.12). Unfortunately, however, this was not the case and we were again unable to achieve satisfactory fits to our high resolution, temperature dependent \( PR \). This again suggests that the model requires some alteration as it is unable to reproduce the intricate lineshapes seen for this VCSEL. We return to this problem in chapter 5.

Fortunately, the \( PR \) lineshape simplifies greatly near 115 \( ^\circ \)C allowing us to fit the spectra over a small range of temperatures (110 - 120 \( ^\circ \)C) with a simple, single fitting function in order to parameterise the symmetry. We use a TDFF lineshape (Eq. 2.14, p. 30) here since it contains a suitable phase parameter. [26] Figure 3.16 shows the fitted \( PR \) spectra for this small range of temperatures. The fits obtained are of a reasonably good quality, considering that we are empirically describing each lineshape with a single TDFF. Figure 3.17 shows the resulting temperature variation of the phase parameter from the fits shown in Fig. 3.16. For this particular TDFF model a phase value of 270\(^\circ\) represents a perfectly anti-symmetric lineshape. A linear fit of the temperature variation of the phase parameter reveals that the phase value becomes 270\(^\circ\) at a temperature of 113.5 \( \pm \) 0.5 \( ^\circ \)C, indicating that this is the precise condition for which the VCSEL is tuned with \( E_{CM} = E_{QW} \). The energy parameter of the closest fit to this temperature (at 114 \( ^\circ \)C) is 1.6298 \( \pm \) 0.0002 eV (760.7 \( \pm \) 0.1 nm). Due to the effects of current heating and band filling within the active region, a VCSEL processed from the wafer studied here would be tuned at a lower ambient temperature, depending
on the level of current applied and the mode of operation (ie continuous or pulsed wave operation). For example, the active region of a VCSEL studied in Ref. [21] was found to heat up by 14.5 K/mA under continuous wave operation.

Finding that the VCSEL wafer is tuned at $\sim 115 \, ^\circ\text{C}$ indicates that a processed device would be suitable for operation in high temperature environments as desired. Also, the tuned wavelength value of 760.7 nm is appropriate for applications of oxygen gas sensing (Fig. 3.1).

In chapter 4 we will look at the carrier recombination mechanisms in 760 nm edge-emitting laser structures with very similar active regions to the VCSEL studied here. This will allow us to assess the suitability of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ material system for operation in elevated temperatures of $T \sim$
3. Photomodulated reflectance of a 760 nm vertical-cavity surface-emitting laser

Figure 3.17: Temperature variation of the phase parameter of the fits shown in Fig. 3.16. For the model used here, a phase of 270° corresponds to a perfectly anti-symmetric lineshape and the linear fit (solid line) indicates that this occurs at 113.5 °C.

As a final finding from these $T$ dependent $PR$ studies we highlight an effect observed in the magnitudes of the signals recorded. In previous VCSEL samples that have displayed the anti-symmetry behaviour when tuned, the PR spectra have not tended to exhibit any noticeable associated resonance in the amplitude of the $PR$. [16] Amplitude resonance provides an alternative way of determining when $E_{CM} = E_{QW}$ for VCSELs in which $\Gamma_{CM} \geq \Gamma_{QW}$. [20] Although the present VCSEL does not satisfy this particular condition, we do see a strong amplitude resonance of the $PR$ near the CM feature in Fig. 3.11. Figure 3.18 shows the variation of this amplitude with temperature, clearly displaying a resonance at $T = 95$ °C. The amplitudes were calculated by subtracting the maximum negative $PR$ signal from the maximum positive signal. This 'resonance', occurring at a different temper-
Figure 3.18: Temperature dependence of the amplitude (Magnitude of maximum positive peak minus magnitude of maximum negative peak) of the photomodulated reflectance spectra for the VCSEL wafer indicating a strong resonance at 95 °C.

ature to which we find $E_{CM} = E_{QW}$, is therefore misleading and should be ignored in terms of deciphering the level of gain-cavity de-tuning. It occurs as a result of the multiplicative effect between the Seraphin coefficients and the modulated dielectric terms, which is more significant as the CM and QW features come closer together. However, when the features are in very close proximity the forms of the lineshapes can cause a reduction in $PR$ signal strength, especially if the width of the CM feature is less than that of the QW. This highlights the need to exercise caution when analysing VCSEL $PR$ results, especially when the VCSEL $PR$ model is unable to fit the measured spectra.
3.6 High resolution angle and temperature dependent reflectance measurements (*The cavity mode broadening effect*)

3.6.1 Introduction

Figure 3.13 in the previous section shows how the $R$ spectrum for the current VCSEL wafer evolves with temperature. This figure was used to demonstrate how the CM energies were obtained at the various temperatures: we did not refer in detail to the shape of the CM features in the $R$ spectra. However, we noticed that the $R$ spectrum changes as the QW feature is tuned through the CM. In this section we pay particular attention to this interesting aspect of the $R$ spectrum. In order to also study the shape of the $R$ spectrum as a function of $\theta$ we undertook specific room temperature $\theta$ dependent $R$ measurements at a much higher instrumental resolution than the initial low-resolution $PR$ measurements of section 3.4 and we study these initially.

3.6.2 High resolution, angle dependent reflectance measurements

Our initial room temperature $\theta$ dependent $PR$ study of section 3.4 was conducted using a low instrumental resolution in order to discern the very weak $e_1h_1$ QW transition $PR$ feature. Consequently the corresponding $R$ measurements (Fig. 3.8) are also of a low resolution and the sharp CM feature of this VCSEL ($\Gamma_{CM} = 0.19$ nm) is barely resolved. Therefore, in order to accurately study the angle dependence of the CM feature we have also conducted much higher resolution $R$ measurements. Spectra for a selection of the measured angles are shown in figure 3.19(a). It is clear from these $R$ spectra that the increased instrumental resolution has resulted in much clearer CM features being observable than in the low resolution spectra of Fig. 3.8. From these sharp CM features it is simple to obtain accurate values for $E_{CM}$ at energies where $R$ is minimum. Using equation 3.2 we can fit the resulting $\theta$ dependence of $E_{CM}$ as shown in figure 3.19(b). From the linear fit to $1/E_{CM}^2$ we extract an effective refractive index for the VCSEL cavity of 3.50±0.02. We can compare this to the refractive index of the cavity material.
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Figure 3.19: (a) High resolution, room temperature reflectance spectra of the VCSEL wafer for a selection of angles of incidence. (b) Variation of the (cavity mode energy)$^2$ with $\sin^2(\theta)$. The fitted straight line yields an effective refractive index of 3.50±0.2 as per Eq. 3.2.

(Al$_{0.386}$Ga$_{0.614}$As), obtained from ellipsometry measurements. [8] Figure 3.20 shows the associated refractive indices in the energy range through which the CM is tuned with $\theta$. It is clear that the literature data for the Al$_{0.386}$Ga$_{0.614}$As refractive index is somewhat lower than our value of 3.50, with the average value being $\sim$3.41. We find that an aluminium concentration of 28% would be required for a value for $n$ of $\sim$ 3.5 from the ellipsometry data [8], and such a difference in composition is too great to be due to uncertainties in the growth parameters of the sample. Such an overestimation of the cavity refractive index could be due to the fact that we are neglecting the presence of the QWs within the cavity when using the model of Eq. 3.2 which yields only an effective refractive index of the whole cavity. However, in order to examine whether the cause is more fundamental, we have conducted angle dependent reflectance simulations using the transfer matrix technique described in section 2.3 for a simple Fabry-Pérot structure in air, such as the one shown in Fig. 3.6. Initially we set the refractive index of the cavity material to an energy-independent value of 3.40 and calculated $R$ between normal incidence to $\theta = 60^\circ$. A fit such as the one shown in Fig. 3.19(b) to the resulting $1/E_{CM}^2$ values gave a fitted value of $n = 3.40 \pm 0.01$, as
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![Refractive Index Data](image)

**Figure 3.20**: Refractive index data for two AlGaAs concentrations taken from Ref. [8] for the energy range in which the cavity mode of the VCSEL is tuned with angle of incidence. The dashed line indicates a refractive index of 3.5, determined to be the effective index of the VCSEL cavity from the fit in Fig. 3.19(b).

expected. We then included some dispersion into the refractive index of the cavity material, so that \( dn/dE = 0.5 \text{ eV}^{-1} \), similar to that shown in Fig. 3.20 (the average value of \( n \) was still \( \sim 3.4 \)). On analysing the \( \theta \) dependence of the CM in this more realistic situation we found a surprising result: the fitted effective refractive index was found to be \( n = 3.56 \pm 0.01 \), nearly 5% higher than the actual average value. These simple simulations show that using the model for the \( \theta \) dependence of the CM energy (Eq. 3.2) for a cavity containing a dispersive refractive index does not yield a refractive index close to the average value of the cavity. Therefore, we expect that Eq. 3.2, when applied to the \( \theta \) dependent \( R \) spectra of VCSEL structures, will yield misleadingly high values for the effective refractive index of the cavity due to the dispersion of the cavity medium. It is possible to explicitly include the dispersion of the refractive index (e.g. using the Cauchy relationship: \( n(E) = A + BE^2 + CE^4 \) [27]) in Eq. 3.2. However, with this inclusion the simple model becomes rather complex and its application becomes more trou-
blesome. Therefore, we recommend that when using Eq. 3.2 to describe the angle dependence of a VCSEL CM, it be realised that the resulting value of $n_{\text{eff}}$ is likely to be an overestimation of the 'true' value by $\sim 5\%$.

### 3.6.3 The cavity mode broadening effect

Looking closely at the high resolution reflectance spectra of the current VCSEL as a function of both angle of incidence (Fig. 3.19(a)) and temperature (Fig. 3.13) it is clear that the CM feature does not just shift with the variable parameter, it also changes in shape somewhat. Here we examine this effect to see if there is any link with the extent of gain-cavity de-tuning in the VCSEL. Figure 3.21 shows a typical CM reflectance feature, highlighting the parameters that can be used to describe the shape. The depth of the CM feature is determined as being $R_{\text{max}} - R_{\text{min}}$. The numerically integrated area can also be determined from the shape as can the FWHM, $\Gamma_{\text{CM}}$.

![Figure 3.21: Representation of the shape in the reflectance spectrum caused by a VCSEL cavity mode. Three measurable quantities related to the shape are shown: the full width at half maximum, $\Gamma_{\text{CM}}$; the integrated area; and the depth of the CM dip.](image)

Figure 3.22 shows the values of the three obtainable CM parameters, taken from the high resolution, $\theta$ dependent $R$ measurements (Fig. 3.19(a)).
The depth parameter shows a slight maximum when $\theta = 32.5^\circ$. It then reduces in magnitude with increasing angle, with a slight plateau around $45^\circ$. The integrated area shows a similar behaviour, however, the maximum here appears at a slightly different angle; $\theta = 35.0^\circ$. Neither of these angles correspond to the conditions for which the VCSEL CM was tuned to QW transitions, as seen in the low resolution $\theta$ dependent $PR$ measurements of section 3.4 (i.e., at $\sim 45^\circ$ and $\sim 60^\circ$). The FWHM of the CM feature $(\Gamma_{CM})$ shows a different behaviour. It increases steadily with increasing angle until $\sim 37.5^\circ$ where it sharply increases to a maximum at $\theta = 45^\circ$. It then decreases rapidly, until a second, less pronounced maximum is seen at around $55^\circ$. What is most interesting about this result is that these two angles at which $\Gamma_{CM}$ shows peaks correspond to the angles at which the low resolution $PR$ investigations of section 3.4 indicate the CM is tuned to QW transitions. A similar behaviour was previously observed in the angle dependent reflectance spectra of an 850 nm VCSEL. [28] In those results...
however, the integrated area, not the FWHM of the CM feature showed peaks as the CM was tuned to three separate QW transitions. It was suggested that the integrated area of the CM could be directly related to the absorption of the QWs ($\alpha_{QW}$) present in the 850 nm VCSEL cavity. However, we believe that it is actually the CM broadening parameter, $\Gamma_{CM}$ that is more closely related to the absorption within the cavity (which is entirely due to the QWs since the cavity material is non-absorbing in this energy region [8]). We believe this because the Q-factor of a cavity is related to the CM broadening by the relationship $Q = E_{CM}/\Gamma_{CM}$, and the Q-factor is also proportional to the average lifetime of resonant cavity photons. [29] If a cavity contains a material with an energy dependent absorption profile (such as the QWs in the present VCSEL) then the lifetime of resonant photons within the cavity would also be a function of their energy. This is because a more strongly absorbing medium would 'capture' more of the resonant photons, reducing the average photon lifetime. Such an effect would lead to a reduced cavity Q-factor, resulting in an increased CM broadening, $\Gamma_{CM}$. So long as the FWHM of the CM in a VCSEL was not too spoilt by other effects, such as low-$R$ DBRs or sample inhomogeneity, such an increased broadening could be discernible in the $R$ measurements. We believe that we are observing this effect here. From Fig. 3.22 it can be seen that $\Gamma_{CM}$ approximately doubles in width in the range $\theta = 22.5° - 45°$. This change is even visible simply by looking at the CM features in Fig. 3.19(a).

Figure 3.23(a) shows the cavity mode broadening of Fig. 3.22 plotted again, but now as a function of $E_{CM}(\theta)$ (with the corresponding $\theta$ values shown on the top scale). If our belief that $\Gamma_{CM} \propto \alpha_{QW}$ is true then this behaviour is representative of the absorption spectrum of the QWs within the cavity of this sample. The two peaks are consistent with excitonic QW absorption features expected at the energies of QW transitions. Figure 3.23(b) shows the modulus spectrum of a normal incidence, room temperature $PR$ measurement, where the energies of the two QW transitions are shown by dashed lines. It can be seen from this that the CM broadening goes through its maximum as the CM is scanned through the energy of the main peak in the modulus spectrum—corresponding to the energy of the $e_{1}hh_{1}$ QW tran-
Figure 3.23: (a) Angle dependence of the cavity mode broadening (full width at half maximum) seen in the reflectance of the VCSEL wafer plotted as a function of the cavity mode energy. The top scale shows the angle of incidence for each $R$ measurement. (b) Modulus spectrum of a PR measurement at normal incidence and room temperature. The energies of two QW transitions are indicated by dashed lines.

sition. The second, less pronounced maximum in $\Gamma_{CM}$ also corresponds with the energy of the $e_1lh_1$ QW transition. It is no surprise that the light-hole feature has a less pronounced effect on $\Gamma_{CM}$ since the oscillator strength of this transition is considerably lower than that of the heavy-hole transition. Also, since the light-hole state is predominantly $z$-like, [23] the interaction
between it and a wave travelling in the $z$-direction (i.e. the CM) will be weak compared to the interaction between the CM and a heavy-hole state.

Figure 3.24 shows a plot equivalent to Fig. 3.23(a) for the CM $R$ feature, but this time for the temperature dependent $R$ measurements (Fig. 3.13). Here $\Gamma_{CM}$ is plotted as a function of $E_{CM}(T)$. A distinct maximum is observed here, as in the $\theta$ dependent data, at a temperature of $T = 115$ °C, when $E_{CM}(T) = 1.631$ eV. Just as in the angle dependence measurements, this also corresponds to the condition at which the VCSEL was determined to have $E_{CM} = E_{QW}$ from $PR$ measurements (section 3.5). This further sug-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.24.png}
\caption{Temperature dependence of the cavity mode broadening (full width at half maximum) of the reflectance cavity mode feature of the VCSEL wafer, plotted as a function of the cavity mode energy. The dashed line shows the position of the maximum at $E_{CM} = 1.631$ eV, when $T = 115$ °C.}
\end{figure}

gests that our belief that $\Gamma_{CM} \propto \alpha_{QW}$ is true. Note, however, that there is a subtle, but important, difference between the data plotted in Fig. 3.23(a) and Fig. 3.24 that should be highlighted: in the $\theta$ dependent $R$ measurements of Fig. 3.23 the QW transition energies are static and thus the measured CM broadening can be compared to the room temperature absorption spectrum of the QWs. However, in the temperature dependent study (Fig. 3.24),
the QW transition energies, oscillator strengths and broadenings are all functions of \( T \) and thus the QW absorption spectrum will be changing. Therefore Fig. 3.24 is not a representation of the QW absorption at a given temperature. However, the maximum in \( \Gamma_{CM} \) will still occur when \( \alpha_{QW}(T) \) is a maximum (i.e. at the transition energy).

It appears from our studies of the high resolution reflectance measurements as a function of both \( \theta \) and \( T \) that we can infer when \( E_{CM} = E_{QW} \) simply by searching for maxima in \( \Gamma_{CM} \) in the \( R \) spectra. A similar method has been used previously in mid-infrared, high-finesse microcavities containing PbSe quantum dot superlattices. [30] There, the broadening of various high-order cavity modes (separated in energy by the free-spectral range of the microcavity) was examined as a function of each of the various cavity mode energies and interpreted as being a sampling of the superlattice absorption. This technique is simple, since their sample had several multiple-order cavity mode dips within a single \( R \) spectra. However, the energy resolution of the absorption sampling was limited by the free spectral range of their cavity and thus the technique is suitable only for samples with long cavity lengths, such as those of mid-infrared microcavity structures. The advantage of our technique of varying the angle of incidence and measuring the broadening of a single CM feature, is that the energy resolution is dependent only upon the experimental setup. This allows detailed absorption profiles (such as Fig. 3.23(a)) to be measured in conventional short-cavity VCSELs exhibiting high-finesse cavities. We return to discuss this topic in further detail in chapter 5.

### 3.7 Conclusions

The low resolution, angle variation \( PR \) study of the 760 nm VCSEL wafer enabled us to observe features from both \( e_1 hh_1 \) and \( e_1 l h_1 \) QW transitions at room temperature. That study also confirmed that the \( PR \) lineshape becomes anti-symmetric when the CM is tuned to the \( e_1 hh_1 \) transition at an angle of \( 45^\circ \), with \( \lambda_{CM} = \lambda_{QW} = 739.8 \pm 0.4 \) nm (1.676 eV). The high-resolution, temperature dependent \( PR \) study (at normal incidence) has
shown that the VCSEL is tuned at a temperature of $113.5 \pm 0.5 \, ^\circ\text{C}$, when $E_{CM} = E_{QW} = 1.6298 \pm 0.0002 \, \text{eV} \,(760.7\pm0.1 \, \text{nm})$. This indicates that an operational VCSEL processed from the wafer tested here would be tuned at a high device temperature as desired. Also, the lasing wavelength, determined by $\lambda_{CM}$, would also be at the desired 760.7 nm for oxygen sensing applications.

Simulations of the angle dependent reflectance of a Fabry-Pérot cavity have shown that the simple model used (Eq. 3.2) to obtain the effective refractive index ($n$) from plots of $E_{CM}^2 \sin^2(\theta)$ in VCSEL samples does not yield correct values for $n$ when the cavity material is dispersive. We comment that users of this equation should be aware that it is likely to overestimate $n$ in a typical VCSEL cavity.

The high resolution reflectance spectra of the VCSEL wafer reveal a very high-finesse CM. Detailed reflectance measurements of the broadening of the CM feature as a function of both angle of incidence and temperature have shown that the broadening becomes enhanced whenever $E_{CM} = E_{QW}$. Monitoring the CM broadening in conventional reflectance measurements could, therefore, provide an additional, non-destructive method for determining when VCSELs are tuned. The CM width enhancement effect is likely to be particularly prominent in devices with cavities of high finesse, such as the one studied here.

Attempts to fit the established VCSEL PR lineshape model to the measured spectra of the current sample have proved unsuccessful. In chapter 5 we return to this problem in an attempt to find a cause for this and ultimately improve upon the understanding of the PR of VCSEL structures.

3.8 References


3. Photomodulated reflectance of a 760 nm vertical-cavity surface-emitting laser

3. Photomodulated reflectance of a 760 nm vertical-cavity surface-emitting laser


4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers

4.1 Introduction

In chapter 3 we conducted PR studies on a 760 nm Al$_2$Ga$_{1-x}$As VCSEL wafer in order to investigate the gain-cavity de-tuning in the sample. From our temperature dependent studies we were able to establish that the cavity mode (CM) energy ($E_{CM}$) of the VCSEL became tuned to the ground state quantum well (QW) transition at a temperature of ~ 115 °C (388 K). At this temperature we found that $E_{CM}$, which defines the lasing energy in a VCSEL, was ~ 1.630 eV (760.6 nm). These conditions were desired for the 760 nm VCSEL since it was designed for oxygen gas sensing applications in high-temperature environments.

In order to gain more insight into how efficiently a processed VCSEL would operate at such a high temperature it is necessary to undertake device studies so that the effect of the elevated temperature on the carrier recombination mechanisms within the device can be investigated.

In a VCSEL, the temperature sensitivity of the threshold current ($I_{th}$) is dependent on both the carrier recombination mechanisms within the active region, and the gain-cavity de-tuning. [1, 2, 3] Figure 4.1 shows an example of the temperature-dependent behaviour of $I_{th}$, for a 665 nm VCSEL. [3] It can be seen that initially, as the temperature increases from 50 K, the threshold current of the VCSEL decreases. This is the opposing trend to that seen in conventional edge-emitting lasers (EELs) [4] and is a result of the increasing CM-QW tuning with increasing temperature, which dominates over the effect of the temperature dependence of the carrier recombination. At approximately 200 K the current reaches a minimum before it eventually begins to increase with temperature due to thermal effects on the carrier recombination.

While analysing such a measurement is possible, a simpler approach would be to somehow remove the effects of the CM-QW tuning so that the
carrier recombination within the active region can be studied independently. We do this here for the 760 nm VCSEL by actually studying the temperature dependence in an edge-emitting laser (EEL) containing an essentially identical active region to the VCSEL. Therefore, by studying the carrier recombination independently we can look at the suitability of the Al$_x$Ga$_{1-x}$As material system for use in high temperature, ~760 nm laser applications.

As well as studying the Al$_x$Ga$_{1-x}$As EEL here, we shall also look at the behaviour of the carrier recombination in an EEL containing compressively strained In$_y$Al$_x$Ga$_{1-x-y}$As ($y = 13.5\%$, $x = 23.1\%$) QWs with relaxed Al$_{0.33}$Ga$_{0.67}$As barriers. This will enable us to quantify any improvements gained by introducing compressive strain into lasers operating near 760 nm.

We begin here by first discussing the structural details of the EELs studied. Then, we look at the temperature dependence of the carrier recombination within the lasers, before finally looking at how the carrier recombination mechanisms change under the application of hydrostatic pressure. By measuring the devices under hydrostatic pressure it may be possible to gain further insight into the key factors affecting the carrier recombination mechanisms, and thus, the suitability of the material system.
4.2 Sample details and calculated band structures

The EELs studied were supplied, along with the 760 nm VCSEL wafer, by the Optoelectronics Research Centre in Tampere, Finland. The 6 nm barriers and 92 nm waveguide layers within the all–Al$_x$Ga$_{1-x}$As EEL are made from Al$_{0.386}$Ga$_{0.614}$As – nominally identical to the barriers and cavity material within the VCSEL sample (see section 3.2, starting on page 50 for details of the VCSEL structure). The cladding layers are made from Al$_{0.636}$Ga$_{0.364}$As, an indirect semiconductor, with both the X and L points at lower energies than the Γ point. While the EEL, like the VCSEL, contains three 8 nm QWs, their aluminium concentrations are slightly different: 15.4% within the VCSEL QWs, and 13.5% within the EEL QWs. This represents the only notable difference between the two active regions and such a small difference means that any findings in this chapter will be reasonably applicable to the VCSEL wafer studied in chapter 3.

Figure 4.2 shows our calculated band lineups at 300 K for the Al$_x$Ga$_{1-x}$As EEL. The procedure we used for the calculations is described below and for simplicity we have ignored the effects of doping and electric fields, showing the bands as flat here. The band gap energies ($E_g$) and bowing parameters used are based on the recommendations given in the review of Vurgaftman et al. [5] and in Refs. [6, 7] In order to determine the valence band offsets (VBOs) between the different materials in the structure the values of the average valence band energies, $E_{v,\text{av}} = (E_{v,\text{hh}} + E_{v,\text{lh}} + E_{v,\text{so}})/3$ are required for each layer, where the subscripts $hh$, $lh$ and $so$ represent the heavy, light and spin split-off valence band edges respectively. $E_{v,\text{av}}$ values for binary semiconductors can be obtained from the model solid theory of Van de Walle [8] and a linear interpolation between the values for GaAs (-6.92 eV) and AlAs (-7.49 eV) leads to a value for the Al$_x$Ga$_{1-x}$As ternary alloy. Using this method we find that the VBO or, valence band discontinuity, between the well and barrier is 143 meV. However, it is known that such a crude linear interpolation of $E_{v,\text{av}}$ values does not yield accurate values for the VBO. For example, measurements of the VBO in Al$_{0.5}$Ga$_{0.5}$As$_{0.04}$Sb$_{0.96}$ / In$_{0.85}$Ga$_{0.15}$As$_{0.94}$Sb$_{0.06}$ heterojunctions, using the capacitance-voltage tech-
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Figure 4.2: Room temperature band lineups for the Al$_x$Ga$_{1-x}$As edge-emitting laser structure. The solid lines show the valence band (VB) and Γ point conduction band energies and the X point conduction band energy is shown by the dashed line. A second solid line in the conduction band shows the L point energies (almost equal to Γ in the barrier). The zero energy has been taken as the lowest energy point – the valence band energy of the cladding layer. Within the wells the calculated confinement energies of the ground state electron ($e_1 = 38.3$ meV), heavy-hole ($hh_1 = 10.1$ meV) and light hole ($lh_1 = 24.6$ meV) are shown. The conduction band offset ratio $Q_c$ is taken to be 68% as explained in the text.

nite, gives a value of 150 meV, [9] while a crude linear interpolation of the binary $E_{v,av}$ values [8] gives a somewhat different value of 174 meV. Unfortunately there is not much literature on the VBOs in Al$_x$Ga$_{1-x}$As / Al$_{x'}$Ga$_{1-x'}$As heterostructures. However, this property has been studied in great detail for Al$_x$Ga$_{1-x}$As / GaAs heterostructures and it has been shown that the conduction band offset ratio ($Q_c$) has a constant value of 68% for $x \leq 45\%$, [10] where $Q_c$ is defined by the equation

$$\Delta E_c = Q_c \Delta E_g$$

(4.1)

Here $\Delta E_c$ is the conduction band discontinuity between the barrier and well and $\Delta E_g = E_{g,\text{barrier}} - E_{g,\text{well}}$ is the difference between the band gaps of the
4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers

We shall assume $Q_c = 68\%$ in the $\text{Al}_{0.135}\text{Ga}_{0.865}\text{As} / \text{Al}_{0.386}\text{Ga}_{0.614}\text{As}$ QWs of the unstrained EEL.

Using the methods described in section 2.1.3 and appendix A, with effective mass and Luttinger parameters obtained from Ref. [5] we calculate the ground state confinement energy of an electron ($e_1$) in the wells of the unstrained device to be 38 meV, a result which we shall call upon later. The heavy-hole ground state energy ($hh_1$) is found to be 10 meV and the light-hole ground state energy $lh_1 = 25$ meV. Accounting for the exciton binding energy (see section 2.1.3) we find that the resulting $e_1 hh_1$ transition energy is 1.668 eV.

The other EEL studied here contains three, 8 nm tri-metal quaternary; compressively strained $\text{In}_y\text{Al}_x\text{Ga}_{1-x-y}\text{As}$ ($y = 13.5\%, x = 23.1\%$) QWs and relaxed $\text{Al}_{0.33}\text{Ga}_{0.67}\text{As}$ barriers of thickness 6 nm. We study this sample here to investigate what advantage is gained by adding strain into the active region of a 760 nm EEL. Although this active region is dissimilar to that of the 760 nm VCSEL studied in chapter 3 it is interesting to study the effects of strain in these EELs here as a separate study.

Adding aluminium to strained InGaAs QWs is a known method for increasing the band gap so that the lasing wavelength can be reduced for a given well width. [11] Therefore, it is possible to fabricate compressively strained devices which emit light near 760 nm. Although this device is not directly related to the VCSEL wafer studied in chapter 3, studying it will allow us to guage the potential benefits of developing an InGaAlAs based VCSEL for oxygen gas sensing. Figure 4.3 shows the band lineups for this EEL. Again we have used band gap parameters taken from ref. [5]. Another group has previously used a value of $Q_c = 67\%$ for the $\text{In}_y\text{Al}_x\text{Ga}_{1-x-y}\text{As} / \text{Al}_x\text{Ga}_{1-x}\text{As}$ material system, [12] and we adopt this value here for this strained EEL. This gives a value of $\Delta E_c = 0.185$ eV since we have here $E_g^{\text{barrier}} = 1.877$ eV and $E_g^{\text{well}} = 1.601$ eV (including the effects of strain).

The strain in the quantum wells arises from the lattice mismatch between the $\text{In}_y\text{Al}_x\text{Ga}_{1-x-y}\text{As}$ wells and GaAs substrate / AlGaAs layers. GaAs has a lattice constant $a_0 = 5.6533$ Å, whereas in the wells the value is larger at $a_0 = 5.7100$ Å. [5] The induced strain in the QWs has a notable effect on
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Figure 4.3: Room temperature band lineups for the edge-emitting laser containing strained In$_x$Al$_{1-x}$Ga$_{1-y}$As quantum wells. The solid lines show the valence band (VB) and Γ point conduction band energies and the X point conduction band energy is shown by the dashed line. The second solid line in the conduction band shows the L point energies. The zero energy has been taken as the lowest energy point – the valence band energy of the cladding layer. Within the compressively strained wells, two energy levels are marked corresponding to the heavy-hole (HH) and light-hole (LH) band edges, which are split by 64 meV due to the strain. The calculated confinement energies of the ground state electron ($e_1 = 39$ meV), heavy-hole ($hh_1 = 12$ meV) and light hole ($lh_1 = 25$ meV) are shown. The conduction band offset ratio $Q_e$ is taken to be 67%. [12]

the conduction and valence bands of the semiconductor and following the methods of Van de Walle [8] and Krijn, [13] we can calculate these effects at the Γ-point. We find that, as a result of compressive hydrostatic strain, the band gap increases, with $E_{v,av}$ decreasing by 15 meV and $E_c$, the conduction band edge, increasing by 68 meV. The shear strain, which breaks the crystal symmetry, splits the heavy and light-hole bands so that they are no longer degenerate at the Γ point. We find that the heavy-hole band edge increases in energy by 142 meV (with respect to $E_{v,av}$) and the light-hole band increase in energy by just 78 meV. This gives a splitting between the two bands of
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64 meV at the $\Gamma$ point in the wells. These effects of strain are included in Fig. 4.3, where the two valence band edges within the well are shown. The 300 K band gap of the well (measured from the conduction band edge to the uppermost valence band edge, the heavy-hole band) is 1.601 meV, compared to the unstrained value of 1.555 meV.

Using the same approach as for the unstrained device we can calculate the electron and hole confinement energies (including the effects of strain). From this we find the ground state confinement energy of an electron in the well to be 39 meV ($e_i$). The heavy-hole (HHI) ground state is found to be 12 meV ($hh_i$) below the HHI valence band edge in the well and the light-hole (LII) ground state is only just confined, lying 89 meV below the HHI valence band edge with $lh_i = 25$ meV. Including exciton binding energy gives a resulting $e_1hh_1$ transition energy of 1.645 eV (753.7 nm).

Both EELs studied here were processed as broad area devices with contact stripe lengths of 1000 $\mu$m and widths of 40 $\mu$m so that current spreading effects can be ignored. [14]

4.3 Temperature dependent studies

4.3.1 Theoretical background

In this section we shall be investigating the temperature ($T$) dependence of the threshold current ($I_{th}$) within the EELs and interpreting the results in terms of the variation of the different carrier recombination processes which may be occurring in the devices. The threshold current can be written as the sum of the different current paths within a device:

$$I_{th} = eV (An_{th} + Bn_{th}^2 + Cn_{th}^3) + I_{leak} \quad (4.2)$$

Here $e$ is the electronic charge and $n_{th}$ the threshold carrier density which we assume to be equal in the conduction and valence bands. For an ideal quantum well, using Boltzmann statistics, it can be shown that $n_{th} \propto T$. [15] $V$ represents the pumped active region volume so that $V \times n_{th}$ represents the number of carriers. We assume here that $V$ is independent of both
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temperature and applied current. This is reasonable since the EELs are broad area devices. The $A_n$ term represents the current due to recombination paths involving one carrier (electron or hole) and defect states, where $A$ is the recombination coefficient for this process and is typically dependent on the density of defects.

The two-carrier, radiative recombination process, described by the term $I_{rad} = eVBn^2_{th}$, represents the current path for carrier recombination resulting in the emission of photons, where $B$ is the recombination coefficient for the process. For ideal quantum wells the relationship $B \propto T^{-1}$ [16] can be used so that we obtain $I_{rad} \propto T$. Therefore, in an EEL containing ideal quantum wells, we expect that $I_{th}$ should increase linearly with temperature when radiative recombination processes dominate over all others.

The three-carrier term, $Cn^3_{th}$, represents carrier recombination through Auger processes. Here, recombining carriers do not release their energy in the form of photons, but rather to other carriers, thus promoting them within the band structure. [17] Auger recombination becomes an issue in narrow gap semiconductors and as such it contributes significantly to $I_{th}$ in longer wavelength lasers. For example, in a typical 1.5 µm laser ~ 80% of the total threshold current may be due to Auger recombination at room temperature. [18] However, the importance of Auger recombination quickly reduces with decreasing wavelength; in 980 nm lasers, for example, the contribution to $I_{th}$ at room temperature has been measured as just ~ 17% [19] and in visible 670 nm lasers no indications of Auger recombination were observed. [20] Therefore, for the 760 nm devices studied here we can assume that the contribution to $I_{th}$ from Auger recombination processes is negligible.

The final term written in Eq. 4.2, $I_{leak}$, is due to the thermally activated leakage of carriers from states in which they can contribute to the lasing process to other states either in the wells, barriers or cladding. Carrier leakage is known to be a problem in visible wavelength lasers [20, 21, 22, 23] and is therefore likely to be a factor in these near-infrared 760 nm devices. Assuming Boltzmann statistics apply then the leakage current may be written
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Using an Arrhenius function:

\[ I_{\text{leak}} = I_0 \exp \left( \frac{-E_a}{k_B T} \right) \]  

(4.3)

Here \( I_0 \) is a temperature independent constant, \( k_B \) is the Boltzmann constant and \( E_a \) is the activation energy of the leakage process. [20] If, for example, a leakage process involves electrons occupying states in the L-minima of a well then \( E_a = E_{\text{well}}^L - E_{fc} \), where \( E_{fc} \) is the conduction band quasi-fermi level.

With all the assumptions made above we can expect that our measured \( I_{th} \) values will exhibit components which vary linearly with temperature due to \( I_{\text{rad}} \), and exponentially with \( T \) due to \( I_{\text{leak}} \) (in the absence of any significant current due to defect recombination). Therefore, we can restate Eq. 4.2 for the case of these 760 nm devices as:

\[ I_{th} = eVBN^2_{th} + I_{\text{leak}} \]  

(4.4)

4.3.2 Experimental technique

Figure 4.4 shows the experimental setup for measuring the light output (L) from a laser device as a function of the applied current (I). Since the laser

![Figure 4.4: Experimental setup used for measuring the L-I characteristics of the devices studied here.](image)
diode has a series resistance of $\sim 2 - 3 \, \Omega$, a $47 \, \Omega$ resistor is included in the circuit to reduce current reflections within the $50 \, \Omega$ impedance coaxial cables. The pulsed current source supplies the lock-in amplifier with a reference frequency at which it drives the laser under test. The light output can then be detected using lock-in amplification, reducing the effects of noise. The other advantage of using a pulsed current source is that the effects of Joule heating within the lasers can be reduced if a low duty cycle is used. Therefore, the ambient temperature, which we measure, and the temperature of the device's active region should be approximately equal. We used a current pulse width of 0.5 $\mu$s and a repetition rate of 10 kHz here. In order to detect the laser emission from the facet of the laser we used either a Si photodiode to measure the integrated emission, or an optical spectrum analyser (OSA) to measure the spectrum.

Figure 4.5 shows a schematic of the mount used to contact the lasers studied here. [24] The device sits on the copper block which acts as both the lower electrical contact and a heat sink. Underneath the device there

![Figure 4.5: Schematic illustration of the spring-loaded clip used to contact the lasers studied in this work. [24] The lower contact is separated from the upper contact by an insulating spacer. It also acts as a heat sink for the laser. The upper contact connects to the upper p-side of the laser chip through the mechanical force of the spring-loaded clip.](image)
is a small drilled hole in the copper so that an optical fibre can be used to measure the spontaneous emission through the substrate if desired. Such a measurement requires a small window to be created in the bottom contact of the laser and this can be achieved using an ion-beam miller. We attempted such measurements here. However, we found that much of the spontaneous emission from these devices is near 760 nm (1.631 eV) and is thus strongly absorbed by the GaAs substrate ($E_g = 1.422$ eV, 870 nm [5]). Therefore, we focus on the measurements of laser light emitted from the facet of the devices in this work.

The upper side of the laser chip is contacted through a spring loaded clip. This gives a good contact to the device, while giving a simple method for releasing the device when the measurements are completed.

To allow us to measure the threshold current of each device as a function of temperature we attached the mount shown in Fig. 4.5 to the cold finger of a liquid nitrogen cryostat. A heater coil was used, connected to a temperature controller, so that we could conduct measurements between 80 – 350 K. An optical fibre was used to couple the facet emission (not shown in Fig. 4.5) into a detector situated outside the cryostat.

In order to determine $I_{th}$ the facet emission is plottedagainst the applied current in what is known as an L-I curve. To demonstrate how we find $I_{th}$ from such a measurement a typical L-I curve is shown in Fig. 4.6. At low currents the measured light is due to spontaneous emission and increases steadily with $I$, but above $I_{th}$ the device begins to lase and the sharp increase in light intensity, due to the onset of the stimulated emission, can be seen. To ensure that we are consistent in determining $I_{th}$ from each L-I curve measured in this study we take $I_{th}$ as being at the intercept of the two linear extrapolations of the separate operating regimes.

4.3.3 Results and discussion

The solid symbols in figure 4.7 show the temperature dependence of the measured $I_{th}$ for the EEL containing the unstrained Al$_x$Ga$_{1-x}$As quantum wells. At room temperature we find that $I_{th} = 0.475$ A. If we divide this
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Figure 4.6: A typical L-I curve for a laser. The threshold current ($I_{th}$) is the current at which the device begins to lase and the light intensity increases sharply at this point. Below $I_{th}$ the measured emission is due to spontaneous emission. $I_{th}$ is determined from the intercept of two linear extrapolations as shown by the dashed lines.

Current by the area of the stripe which makes the upper contact for the laser (40 $\mu$m $\times$ 1000 $\mu$m $\equiv$ 4 $\times$ 10$^{-4}$ cm$^2$) we obtain the threshold current density, $J_{th} = 1190$ Acm$^{-2}$. This can be compared to values measured for other devices of differing dimensions. We find it to be consistent with other Al$_x$Ga$_{1-x}$As 760 nm EELs; for example, a distributed feedback device also designed for O$_2$ gas sensing has a reported value of $J_{th} = 1250$ Acm$^{-2}$ for example. [25] This suggests that our EEL device is both functioning well, and fairly typical.

At low temperatures we see from Fig. 4.7 that $I_{th}$ varies linearly with $T$, consistent with the current being dominated by radiative recombination processes. For these low temperatures ($T < 175$ K) we fit our data with a linear model shown in Fig. 4.7 by the solid line. We find that this fit goes very close to zero current when $T = 0$ K which is an indication that there is no significant contribution from defect recombination. Therefore, we can assume that after $I_{rad}$ the only other contribution to $I_{th}$ is from $I_{leak}$ – the
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Figure 4.7: The solid symbols show the measured threshold current ($I_{th}$) values of the unstrained Al$_x$Ga$_{1-x}$As quantum well edge-emitting laser as a function of temperature. The solid line is a linear fit to $I_{th}$ below 175 K, where the current is dominated by radiative recombination. The dashed curve is then the difference between the measured $I_{th}$ values and the fitted $I_{rad}$ line and represents $I_{leak}$. This is fitted with an exponential (Eq. 4.3) which is added to the fit of $I_{rad}$ to give the fitted $I_{th}$ curve (solid curve). These fits are extrapolated up to the temperature at which the PR studies of chapter 3 showed the VCSEL to be tuned ($T = 388$ K).

Above 250 K we see that $I_{th}$ begins to increase at a rapid rate and the separation between it and the linear fit to $I_{rad}$ grows as a result. The difference between $I_{th}$ and $I_{rad(fitted)}$ is shown by the dashed curve in Fig. 4.7. We find that this follows an exponential curve, as expected for a thermally activated leakage process obeying Boltzmann statistics (Eq. 4.3, p97) and we fit it with such a term. The sum of our fitted linear $I_{rad}$ term and the fitted exponential $I_{leak}$ term is shown in Fig. 4.7 as the solid curve. It is clear that there is a very good agreement between our measured data and the fitted model; evidence that our assumption that $I_{th} = I_{rad} + I_{leak}$ is appropriate for this 760 nm device.

Figure 4.8 shows the natural log of $I_{leak} = I_{th} - I_{rad(fitted)}$ against $1000/T$ (solid symbols). Eq. 4.3 shows that the gradient of a linear fit to this should
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Figure 4.8: The natural log of the leakage current (see Fig. 4.7) in the edge-emitting laser containing unstrained Al$_x$Ga$_{1-x}$As quantum wells plotted as a function of inverse temperature (solid symbols). The solid line is a linear fit to the data and yields an activation energy ($E_a$) of 255 ± 5 meV using Eq. 4.3.

equal $-E_a/k_B$. From the linear fit in Fig. 4.8 we obtain a value for the leakage process of $E_a = 255 ± 5$ meV. From our data used to generate the band lineup diagram in Fig. 4.2 (p92) for the EEL we find that the energy separation between the electron ground state in the well and the X-minima of the barrier/waveguide conduction band is 220 ± 10 meV. The reasonably close agreement between the two numbers indicates that the leakage process occurring here is likely, therefore, to involve electrons escaping into the X-minima states of the barrier and waveguide layers. Due to the high density of states at the X-minima (caused by the large effective mass and a multiplicity of six—see section 2.1) the number of available states is significant even with an activation energy ~10 times larger than $k_BT$. Hence such a leakage process has a large impact on the thermal dependence of $I_{th}$.

Since lasing actually occurs from the quasi-Fermi level within the conduction band of the well, which will be slightly above the electron ground state, the expected leakage activation energy will be slightly lower than the 220 meV noted above. However, since the splitting between the confined electron state and the quasi-Fermi level would be relatively small, this would not greatly affect things here.
Although we have suggested that the leakage may involve electrons undergoing thermal diffusion from the wells into the X-minima of the barrier and waveguide layers, it is possible that the leakage could also occur between other states. Looking again at Fig. 4.2 on page 92 we see that the L-minima in the barriers/waveguide occur at an energy slightly lower than the X-minima (by \(\sim 30\) meV). Therefore, we would expect some leakage into these states too. It is not possible to tell which state the carriers are leaking into from our temperature dependent measurements alone. We may study the pressure dependence of \(I_{th}\) in order to ascertain which states are most significant in the leakage process and we do this in the next section.

From Fig. 4.2 on page 92 it can also be seen that the X-minima of the cladding layers are below those of the barrier/waveguide layers. Therefore, it is possible that carriers may be leaking into these states since, in terms of energy, they are closer to the quasi Fermi level in the conduction band. However, the cladding layers are separated from the QWs by the waveguide layers, which have a thickness of 92 nm, and so carriers must traverse this distance via drift processes. In order to calculate the extent of this leakage process a full drift-diffusion model [26] would need to be used here. However, this is beyond the scope of the present work.

Looking again at Fig. 4.7 we return to the point that the leakage causes a super-linear increase in \(I_{th}\) above \(T \sim 250\) K. From our fit to the data we find that at room temperature 25% of \(I_{th}\) is due to this heterobarrier leakage process. In our PR studies of chapter 3 on the 760 nm VCSEL wafer containing an almost identical active region to this EEL we determined that the cavity mode and QW ground state transition were tuned when \(T \approx 115\) °C (388 K). Therefore, we are particularly interested in the threshold current of the EEL at this temperature. By extrapolating our fit to \(I_{th}\) beyond our highest measured temperature (350 K) we find that when \(T = 388\) K, \(I_{th} \approx 1.7\) A, with \(\sim 85\%\) of this due to \(I_{leak}\). Therefore, we can say that a device processed from the VCSEL wafer studied in chapter 3 would also suffer significantly from carrier leakage at the desired temperature of operation. Problems caused by such leakage would be exacerbated in a VCSEL since it would increase the density of free carriers in the distributed Bragg reflectors,
reducing their reflectivity and thus increasing the round-trip losses of the cavity. [27] Furthermore, the high threshold current required to overcome the leakage process would cause significant self-heating in the small VCSEL cavity, [3] which would further reduce the efficiency of the laser.

A further problem that the leakage current causes for the device is thermal instability. Looking at the exponential behaviour of \( I_{th} \) above room temperature in Fig. 4.7 it is clear that small fluctuations in the ambient temperature would cause relatively large changes to \( I_{th} \) for a laser. Therefore, a VCSEL processed from the wafer studied in chapter 3 operating as an oxygen sensor may struggle to give a steady output intensity in an environment where the ambient temperature was fluctuating. This would reduce the sensitivity and accuracy of an oxygen sensing system using such a laser.

The temperature instability can be quantified by the characteristic temperature, \( T_0 \), defined as:

\[
T_0(I_{th}) = \left( \frac{d \ln(I_{th})}{dT} \right)^{-1}
\]

(4.5)

The ideal scenario for any laser would be for \( I_{th} \) to be independent of temperature since its light output would then be unaffected by changes in temperature, making it completely stable. This corresponds to an infinite \( T_0 \) value. In an ideal QW EEL, however, \( I_{rad} \propto T \) and as such \( T_0(I_{rad}) = T \). Similarly, thermally activated carrier leakage has a characteristic temperature given by

\[
T_0(I_{leak}) = \frac{T}{(E_a/k_BT)} = \frac{k_BT}{E_a}.
\]

For our measured \( I_{th} \) values in Fig. 4.7 we can numerically calculate values for \( T_0 \) by using a moving five-point differential technique. Figure 4.9 shows the calculated \( T_0(I_{th}) \) values for this unstrained Al\(_x\)Ga\(_{1-x}\)As QW EEL (solid symbols). Also shown, by the solid line, is \( T_0(I_{rad}) \); a simple \( T_0 = T \) relationship. It can be seen that up to \( \sim 200 \) K, where \( I_{th} \) is dominated by radiative recombination (see Fig. 4.7), our calculated \( T_0(I_{th}) \) values follow this relationship as expected. However, as the temperature increases our \( T_0(I_{th}) \) values decrease below \( T \) due to the onset of the thermally activated leakage. The dashed curve in Fig. 4.9 shows our \( T_0(I_{leak}) \) values as determined from the numerical differentiation of the fit to \( I_{leak} \) shown in Fig. 4.7. The solid curve shows the corresponding fit
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Figure 4.9: Temperature variation of the characteristic temperature $T_0$ of the measured threshold current, $I_{th}$ (solid symbols) for the unstrained Al$_x$Ga$_{1-x}$As QW edge-emitting laser of Fig. 4.7 obtained using Eq. 4.5. The solid line and dashed curve show the $T_0$ values of the fitted radiative and leakage current components as explained in the text. The solid curve shows $T_0$ obtained from the fit to $I_{th}$ in Fig. 4.7 and Eq. 4.5.

It is clear, then, that the unstrained Al$_x$Ga$_{1-x}$As QW EEL demonstrates poor thermal stability due to electron leakage into the barrier/waveguide layers. In order to reduce this problem the separation between the quasi Fermi-level and the X and L-minima of the barriers/waveguide layers would have to be increased (increasing $E_a$). Unfortunately, material choices for this wavelength region are limited and such a change is not readily achievable. One inclusion, however, that may improve the performance of a 760 nm EEL could be to introduce strain into the QWs. This will reduce the in-plane effective mass of the carriers in the heavy-hole band, leading to a reduction in the density of states, and therefore reducing threshold carrier concentrations. [28] Such an effect could help to lower the impact of carrier leakage.

to $T_0(I_{th})$ – calculated from Eq. 4.5 and the fit to $I_{th}$ in Fig. 4.7. At room temperature we find that the EEL has $T_0 = 70 \pm 2$ K. This low value is a representation of the temperature instability at room temperature a direct result of the carrier leakage.
leakage.

We have already introduced the details of the 760 nm EEL containing compressively strained, In$_y$Al$_x$Ga$_{1-x-y}$As QW EEL in section 4.2. To reiterate, this sample is studied here so that the effect of incorporating compressive strain in the active region of a device operating at ~760 nm can be quantified. The results of this sample are not relevant to the potential performance of the unstrained oxygen sensing VCSEL wafer studied in chapter 3 since the active regions are dissimilar.

Comparing the band lineups of this active region (Fig. 4.3) to that of the EEL containing unstrained Al$_x$Ga$_{1-x}$As QWs (Fig. 4.2) we see that the two are quite similar. In the unstrained EEL the energy difference between the calculated electron ground state and the barrier/waveguide X-minima was 220 meV and for the L-minima this energy separation was 190 meV. In this strained tri-metal quaternary device we find the energy difference between the electron ground state and X-minima in the barriers/waveguide to be only slightly different at 240 ± 10 meV. The L-minima lie ~ 55 meV below the X-minima so that the splitting between the electron ground state and the L-minima in the barriers/waveguide is just 185±10 meV. This would suggest that this strained device will suffer from similar carrier leakage problems as the unstrained device. We shall study the temperature dependence of $I_{th}$ to see if this is the case, and if any significant improvements have been gained from introducing strain into the active region.

Figure 4.10 shows the measured temperature dependence of $I_{th}$ (solid symbols) for the strained EEL. Comparing this with the behaviour of $I_{th}$ in the unstrained EEL (Fig. 4.7, p101) it can be seen that the two are very similar — indicating that carrier leakage is indeed a problem in both material systems. At low $T$, $I_{th}$ again increases linearly due to radiative recombination, and, when $T > 250$ K, $I_{th}$ increases rapidly due to the leakage. In Fig. 4.11 we plot the characteristic temperature, $T_0$ for this device as we did for the unstrained laser (Fig. 4.9, p105). In many ways it is also similar to the $T_0$ behaviour seen in the unstrained device. We even find that this device has a room temperature $T_0$ value of 70±3 K, equal to the value of the unstrained laser. This shows that in both lasers the temperature stability is affected to
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Figure 4.10: The solid symbols show the measured threshold current ($I_{th}$) values of the compressively strained In$_y$Al$_{x}$Ga$_{1-x-y}$As quantum well edge-emitting laser as a function of temperature. The solid linear line is a fit to $I_{th}$ below 200 K, where the current is dominated by radiative recombination. The dashed curve is the difference between the measured $I_{th}$ values and the fitted $I_{rad}$ line and represents $I_{leak}$. This is fitted with an exponential (Eq. 4.3, p97) which is added to the fit of $I_{rad}$ to give the fitted $I_{th}$ curve (solid line). These fits are extrapolated up to the temperature at which the PR studies of chapter 3 showed the VCSEL to be tuned ($T = 388$ K).

a similar degree as a result of the leakage processes. However, the behaviour of $T_0$ is slightly different at low temperatures, where we observe that $T_0 > T$ in the strained device. This indicates the presence of a current process with a sub-linear temperature dependence (see Eq. 4.5, p104). From our studies it is not possible to determine the exact nature of this current path. However, it is known that current occurring in devices as a result of defect recombination can exhibit a very weak temperature dependence. [29] If we make a simple assumption that there is a current path due to the presence of defect states, and that the amount of leakage is independent of temperature, we can simply subtract this current from the measured $I_{th}$ values shown in Fig. 4.10. It can be seen from Fig. 4.10 that the fit to $I_{rad}$ does not go through zero

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Figure 4.11: Temperature variation of the characteristic temperature $T_0$ of the measured threshold current $I_{th}$ (solid symbols) for the strained In$_x$Al$_{1-x}$Ga$_{1-2y}$As QW edge-emitting laser. The solid line and dashed curve show the $T_0$ values of the fitted radiative and leakage current components. The solid curve shows $T_0$ obtained from the fit to $I_{th}$.

When $T = 0$ K for this strained QW device, contrary to the behaviour in the unstrained device (see Fig. 4.7, p.101). We take the intercept value of $\sim 22$ mA in Fig. 4.10 to be the constant defect current value ($I_{defect}$) which we subtract from $I_{th}$. We now recalculate the $T_0$ behaviour for $I_{th} - I_{defect}$ and this is shown in Fig. 4.12.

Looking at the temperature dependence of $T_0$ for $I_{th} - I_{defect}$ in Fig. 4.12 we see that by subtracting the constant term $I_{defect} = 22$ mA , the low temperature $T_0$ values are now $\sim T$, indicating that the remaining current is completely dominated by radiative current. Fortunately, since this defect current is only small it will not have a significant impact on the values of $I_{th}$ at and above room temperature. Therefore, its presence should not affect our analysis of the thermally induced leakage current.

For the unstrained device we were able to derive a value for the activation energy of the leakage process (see Fig. 4.8, p.102) and we follow the same procedure here. Figure 4.13 shows the natural log of the leakage current plotted against inverse temperature. From the gradient of the linear fit (solid
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Figure 4.12: Temperature variation of the characteristic temperature $T_0$ of the measured threshold current, with a constant current due to defect recombination subtracted: $I_{th} - I_{defect}$ (solid symbols) for the strained In$_y$Al$_z$Ga$_{1-z-y}$As QW edge-emitting laser. The solid line and dashed curve show the $T_0$ values of the fitted radiative and leakage current components. The solid curve shows $T_0$ obtained from the fit to $I_{th} - I_{defect}$.

At room temperature we find from Fig. 4.10 that $\sim 18\%$ of $I_{th}$ is due to $I_{leak}$. This is slightly less than the value obtained for the unstrained EEL, where $E_a$ was found to be $255 \pm 5$ meV. It is also somewhat larger than the separations between the electron ground state energy and either the X or L-minima in the barrier/waveguide layers, which from Fig. 4.3 (p94) we determine to be 240 meV and 185 meV respectively. This difference appears to be too large to be explained solely as a result of uncertainties in the material parameters used to calculate the expected value for $E_a$.

We obtain a value of $E_a = 310 \pm 10$ meV using Eq. 4.3 on page 97. This is higher than the value obtained for the unstrained EEL, where $E_a$ was found to be $255 \pm 5$ meV. It is also somewhat larger than the separations between the electron ground state energy and either the X or L-minima in the barrier/waveguide layers, which from Fig. 4.3 (p94) we determine to be 240 meV and 185 meV respectively. This difference appears to be too large to be explained solely as a result of uncertainties in the material parameters used to calculate the expected value for $E_a$.

At room temperature we find from Fig. 4.10 that $\sim 18\%$ of $I_{th}$ is due to $I_{leak}$. This is slightly less than the value obtained for the unstrained device, where 25% of $I_{th}$ was due the leakage current. This indicates a slight improvement in the strained device. Comparing the absolute values of $I_{th}$ at room temperature in the strained ($I_{th} = 330$ mA, Fig. 4.10, p. 107) and unstrained ($I_{th} = 475$ mA, Fig. 4.7, p. 101) devices we find that the threshold current is reduced by some $\sim 30\%$ as a result of the incorporation of compressive
4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers

Figure 4.13: The natural log of the leakage current in the edge-emitting laser containing strained In$_y$Al$_{x}$Ga$_{1-x-y}$As quantum wells plotted as a function of inverse temperature (solid symbols). The solid line is a linear fit to the data and this yields an activation energy ($E_a$) of 310 ± 10 meV using Eq. 4.3.

strain. Therefore, our studies suggest that adding indium into the wells of ~760 nm lasers will result in lower threshold current values.

4.4 Pressure dependent studies

4.4.1 Theoretical background

In the previous section we measured the threshold current of the two EELs as a function of temperature. These results showed an exponential increase in $I_{th}$ with $T$ leading to poor temperature stability within the lasers. In both devices we suggested that the exponential increase was caused by thermal leakage of electrons into the X and/or L-minima of the barrier/waveguide layers since the activation energy of the leakage process, $E_a$, was close to the difference between these energies and the electron ground state in the wells. In this section we shall look at the variation of $I_{th}$ with hydrostatic pressure to attempt to determine the exact leakage process that causes the exponential rise in $I_{th}$. This is possible due to the differing pressure coefficients of the barrier X-minima and L-minima levels and the $\Gamma$ point level
within the well. Figure 4.14 shows a schematic of how the band lineups in a semiconductor heterojunction change under the application of hydrostatic pressure. Fig. 4.14 (a) shows the normal situation at atmospheric pressure

(a) --- (b)

\[
\begin{align*}
E_a & \quad E_a^X \\
\Gamma & \quad \text{Barrier} \\
\downarrow & \quad \Delta E_v \\
\text{Quantum well} & \quad \text{Barrier} \\
\h^+ & \quad \text{VB}
\end{align*}
\]

\[
\begin{align*}
E_b & \quad E_b^X \\
\Gamma & \quad \text{Barrier} \\
\downarrow & \quad \Delta E_v \\
\text{Quantum well} & \quad \text{Barrier} \\
\h^+ & \quad \text{VB}
\end{align*}
\]

Figure 4.14: Schematic of the pressure dependence of the energy bands in a III-V semiconductor heterojunction. (a) shows the band lineups at room temperature and atmospheric pressure. (b) shows the band lineups at room temperature and some pressure greater than atmospheric conditions.

\(~1 \times 10^{-3} \text{ kbar}\). For simplicity we have shown the two activation energies to be between the electron ground state in the well (rather than the quasi-Fermi level of the conduction band) and either the barrier X-minima \((E_a^X)\) or the barrier L-minima \((E_a^L)\). Fig. 4.14 (b) shows the same heterojunction, now under the influence of a larger hydrostatic pressure. In a III-V semiconductor the \(\Gamma\)-point in the conduction band is known to increase linearly in energy with applied pressure (over the pressure range of interest here), as do the L-minima. [30] Therefore, the direct band gap and indirect L-gap both increase with increasing pressure. The X-minima in the conduction band move in the opposing direction, so the indirect X-band gap decreases linearly with increasing pressure. [30] Therefore we can write an expression for the rate of change of activation energy with pressure, which will be constant.

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due to the linear nature of the band energy pressure coefficients:

\[
\frac{dE^{X,L}_a}{dP} = \frac{dE^{X,L}_{\text{barrier}}}{dP} - \frac{dE^{r}_{\text{well}}}{dP}
\]  

(4.6)

In Eq. 4.6 we make the assumption that the relative positions of the valence bands are preserved (i.e. the valence band offsets are independent of pressure) and that the pressure principally affects the conduction band levels. This approximation is acceptable here since it has been shown previously that the valence band offset ratio \(Q_v\) in AlGa/GaAs heterojunctions varies by just \(\sim 1\%\) kbar\(^{-1}\). [31] This is small compared to the relative changes between the \(E^{X,L}_{\text{barrier}}\) energies and the electron ground state in the well.

We can determine the \(dE^{X,L}_{\text{barrier}}/dP\) values from literature reported values for our two devices and the second term in Eq. 4.6 can be inferred directly by measuring the energy of the photons involved in stimulated emission \((E_{\text{las}} \sim E^{r}_{\text{well}})\). This gives us the pressure dependence of \(E_a\) for a particular leakage process.

The differential in Eq. 4.6 can be integrated with respect to pressure and substituted into Eq. 4.3 (p. 97) to give Eq. 4.7 for the leakage current at some pressure \(P\) above atmospheric pressure, where \(I_0\) is a pressure independent constant, containing the activation energy at zero pressure:

\[
I_{\text{leak}}^{X,L} = I_0^{X,L} \exp \left( -\frac{P}{k_B T} \frac{dE^{X,L}_a}{dP} \right)
\]  

(4.7)

Eq. 4.7 gives us a simple method for quantifying the variation of \(I_{\text{leak}}\) with pressure. In order to model the complete pressure dependence of \(I_{\text{th}}\) we must also consider how \(I_{\text{rad}}\) changes. In a QW it can be shown that \(n_{\text{th}}^2\) is proportional to the conduction band effective mass, which in turn is approximately proportional to \(E_g\). [30] We use the approximation that \(m_e \propto E_g\) here, although from \(k \cdot p\) theory it can be seen that this is only true when the spin-orbit splitting energy \((\Delta_0)\) is much larger than \(E_g\). In Al\(_x\)Ga\(_{1-x}\)As this is not the case and \(\Delta_0 \sim E_g/4\). [5] Therefore, to illustrate the accuracy of the approximation that \(m_e \propto E_g\) in these 760 nm devices we
4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers

<table>
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<th>Value</th>
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</tr>
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<td>$E_p$ (eV)</td>
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</tr>
<tr>
<td>$s (m_0)$</td>
<td>-2.5</td>
</tr>
</tbody>
</table>

Table 4.1: Parameters for Al$_{0.135}$Ga$_{0.865}$As at atmospheric pressure required for calculating the conduction band effective mass using equation 4.8.

give a relation for $m_e$ based on an eight-band $k \cdot p$ model: [32]

$$m_e^{-1} = s + \frac{E_p}{3} \left[ \frac{2}{E_g} + \frac{1}{E_g + \Delta_0} \right]$$ (4.8)

The parameter $s$ is a second order perturbation term, and $E_p$ is related to the Kane momentum matrix element. From Ref. [5] we obtain the parameters for the material of the quantum wells in the unstrained device (Al$_{0.135}$Ga$_{0.865}$As) required in Eq. 4.8. These are given in table 4.1. Using these parameters we obtain a value for the conduction band effective mass of $m_e = 0.0736$ (units of free electron mass, $m_0$). In order to determine the validity of the approximation $m_e \propto E_g$ we can simply vary $E_g$ and re-calculate $m_e$. Figure 4.15 shows the calculated $m_e$ values over a range of band gap values (solid symbols). The solid line in Fig. 4.15 is a linear fit to the variation of $m_e$ with $E_g$. It is clear that the linear fit is of a good quality, indicating that we can indeed make the approximation that $m_e \propto E_g$ here.

The radiative recombination coefficient, $B$, is also known to exhibit a linear dependence on $E_g$, [30] therefore, from the radiative current $Bn_h^2$ term we find that $I_{rad} \propto E_g^2$. By measuring the energy of photons emitted at threshold we can measure $E_g$ (approximately) as a function of pressure. This gives us the pressure variation of $I_{rad}$. In order to model the pressure variation of $I_{th}=I_{rad}+I_{leak}$ we sum the relation $I_{rad} \propto E_g^2$ and the relation for $I_{leak}$ (Eq. 4.7) using a variable parameter, $x$, to describe the relative contribution due to leakage current at atmospheric pressure and room temperature. This
4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers

![Graph showing the calculated variation of the conduction band effective mass in Al$_{0.135}$Ga$_{0.865}$As, the material of the quantum wells in the unstrained devices studied in this chapter (solid symbols). The solid line shows a linear fit to the effective mass parameter, indicating that $m_e \propto E_g$.]

**Figure 4.15:** Calculated variation of the conduction band effective mass in Al$_{0.135}$Ga$_{0.865}$As, the material of the quantum wells in the unstrained devices studied in this chapter (solid symbols). The solid line shows a linear fit to the effective mass parameter, indicating that $m_e \propto E_g$.

is shown in Eq. 4.9.

$$\frac{I_{th}(P)}{I_{th}(0)} = x \exp \left( -P \frac{dE_d}{k_BT} \frac{dP}{P} \right) + (1 - x)E_g^2 \quad (4.9)$$

By writing the expression in terms of the normalised threshold current ($I_{th}(P)/I_{th}(0)$) any constants of proportionality divide out. This allows us to define a variable fitting parameter, $x$, the fraction of $I_{th}$ that is due to $I_{leak}$ at room temperature and atmospheric pressure. The aim is then to use Eq. 4.9 to fit the pressure dependence of $I_{th}$ for a certain leakage process, giving a percentage of leakage that agrees with the value seen in the temperature dependent studies.

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4.4.2 Experimental Technique

Figure 4.16 shows a diagram of the pressure system used to study the devices in this work. Hydrostatic pressure is exerted on a device using a piston in cylinder system with the pressure being transmitted through a liquid medium within the cylinder. The cylinder is made from hardened, pre-stressed steel and has an inner bore diameter of \( \sim 3 \) cm. [24] The bottom hardened steel piston remains fixed in place while the upper piston, which holds the laser being studied, is placed in the cylinder once filled with the pressure transmitting medium. The pressure transmitting medium used here is a hydrocarbon fluid known as 'Essence-F'.

In order to increase the pressure within the cylinder a load is applied to the upper piston using a hydraulic ram. This allows us to generate pressures of up to 10 kbar. To measure the applied pressure a coil of manganin wire is present in the cylinder and the resistance of this is measured via the electrical feedthroughs in the bottom piston. This resistance can be related to a pressure since the relationship between the two in manganin is well known. [33, 34] When changing pressure by increasing the force applied by the hydraulic ram, care is taken to ensure that the system reaches thermal equilibrium after the adiabatic compression before measurements of the threshold current are made.

The upper piston has feedthroughs so that an optical fibre can be used to couple the light emitted from the facet of the laser to a detector outside of the pressure system. Electrical connections are also present, allowing us to supply the device under investigation with a current.

4.4.3 Results and discussion

Figure 4.17 shows the variation of \( I_{th} \) with hydrostatic pressure for the unstrained edge-emitting laser (solid symbols). The threshold currents have been normalised (i.e. each measured value has been divided by the threshold current at atmospheric pressure) so that we can model the variation of \( I_{th} \) using Eq. 4.9 on page 114. It is clear that \( I_{th} \) increases with pressure and at 7.5 kbar we see that \( I_{th} \) has increased by around 3.5 times the value at
4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers

Figure 4.16: Diagram of the hydrostatic pressure system used to investigate laser threshold currents. [24]
4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers

Figure 4.17: Variation of the threshold current (normalised to atmospheric pressure value) with hydrostatic pressure in the unstrained edge-emitting laser (solid symbols). The solid curve shows a fit using Eq. 4.9 and varying $x$ as explained in the text. The resulting percentage of leakage current is determined to be 18%, assuming the leakage involves the X-minima of the barrier/waveguide layers.

As explained in section 4.4.1, in order to model the increase observed in $I_{th}$ it is necessary to measure the variation of $E_{lase}$ ($\sim E_{well}^T$) with pressure. Figure 4.18 shows this for the unstrained device (solid symbols). The solid line shows a linear fit to the data, giving a value of $dE_{lase}/dP = 8.1 \pm 0.5$ meV/kbar. We enter this value in Eq. 4.6 on page 112 to give us the second term ($dE_{well}^T/dP$) in the relationship for $dE_a/dP$. It is adequate to assume here that $dE_{lase}/dP \approx dE_{well}^T/dP$ since the main pressure dependence of the lasing energy will be the pressure coefficient of the band gap in the well. For the first term in Eq. 4.6, if we assume the leakage involves the X-minima of the barriers/waveguide, we use a value of -1.2 meV/kbar for $dE_{barrier}^X/dP$, the average of three values obtained from different sources: -0.8 meV/kbar [7], -1.3 meV/kbar [31] and -1.5 meV/kbar. [35] This then gives us a value of $dE_a^X/dP = -1.2 - 8.1 = -9.3 \pm 0.5$ meV/kbar, which we can
4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers

Figure 4.18: Variation of the lasing energy in the unstrained edge-emitting laser with hydrostatic pressure (solid symbols). The gradient of the fitted linear line gives $\frac{dE_{\text{las}}}{dP} = 8.1 \pm 0.5 \text{ meV/kbar}$.

enter into Eq. 4.7 on page 112, allowing use to calculate the leakage current at a given pressure. This may then be substituted into Eq. 4.9 (p. 114), so that the equation may be used to fit the pressure dependence of $I_{th}$ in Fig. 4.17. As mentioned in section 4.4.1 the radiative current should be approximately proportional to $E_g^2$ (where $E_g$ is the band gap of the well) and we can approximate the pressure variance of $E_g$ from Fig. 4.18. This leads us to the remaining component describing how $I_{th}$ varies with pressure in Eq. 4.9, allowing us to fit $I_{th}$ in Fig. 4.17 (p. 117) by varying the relative amount of leakage current at atmospheric pressure, $x$. The result of the fit obtained for this EEL is shown by the solid curve in Fig. 4.17, where $x = 18 \pm 2\%$. The uncertainty is dominated by the uncertainty in the $\frac{dE_g^X}{dP}$ value, obtained from a range of literature sources.

A fitted leakage percentage of 18% is reasonably consistent with the amount of leakage current seen in the temperature dependent studies at room temperature (Fig. 4.7, p101). There we saw that 25% of $I_{th}$ was due $I_{\text{leak}}$. The small difference between the two values may be due to the presence of multiple, competing leakage processes. For example, electrons may be leaking at different rates into the barrier/waveguide $\Gamma$, $X$ and $L$ points in
the conduction bands. Since each of these processes has a unique pressure dependence the results in Fig. 4.17 may contain aspects of each of these. It is not easy to account for this when modelling the pressure dependence of $I_{th}$. However, since the two percentages agree reasonably well we can assume that the majority of leakage is due to leakage into the X-minima states.

Figure 4.19 shows the pressure dependence of $I_{th}$ (again normalised to the atmospheric pressure value) in the strained QW device. Similar to Fig. 4.17,

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.19.png}
\caption{Variation of the threshold current (normalised to atmospheric pressure value) with hydrostatic pressure in the strained edge-emitting laser (solid symbols). The solid curve shows a fit using Eq. 4.9 as explained in the text. The resulting percentage of leakage current is determined to be 5.5%.
}
\end{figure}

it shows an increasing $I_{th}$ with increasing pressure. However, the increase is not so marked as in the unstrained device; at 7 kbar, for example, the normalised threshold current is just $\sim 1.7$ times greater than the atmospheric value. However, in the unstrained device the threshold current had increased by approximately 3.1 times at this pressure (Fig. 4.17). This indicates that the leakage current is not as sensitive to pressure change in the strained device compared to the unstrained device.

By monitoring the energy of the lasing mode with pressure in this strained device we obtain a value of $dE_{\text{lase}}/dP = 7.7 \pm 0.5 \text{ meV/kbar}$, shown by the fit in figure 4.20. Using this value, and the same value for $dE_{\text{barrier}}/dP$
as in the unstrained device (-1.2 meV/kbar) gives a value of \( \frac{dE_a}{dP} = -8.9 \pm 0.5 \text{ meV/kbar} \), which we enter into Eq. 4.7 to give the amount of leakage current at a given pressure. Using this value in Eq. 4.9 and fitting the behaviour of \( I_{th} \) in Fig. 4.19 (solid line) yields a leakage current percentage of just 5.5%. This is somewhat lower than the value determined from the temperature studies, where the value obtained was 18% (Fig. 4.10, p. 107). The difference between the two appears to be too large to be explained as a result of the uncertainties in the various material parameters used to model the pressure dependence, and it may suggest that the leakage process involves not the X-minima of the barriers/waveguide, but some other state.

In order to check this we use another approach to analyse the pressure dependence of \( I_{th} \) in Fig. 4.19. Now, rather than varying the amount of leakage at atmospheric pressure (\( x \)) in Eq. 4.9, we vary the pressure dependence of the leakage activation energy (\( \frac{dE_a}{dP} \)) when fitting the data in Fig. 4.19 and fix \( x \) at 18% - the value obtained from the temperature dependent study of \( I_{th} \). This gives a fitted value of \( \frac{dE_a}{dP} = 4.7 \text{ meV/kbar} \). Since we know \( \frac{dE_{cel}}{dP} \approx \frac{dE_{lase}}{dP} = 7.7 \text{ meV/kbar} \) in this device (Fig. 4.20) we find that the energy of the state into which leakage is occurring must be increas-
4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers

...ing in energy with pressure at a rate of 3.0 meV/kbar (Eq. 4.6, p. 112). This is very close to the value of \( dE_{\text{barrier}}^L/dP = 2.8 \text{ meV/kbar} \) obtained from literature [7] and suggests therefore that the leakage is actually occurring between the quasi-Fermi level in the conduction band and the \( L \)-minima of the barrier/waveguide layers in this strained device. This could be due to the fact that the X-L splitting in the barrier is larger in the strained device compared to the unstrained device.

4.5 Conclusions

The principal aim of this chapter was to determine how effectively a VCSEL processed from the wafer studied in chapter 3 would perform at high temperatures \((T > 100 \, ^\circ\text{C})\). We did this here by actually studying the carrier recombination mechanisms in an unstrained edge-emitting laser with essentially the same active region as the VCSEL wafer. Our measurements of the temperature dependence of the threshold current in this edge-emitting laser have revealed that for devices operating near 760 nm the Al\(_x\)Ga\(_{1-x}\)As material system is particularly susceptible to carrier leakage effects. This was seen as a rapid exponential increase in \( I_{\text{th}} \) when \( T > 200 \, \text{K} \) (see Fig. 4.7 on page 101). Analysis of this behaviour suggested an activation energy for the leakage process of 255 meV, not greatly different to the energy separation between the electron ground state in the well and the X-minima of the barrier and waveguide layers. Therefore, we suggested that the sharp increase in \( I_{\text{th}} \) was due to the thermal excitation of electrons from within the QWs out into the X-minima of the barrier/waveguide layers. As a result of this leakage we found that at room temperature 25% of \( I_{\text{th}} \) was due to the leakage current. Furthermore, the exponential increase in \( I_{\text{th}} \) caused by the current leakage resulted in a large reduction in the thermal stability of the laser, with a \( T_0 \) of just 70 K at room temperature (Fig. 4.9, p. 105).

In order to check that the leakage process involved the aforementioned states we also studied \( I_{\text{th}} \) as a function of hydrostatic pressure. Using literature values for the pressure dependence of the X-minima in the barriers/waveguides we were able to determine the percentage of leakage at atmo-
spheric pressure and room temperature by fitting a simple model (Eq. 4.9, p. 114) to the pressure dependent data. This suggested that if the leakage was due entirely to X-minima states in the barriers and waveguides then the amount of leakage current was $18 \pm 2\%$ of $I_{th}$ at room temperature.

In a separate study we also measured the temperature and pressure dependence of the threshold current in a 760 nm edge-emitting laser containing compressively strained $\text{In}_{y}\text{Al}_{z}\text{Ga}_{1-x-y}$As quantum wells in order to quantify the advantage of incorporating strain in this wavelength region. The temperature dependence of $I_{th}$ (Fig. 4.10, p. 107) showed a similar trend to that of the unstrained laser, again indicating that electron leakage was a problem in the strained system. However, our pressure dependent studies were consistent with a leakage of electrons into the L-minima of the barrier layers, rather than the X-minima as in the unstrained device. This was explained since the X-L splitting in the barriers of the strained device was larger than in the unstrained device, meaning that L-minima states could become preferentially occupied.

When we compared the measured room temperature threshold currents of the strained and unstrained devices we found that the current was reduced by $\sim 30\%$ as a result of incorporating the strain. This indicates that using compressively strained $\text{In}_{y}\text{Al}_{z}\text{Ga}_{1-x-y}$As quantum wells in 760 nm devices will result in lower threshold currents compared to devices containing unstrained $\text{Al}_{z}\text{Ga}_{1-x}$As wells.

### 4.6 References


4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers


4. Temperature and pressure studies of the carrier recombination mechanisms in 760 nm edge-emitting lasers


[29] S.J. Sweeney, private communication


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5 An enhanced modulated reflectance lineshape theory for vertical-cavity surface-emitting lasers

5.1 Introduction

In chapter 3 we reported on the photomodulated reflectance (PR) studies of a 760 nm VCSEL wafer with a very high-finesse cavity mode (CM). Although the sample yielded strong, clear PR signals we found that we were unable to fit the measured PR spectra with the established VCSEL PR lineshape model described in section 2.2.4. We believed that the reason for this failure, when attempting to fit our angle dependent measurements (section 3.4), was partly due to the convolution of the lineshapes resulting from the low instrumental resolution used. However, we also found that the model could not be fitted to the high resolution temperature dependent measurements of section 3.5 indicating that something more fundamental was the cause.

Figure 5.1(a) shows an example of an attempted fit to a high resolution PR measurement at normal incidence recorded at a temperature of 150 °C. For this fit the energy parameters of the two QW transitions—the ground state electron to heavy-hole and light-hole transitions ($e_{1}hh_{1}$ and $e_{1}lh_{1}$) were allowed to vary unconstrained along with the other variable parameters in the model. We see from Fig.5.1(a) that in the region of the CM this fit appears to be of a good quality, reproducing the form of the lineshape. However, in the region of the $e_{1}hh_{1}$ QW transition it can be seen that the fit is of a very poor quality. The values of the the $e_{1}hh_{1}$ and $e_{1}lh_{1}$ energies obtained from this fit are 1.6215 and 1.6253 eV respectively and these energies are marked on the upper scale. They are both close to the CM energy ($E_{CM}$) and this is caused by the least squares fitting routine’s attempts to reproduce the PR lineshape, which is strongest in the CM region. Although this does create a good fit here, it is at the expense of the fit in the region of the weaker $e_{1}hh_{1}$ feature. Furthermore, we can show that the two fitted energies of the QW transitions are not consistent with the values obtained in chapter 3: for example, from figure 3.14 on page 70 we can estimate the energy of the $e_{1}hh_{1}$
Figure 5.1: (a) Measured normal incidence PR of the 760 nm VCSEL recorded at 150 °C (filled symbols). The $e_{1/2}h_{1}$ transition region below 1.618 eV has been magnified for clarity. The unconstrained least squares fit achieved using the established lineshape model (Eq. 2.18, p. 37) is also shown (solid curve). (b) The same PR spectrum fitted with established model, where the parameters have been constrained near their approximate values, as determined from the PR studies of chapter 3. The labelled arrows mark the respective energies of the three features obtained from the fits.
Parameter Fit #1 Fit #2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fit #1</th>
<th>Fit #2</th>
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<tbody>
<tr>
<td>$I_a \times 10^{-3}$</td>
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</table>

Table 5.1: Parameters of the unconstrained fit (Fit #1) and constrained fit (Fit #2) shown in Fig. 5.1 for the normal incidence, 150 °C PR spectrum of the 760 nm VCSEL wafer.

The QW transition at $T = 150$ °C to be $1.613 \pm 0.005$ eV and this is some 8.5 meV lower than the fitted value.

In order to produce a fit that was more physically meaningful we constrained the energy parameters so that they were close to the values shown in Fig. 3.14 at $T = 150$ °C (the $e_{1lh_1}$ value was taken to be $\sim 14$ meV greater than the $e_{1hh_1}$ energy since this was their energy separation measured from Fig. 3.7 on p59). This constrained fit is shown in figure 5.1(b). It is clear from this that the fit is of a poor quality; by ensuring that the QW transition energies are near their pre-determined positions we have made it impossible for the established model to reproduce the negative-going side-lobes that surround the central peak near $E_{CM}$. Similarly the model fails to reproduce the lineshape in the region of the $e_{1hh_1}$ QW transition. Table 5.1 shows the parameters used in the two fits, where Fit #1 is the unconstrained fit and Fit #2 is the constrained fit. All the parameters are explained in detail in section 2.2.4. The first four parameters in the table are associated with
the CM Seraphin coefficients and the next four are the $e_1h_1$ QW transition TDFF parameters. The amplitude of this TDFF is absorbed into the $I_\alpha$ and $I_\beta$ amplitude terms of the CM. The final five parameters are associated with the $e_1l_1$ TDFF—this feature has a separate intensity parameter ($I$) and its value represents the relative magnitude of the TDFF with respect to the first $e_1h_1$ TDFF. In Fit #1 the intensity of the $e_1l_1$ TDFF is 1.84, and this implies that the $e_1l_1$ PR feature is stronger than the $e_1h_1$ feature. We know this is not the case here (see Fig 3.7) and this further demonstrates that this unconstrained fit is not physically meaningful, despite reproducing the PR lineshape near the CM. In both Fit #1 and Fit #2 the value of the exponent ($n$) used in the two TDFFs is fixed at 2.0; an appropriate value for excitonic QW transitions (see section 2.2.2).

Fortunately, despite not being able to fit the established model to our measured PR spectra of the 760 nm VCSEL wafer, we were still able to characterise the gain-cavity de-tuning of the sample by monitoring the symmetry of the measured lineshapes. Here we utilised the theory that in VCSELs such as this one, where the CM FWHM, $\Gamma_{CM}$ is less than that of the $e_1h_1$ transition, the PR lineshape becomes anti-symmetric when the CM and QW are in resonance (see section 2.2.4). This allowed us to determine that the VCSEL was tuned with $E_{CM} = E_{QW}$ at room temperature when the angle of incidence was 47° (Fig. 3.10, p63), or at normal incidence, when the temperature was 113.5 °C (Fig. 3.17, p75).

Although we were able to use the existing symmetry theory to characterise the gain-cavity de-tuning in the sample the question still remained as to why we were unable to fit the measured PR spectra with the currently accepted model. Therefore, in this chapter we return to the problem, in an attempt to enhance the VCSEL PR lineshape model. Our approach will be to first simulate the reflectance and Seraphin coefficients of a VCSEL similar to the 760 nm sample studied in chapter 3. Then, analysis of these simulations will hopefully lead to a suitable lineshape model for the Seraphin coefficients, which can be included into an new PR model for VCSELs. We can then test the model by attempting to fit the measured PR spectra of the 760 nm VCSEL.
5.2 Simulating the reflectance spectra and Seraphin coefficients of a VCSEL

When the established VCSEL PR lineshape model was originally formulated it was found empirically that measured spectra could be fitted by using the real and imaginary parts of a complex Lorentzian to describe the Seraphin coefficients. [1] The equations for these, which are included in the VCSEL PR model discussed in section 2.2.4, are repeated here in Eq. 5.1.

\[
\alpha = I_\alpha \frac{\Delta_{CM}}{\Delta_{CM}^2 + \gamma_{CM}^2} \quad \text{and} \quad \beta = I_\beta \frac{\gamma_{CM}}{\Delta_{CM}^2 + \gamma_{CM}^2}
\]  

(5.1)

Here, \( \gamma_{CM} = \Gamma_{CM}/2 \) is the half width at half maximum (HWHM) of the CM PR feature and \( \Delta_{CM} = E - E_{CM} \), where \( E_{CM} \) is the CM energy.

In these original studies the Reflectance (R) spectra of various VCSEL structures were simulated, allowing the Seraphin coefficients to be calculated numerically using Eq. 5.2.

\[
\alpha \approx \frac{R(\varepsilon_1 + \delta\varepsilon_1, \varepsilon_2) - R(\varepsilon_1, \varepsilon_2)}{R(\varepsilon_1, \varepsilon_2)\delta\varepsilon_1} \quad \text{and} \quad \beta \approx \frac{R(\varepsilon_1, \varepsilon_2 + \delta\varepsilon_2) - R(\varepsilon_1, \varepsilon_2)}{R(\varepsilon_1, \varepsilon_2)\delta\varepsilon_2}
\]  

(5.2)

In this equation \( \delta\varepsilon_1 \) and \( \delta\varepsilon_2 \) are infinitesimally small changes to the dielectric function of the material for which the Seraphin coefficients are being calculated. These early studies showed that the numerically calculated VCSEL Seraphin coefficients were well represented by the lineshapes of Eq. 5.1. However, in these simulations, the dielectric functions of the QW layers in the cavities of VCSELs were approximated as being the same as their bulk materials—i.e. ignoring the effects of quantum confinement. [2]

In order to try to develop an enhanced PR model for VCSELs we include here an accurate model for the dielectric functions of the QWs that will be included in the structure, so that a closer approximation to the true effect of the QWs can be simulated. We use the transfer matrix technique described in section 2.3 to calculate the R spectra as a function of angle of incidence. This allows us to observe the changes to the simulated R and the Seraphin coefficients as the CM is tuned through the included QW
transitions. This approach is much simpler than attempting the study the problem as a function of temperature since this would require a detailed inclusion of the thermal dependence of the dielectric functions of all the materials involved. The structure of the VCSEL used in the simulations is identical to the 760 nm VCSEL studied in chapter 3 and a description is given in section 3.2. In order to simplify the analysis of the simulated \( R \) spectra we omitted the GaAs cap layer from the structure which caused the unusual, broad dip in the reflectance stop band (Fig. 3.5, p55). This allows us to develop a general theory, applicable to VCSELs which do not show perturbed \( R \) spectra resulting from poorly designed cap layers.

The dielectric functions of the various bulk materials were obtained from ellipsometry measurements. [3]

5.2.1 Modelling the dielectric function in quantum wells

In this section we describe the model used for the complex dielectric function of the QWs included in our VCSEL structure. The model was developed by Tanguy et al. [4] and is based on the dielectric function of Wannier excitons in non-integer, or ‘fractional’ dimensions.

An ideal, two-dimensional system has a dimensional integer \((d)\) of two, compared to a value of three for a conventional bulk system. Using non-integer dimensions \((2.0 < d < 3.0)\) to describe effects in real quantum confined systems has proven popular due to the good agreements between theory and experiments, [5, 6, 7] and the low computational effort required compared to complex numerical calculations. [8]

The relative, energy dependent complex dielectric function \((\varepsilon = \varepsilon_1 + i\varepsilon_2)\) of a Wannier exciton in a non-integer dimension \(d\) can be written as equation 5.3: [4]

\[
\varepsilon_d^\lambda(E) = \frac{A_d R^{(d/2)-1}}{(E + i\gamma)^2} [g_d(\xi(E + i\gamma)) + g_d(\xi(-E - i\gamma)) - 2g_d(\xi(0))] \quad (5.3)
\]

Here \(\gamma\) is the Lorentzian broadening (HWHM), \(A_d\) is related to the oscillator strength of the transition, and \(R\) is the excitonic binding energy in three
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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Heavy hole</th>
<th>Light hole</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_d$</td>
<td>0.7</td>
<td>0.28</td>
</tr>
<tr>
<td>$R$ (meV)</td>
<td>6.0</td>
<td>4.0</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>1.6851</td>
<td>1.6955</td>
</tr>
<tr>
<td>$\gamma$ (meV)</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>$d$</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 5.2: Parameters of the model for the complex dielectric function of Wannier excitons in non-integer dimensions used to generate the dielectric function of the QWs included in the VCSEL reflectance simulations of this work. The heavy and light hole ground state transitions are included.

dimensions. The function $\xi(q)$ is given by Eq. 5.4, where $E_g$ is described by Tanguy et al. as being the absorption threshold energy. [4]

$$\xi(q) = \left(\frac{R}{E_g - q}\right)^{1/2}$$  \hspace{1cm} (5.4)

$g_d(\xi)$ is given by Eq. 5.5, where $D = d - 1$ and $\zeta(x)$ is the Euler Gamma function, with argument $x$.

$$g_d(\xi) = \frac{2\pi\zeta(D/2 + \xi)}{\zeta(D/2)^2\zeta(1 - D/2 + \xi)}\left[\cot(\pi(D/2 - \xi)) - \cot(\pi D)\right]$$ \hspace{1cm} (5.5)

In order to solve the Euler Gamma function we have used the approach described by Spouge. [9] This then enables us to calculate the complex dielectric function for a given excitonic transition.

In order to select appropriate parameters for the model we take guidance from Ref. [4] and our PR measurements on the 760 nm VCSEL (Fig. 3.7, p59) as a guide to the appropriate values of $\gamma$ and $E_g$. We include the excitonic effects of both the $e_1h_1$ and $e_1l_1$ transitions, requiring us to sum the contributions of two separate $\varepsilon_d$ functions from Eq. 5.3 (i.e. $\varepsilon_d = \varepsilon_d^{hh} + \varepsilon_d^{lh}$). The values of the parameters used are shown in table 5.2.

In their work on excitonic binding energies in non-integer dimensions, Mathieu et al. [10] give a simple method for calculating $d$ for an infinite
quantum well:

\[ d = 3 - \exp(-L_w/2a_0) \]  

(5.6)

Here \( L_w \) is the width of the quantum well (8 nm), \( a_0 = \varepsilon_1 a_H/\mu \) is the effective Bohr radius, \( a_H \approx 0.053 \text{ nm} \) is the Bohr radius and \( \mu = (1/m_e + 1/m_h)^{-1} \) is the reduced mass (in units of the free electron mass, \( m_0 \)). Using effective mass parameters from the review of Vurgaftman et al. [11] and a value for \( \varepsilon_1 = 13.3 \) based on the dielectric function data from ellipsometry measurements [3] gives a value of \( d \approx 2.3 \). In order to account for the wavefunction penetration into the barriers of our finite quantum wells we have increased this value of \( d \), using a value of 2.5 here.

Our applied \( E_g \) values are chosen to yield excitonic peaks in \( \varepsilon_2 \) at energies based on the two room temperature energies \( \varepsilon_1 hh_1 \) and \( \varepsilon_1 lh_1 \) of the 760 nm VCSEL as determined from Fig 3.7 (1.675 and 1.689 eV). However, we have slightly red-shifted the heavy hole transition from the light hole transition in our model so that the two excitonic peaks are clearly resolvable. Therefore, our generated excitonic absorption peaks occur at 1.671 and 1.689 eV for the \( \varepsilon_1 hh_1 \) and \( \varepsilon_1 lh_1 \) transitions. Comparing these energies with the values of \( E_g \), the absorption threshold energy, used in the dielectric function model (table 5.2) we see that the excitonic features occur at lower energies than \( E_g \). This is due to the exciton binding energies and carrier confinement effects. [4]

The excitonic features can be seen in figure 5.2, which shows the separate dielectric functions of the two Wannier excitons associated with both transitions calculated from Eq. 5.3. The imaginary parts (\( \varepsilon_2 \)) are shown by the dashed curves. It can be seen that the dielectric function of the \( \varepsilon_1 lh_1 \) transition is smaller than the corresponding \( \varepsilon_1 hh_1 \) function, due to the larger \( A_d \) value used for the heavy-hole transition (see table 5.2). At energies below the excitonic peaks both transitions display absorption tails resulting from the Lorentzian broadening, \( \gamma \) included in Eq. 5.3. Above the absorption peaks however, \( \varepsilon_2 \) does not go to zero for either transition. This is due to the inclusion of effects from higher energy bound states and unbound continuum states in the model of Eq. 5.3. [4] The corresponding real parts of the dielectric functions (\( \varepsilon_1 \)) are shown by solid curves. Since these must be
the Kramers-Kronig counterparts of the $\varepsilon_2$ terms, taken together $\varepsilon_1 + i\varepsilon_2$ exhibit lineshapes which resemble the real and imaginary parts of complex Lorentzian lineshapes near the excitonic absorption peak energies.

The dielectric functions in figure 5.2, when summed, will give the total dielectric function contribution of the two included QW transitions. However, in order to get a full description of the QW dielectric function we must include a background $\varepsilon_1$ term that results from transitions near the $X$ and $L$ points in the bandstructure, far above $E_g$. [4] This addition must not be in contradiction to the causality principle and so the real and imaginary parts of the dielectric function must remain Kramers-Kronig pairs over the entire energy spectrum. Fortunately, in the narrow energy region near $E_g$ it is permissible to add a linear term such as $a + bE$ to $\varepsilon_1$ without breaking this condition. [4] Therefore, we added a linear background to $\varepsilon_1$ consistent with the real $\varepsilon_1$ data of the QW bulk material (Al$_{0.154}$Ga$_{0.846}$As) obtained from ellipsometry measurement data. [3] (not shown in Fig. 5.2) This seemed like
an appropriate choice since this background term, arising from transitions near $X$ and $L$, will be relatively unaffected by the effects of quantum confinement. The resulting QW dielectric function is shown in figure 5.3. Now, the QW dielectric function exhibits two peaks in $\varepsilon_2$ due to the two included QW transitions and $\varepsilon_1$ shows the combination of the excitonic effects as well as the included linear background term. This then is the dielectric function we employed to describe the three quantum wells in the structure used in the $R$ simulations of this study. For simplicity we have assumed all three QWs to be identical.

### 5.3 Results of the angle dependent reflectance simulations

Figure 5.4 shows the simulated reflectance of the VCSEL structure at normal incidence using the dielectric functions of the bulk materials of the structure [3] and the QW dielectric function described in the previous section, shown in Fig. 5.3. The structure used in the simulations is the same as the
760 nm VCSEL wafer studied in chapter 3 and is described in section 3.2. As mentioned previously, we have omitted the GaAs cap layer from the structure in order to simplify the form of the spectra and give an opportunity to develop a new PR lineshape model for general use. Therefore, the $R$ spectrum does not exhibit the unusual, broad dip across the stop band as in the measured $R$ spectrum of the 760 nm VCSEL wafer (Fig. 3.2, p51). We see a sharp feature in Fig. 5.4 due to the cavity mode at $E_{CM} = 1.6425$ eV (754.9 nm), near the centre of the high reflectance stop band ($R = 99.998\%$).

Figure 5.5 shows the calculated $R$ spectrum in the region of the CM. From this figure the true lineshape of the CM $R$ feature can be seen. In order to describe its shape, we have fitted it with an inverted Lorentzian peak, described by equation 5.7.

$$ R_{CM} \approx 1 - \frac{I_{\gamma_{CM}}}{\Delta_{CM}^2 + \gamma_{CM}^2} \quad (5.7) $$
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Figure 5.5: Simulated normal incidence, room temperature reflectance of the VCSEL structure in the cavity mode region (open symbols). A fit using the imaginary part of a complex Lorentzian (Eq. 5.7) is also shown (solid curve), giving $E_{CM} = 1.6425$ eV and $\Gamma_{CM} = 2\gamma_{CM} = 0.176$ meV.

Here $\gamma_{CM} = \Gamma_{CM}/2$ is the half width at half maximum (HWHM) and $\Delta_{CM} = E_{CM} - E$. $I$ is an intensity parameter describing the depth (minimum reflectance) to which the CM dip falls. It is clear from Fig. 5.5 that the fit obtained using Eq. 5.7 is of a very high quality, indicating that the Lorentzian peak is an appropriate choice for the profile of the CM feature. The fitted value for $E_{CM}$ here is 1.6425 eV and $\gamma_{CM} = 0.088$ meV. This is now our starting point for developing a model to describe the lineshapes of a VCSEL's Seraphin coefficients. By asserting that $R_{CM}$ follows a Lorentzian profile we can state that the Seraphin coefficients will be related to this form.

Before looking at the simulated Seraphin coefficients, however, we shall look at the simulated angle dependence of the CM feature in order to observe the changes that occur as the CM is tuned through the two transitions included
Looking at the dielectric function of the QWs used in the structure (Fig. 5.3, p. 134) it can be seen that at normal incidence $E_{CM}$ (1.6425 eV) occurs in a region of low absorption, on the Lorentzian tail of the 1.671 eV exciton peak. By increasing the angle of incidence ($\theta$) away from the normal we can blue shift $E_{CM}$, moving it up the absorption tail and towards the two excitonic peaks. Figure 5.6 shows a selection of the simulated $R$ spectra, from normal incidence up to $\theta = 30^\circ$. The spectra are plotted as a function of $E - E_{CM}$ so that the position of each CM dip appears at zero on this scale—allowing for an easy comparison between the features. It is clear from Fig. 5.6 that with increased angle of incidence the depth ($I$) of the CM $R$ dip reduces while its width ($\gamma_{CM}$) increases. We find that the CM is tuned from an energy of 1.6425 to 1.7022 eV as $\theta$ is increased from 0 – 70°. Comparing this range of energies to the horizontal scale of Fig. 5.3 it is clear that our
simulations have been able to tune the CM through the energies of the two QW transitions. Now we look at the values of our fitted parameters to see if any indication of the CM-QW tuning can be observed in these results.

Figure 5.7 shows the CM feature width, integrated area, and depth as a function of the incidence angle. In this figure the CM width (filled circles) is plotted as the FWHM (i.e. $\Gamma_{CM} = 2\gamma_{CM}$), showing two pronounced peaks, similar to the behaviour seen in the measured $R$ spectra of the 760 nm VCSEL (Fig. 3.22, p81). Also plotted (filled triangles) is the depth, $I$, multiplied by $\pi$. The reason for this multiplication is due to the fact that a standard Lorentzian (with an amplitude equal to one) has an integrated area of $\pi$. Therefore, if our simulated CM $R$ features are exact Lorentzians, their areas should equal $\pi \times I$. In order to check this we have also plotted the numerically integrated area of the simulated features (filled squares). There is a generally good agreement between the two values, which is further evidence that using a Lorentzian to describe the CM $R$ features is justifiable. However, there is a slight discrepancy between the two; near the energy at which the FWHM
becomes maximum, \( I \) appears to display a small peak between \( \theta = 35 - 45^\circ \), but this is not the case for the integrated area parameter. This suggests that in this region the lineshape deviates slightly from a true Lorentzian shape. Indeed, this can be seen in figure 5.8, where the fit using Eq. 5.7 to the simulated \( \theta = 40^\circ \) \( R \) spectrum is shown. Here the slight deviation from a true Lorentzian can be seen since the Lorentzian fit is unable to describe perfectly the simulated lineshape. We believe that this is due to the fact that at \( \theta = 40^\circ \) the CM (\( E_{CM} = 1.6695 \) eV) is in a region where the QW absorption (\( \sim \varepsilon_2 \)) is rapidly varying with energy (see Fig. 5.3 on p134). Therefore, if the CM broadening is affected by the QW absorption and the absorption is changing across the CM feature, then it follows that the CM
feature will have an energy dependent width. We shall mention this effect again when talking about the corresponding Seraphin coefficients of such a reflectance feature.

Figure 5.7, showing the parameters describing the CM feature of the simulated R spectra, has notable similarities with Fig. 3.22 on p81, showing the same parameters for the measured R spectra of the 760 nm VCSEL wafer (although the depths of the measured R spectra are not multiplied by $\pi$). In section 3.6.3 we also plotted the angle dependence of the CM FWHM as a function of the CM energy and compared it to a PR modulus spectrum showing the positions of the two QW transitions (Fig. 3.23, p83). We suggested that the agreement between the energies at which the CM FWHM was maximised and the energies of the two QW transitions was an indication that the CM broadening was related to the amount of QW absorption ($\alpha_{QW}$) at the CM energy. This follows from the fact that an optical cavity's Q-factor ($Q = E_{CM}/\Gamma_{CM}$) is related to the lifetime of the resonant photons within the cavity. [12] We can now analyse our simulated data to see if $\Gamma_{CM} \propto \alpha_{QW}$ since $\alpha_{QW}$ can be calculated using the dielectric function shown in Fig. 5.3 and $\Gamma_{CM} = 2\gamma_{CM}$ can be obtained from Fig. 5.7. Figure 5.9 displays $\Gamma_{CM}$ of the simulated CM features plotted as a function of their CM energies (filled symbols). The upper scale shows the corresponding angle of incidence at which each simulation was conducted. The solid curve shows the absorption of the three QWs used in the structure for which the R spectra were simulated (calculated from the $\varepsilon_2$ in Fig. 5.3). This figure shows an unmistakable relationship between the two values, with $\Gamma_{CM} \propto \alpha_{QW}$ and it confirms our observations of Fig. 3.23 of an absorption-induced cavity mode broadening effect seen in the 760 nm VCSEL. This adds further evidence that the effect may prove useful as a simple, non-destructive method for determining when VCSELs with high-quality cavities are tuned, with $E_{CM} = E_{QW}$.
Figure 5.9: Measured broadening ($\Gamma_{CM}$, FWHM) of the cavity mode feature in the simulated reflectance spectra of the VCSEL structure plotted as a function of the cavity mode energy (closed symbols). The upper axis shows the corresponding angles for which the simulations were conducted. Also plotted (solid curve) is the absorption ($\alpha_{QW}$) of the quantum wells used in the structure for which the reflectance was simulated.

5.3.1 Modelling the simulated Seraphin coefficient lineshapes

As was shown in figure 5.5, we can model our simulated $R_{CM}$ spectra using a Lorentzian peak shape (Eq. 5.7). To see how this relates to the corresponding Seraphin coefficients we repeat the equations for these here.

\[
\alpha = \frac{1}{R} \frac{\partial R}{\partial \varepsilon_1} = \frac{\partial (\ln R)}{\partial \varepsilon_1} \tag{5.8}
\]

\[
\beta = \frac{1}{R} \frac{\partial R}{\partial \varepsilon_2} = \frac{\partial (\ln R)}{\partial \varepsilon_2} \tag{5.9}
\]

Writing the Seraphin coefficients in terms of the natural log of the reflectance ($\ln R$) simplifies our analysis as will become clear shortly. Now the Seraphin coefficients become differentials of $\ln R$ with respect to the complex
dielectric function. Therefore, in order to find an appropriate lineshape for these differentials we must find an appropriate form for \( \ln R \). Using the form of Eq. 5.7 for \( R \) we can see that \( \ln R \) is the natural log of \( 1 + L_i \), where \( L_i \) is the imaginary part of a complex Lorentzian. Here we have taken \( L_i \) to be a negative dip shape rather than a positive peak shape. Figure 5.10 shows the natural log of the CM reflectance at normal incidence \( (R \) is shown in Fig. 5.5). It can be seen from this that \( \ln R \) is also a simple dip shape in the region of the CM. The form of \( \ln R \approx \ln(1 + L_i) \) can be found by writing the natural log as a Taylor expansion. However, this becomes rather lengthy, with high powers of \( L_i \) being required. Fortunately our analysis of the different CM \( R \) features simulated in this study has enabled us to show that \( \ln R \) can also be fitted with a Lorentzian dip. The normal incidence \( \ln R \) spectrum in Fig. 5.10 is fitted very successfully with such a lineshape and

Figure 5.10: Natural log of the simulated normal incidence, room temperature reflectance of the VCSEL structure in the cavity mode region (open symbols). A fit using the imaginary part of a complex Lorentzian (Eq. 5.10) is also shown (solid curve).
the form of the model for \( \ln R \) is given by equation 5.10.

\[
\ln(R_{CM}) \approx -\frac{B\gamma'_{CM}}{\Delta^2_{CM} + \gamma'^2_{CM}}
\]

(5.10)

Here \( B \) is the intensity and \( \gamma'_{CM} \) is the HWHM of \( \ln R \), which differs from the HWHM of \( R \), \( \gamma_{CM} \). \( \Delta_{CM} = E_{CM} - E \) is the same as in Eq. 5.7, with the minima occurring at the same value of \( E_{CM} \) in both spectra. When fitting our calculated \( \ln R \) spectra with Eq. 5.10 we treated the three parameters as variable fitting parameters, with no enforced correlation to the values obtained from the fits to the \( R \) spectra. We should mention however, that a detailed mathematical analysis gives an approximate relationship between these parameters, [13] and we give these relationships here for those interested.

\[
B \approx \ln(1 - I)
\]

(5.11)

\[
\gamma'_{CM} \approx \gamma_{CM} \sqrt{\frac{\ln(1 - I/2)}{\ln(1 - I) - \ln(1 - I/2)}}
\]

(5.12)

The important finding from this is that width of the CM feature in \( \ln R \), \( \gamma'_{CM} \), is less than that in the conventional \( R \) spectrum. For example; the normal incidence \( R \) spectrum has a fitted amplitude \( (I) \) of 0.693. Therefore the square root factor in Eq. 5.12 is 0.75. Using the width of \( \gamma_{CM} = 0.088 \) meV (from Fig. 5.7) we obtain a width of \( \gamma'_{CM} = 0.066 \) meV for the corresponding \( \ln R \) spectrum. Our fit to the \( \ln R(0^\circ) \) spectrum shown in Fig. 5.10 has a HWHM of 0.067 meV and this in in good agreement with the predicted value using the relationship of Eq. 5.12. We find a similar agreement with the fitted intensity of this \( \ln R \) spectrum, where \( B = -1.172 \), and the value calculated using Eq. 5.11 gives \( B = -1.181 \).

Now that we have an appropriate form for \( \ln R \) we can develop a model for the \( \alpha \) Seraphin coefficient based on the relationship in Eq. 5.8 on page 141. To do this we relate the derivative with respect to \( \varepsilon_1 \) to a derivative with respect to \( E_{CM} \) since the CM energy depends on the optical thickness of the cavity through the relationship \( \lambda_{CM} = nd \), where \( n \) is the effective refractive index of the cavity and \( d \) is the cavity thickness. Therefore, we may write \( \alpha \)
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in terms of a differential change in $E_{CM}$:

$$\alpha = \frac{\partial (\ln R)}{\partial \varepsilon_1} \approx \frac{\partial (\ln R)}{\partial E_{CM}}$$  \hspace{1cm} (5.13)$$

This differential of $\ln R$ can be calculated analytically from Eq. 5.10, giving us a new lineshape function for $\alpha$:

$$\alpha = \frac{-2C\gamma_{CM}\Delta_{CM}}{(\Delta_{CM}^2 + \gamma_{CM}^2)^2}$$  \hspace{1cm} (5.14)$$

Here, $C$ is a positive amplitude and the other parameters are the same as those that apply to the fits of the $\ln R$ spectra (Eq. 5.10). Comparing this equation to the form used for $\alpha$ in the established model (Eq. 5.1, p129) we see that the two are not identical. The primary difference between the two is the raised power in the denominator of the new $\alpha$ lineshape: this will give a sharper feature than in the established model. However, their general lineshape will be similar, exhibiting a dispersive-like shape due to the $\Delta_{CM}$ term in the numerator.

Our approach here of using $\alpha \sim \partial (\ln R)/\partial E_{CM}$ is similar to that used when developing the established VCSEL PR lineshape model. However, in that early study the lineshape for $\alpha$ was approximated as simply being the real part of a complex Lorentzian since it was found that this was adequate for fitting the $PR$ spectra of VCSELs studied at the time. [1]

Figure 5.11 shows the simulated $\alpha$ coefficient of the VCSEL structure at normal incidence (open symbols). The calculation was done numerically using Eq. 5.2 on page 129, where the term $\delta \varepsilon_1$ was added to $\varepsilon_1$ of the three QWs in the structure. The size of $\delta \varepsilon_1$ used ($\delta \varepsilon_1 = \varepsilon_1 \times 1 \times 10^{-5}$) was small enough for our calculations to be within the correct limit to yield a good approximation to the true differential lineshapes, while large enough to maintain computational stability. It is clear from Fig. 5.11 that $\alpha$ has the expected dispersive form, resulting from the shifting of $E_{CM}$ caused by the differential change in the optical thickness of the cavity. The solid curve shows the fit using Eq. 5.14 and it is clear that it is of a very high quality. This shows that Eq. 5.14 is suitable for use as part of our development of a
new VCSEL PR model.

Figure 5.12 shows the simulated $\beta$ coefficient of the VCSEL structure, also at normal incidence (open symbols). Again we used the approach of taking $\delta \varepsilon_2 = \varepsilon_2 \times 1 \times 10^{-5}$ in order to numerically calculate $\beta$. Our simulated $\beta$ lineshape is similar to the form used in the established model, displaying a peak at $E_{CM}$ and symmetric about that point (see Fig. 2.11, p. 36). However, it does differ from this, displaying two negative-going side-lobes approximately seven times weaker than the amplitude at $E_{CM}$. These side-lobes are not reproducible using the established equation for $\beta$ (Eq. 5.1, p129) and as such we must derive a more appropriate lineshape function. In the case of the $\alpha$ coefficient this was simple since we were able to use the relationship between $E_{CM}$ and $\varepsilon_1$ in order to relate the differential with respect to the dielectric function to that involving $E_{CM}$. However, in the case of the $\beta$ coefficient, such a relationship is not immediately clear. However, we can use an inter-
An enhanced modulated reflectance lineshape theory for vertical-cavity surface-emitting lasers

Figure 5.12: Simulated room-temperature, normal incidence $\beta$ Seraphin coefficient of the VCSEL structure (filled symbols). The solid line shows the least squares fit using Eq. 5.17

We notice that the amplitudes of the two Seraphin coefficients are similar for all the simulated data, and that the two lineshapes appear to resemble a Kramers-Kronig (KK) pair. In order to test this we numerically calculated the KK transforms of the simulated Seraphin coefficients using the method described in section 2.2.2. The energy range for each integration involved in the KK transforms covers the range where the Seraphin coefficients are non-zero. Fortunately, the coefficients quickly go to zero and so we can perform these finite-energy-range KK transforms without difficulty. We find an excellent agreement between the KK transforms (open symbols) and the Seraphin
coefficients as shown in Fig. 5.13, with the relationships given below:

\begin{equation}
KK_r \rightarrow -i [\alpha] = -\beta \\
\end{equation}

\begin{equation}
KK_r \rightarrow -i [\beta] = \alpha
\end{equation}

Here \( KK_r \rightarrow -i \) implies that the transform used is of the form that converts a real component into an imaginary one. The small disagreement between the numerically calculated KK transforms and the simulated Seraphin coefficients shown in Fig. 5.13 is simply an artefact of the low number of data points chosen for our simulated Seraphin coefficients near to \( E_{CM} \), which affects the accuracy of the Kramers-Kronig transformations.

Although the lineshapes for the Seraphin coefficients used in the established \( PR \) model (Eq. 5.1, p129) are also related by KK transforms, in prac-
five enhanced modulated reflectance lineshape theory for vertical-cavity surface-emitting lasers

There was no enforced connection applied between $I_\alpha$ and $I_\beta$ when using this model to fit PR spectra, meaning that they were not assumed to be a KK pair. However, our simulations show that the coefficients are KK pairs, and therefore the amplitude parameters of the two coefficients must be equal. Although this strict constraint could make fitting certain VCSEL PR line-shapes very difficult, it does have the advantage of reducing the number of possible variable fitting parameters and this is always beneficial in least squares fitting algorithms.

This study is the first time that a relationship between the Seraphin coefficients of a VCSEL and their KK transforms has been established and so it is interesting to try to establish its theoretical origin. In appendix B we present a mathematical explanation as to why the $\alpha$ and $\beta$ Seraphin coefficients of a VCSEL could be a KK pair in the vicinity of the CM. Since this, along with our simulations here, show that the Seraphin coefficients are related by KK transforms we must ensure that the lineshape model used to describe $\beta$ is the analytical KK counterpart of the form used for $\alpha$ (Eq. 5.14, p144). This leads us to describe $\beta$ as being $\partial \ln R / \gamma_{CM}$ (see appendix B) and this relationship is given by equation 5.17, where the amplitude, $C$, is the same as in Eq. 5.14 for $\alpha$.

$$\beta = C \frac{\gamma_{CM}^2 - \Delta_{CM}^2}{(\Delta_{CM}^2 + \gamma_{CM}^2)^2}$$ (5.17)

We can understand qualitatively why $\beta$ should be $\sim \partial \ln R / \gamma_{CM}$ by looking at Fig. 5.9 on page 141. This figure shows a clear relationship between the QW absorption ($\sim \varepsilon_2$) and the CM width in $R$, $\gamma_{CM}$. We have also shown that this width can be related to the widths of $\ln R$ and the Seraphin coefficients ($\gamma_{CM}$) with a relation between the two being given in Eq. 5.12 on page 143. Therefore, we can state that $\gamma_{CM} \sim \varepsilon_2$ and so $\beta = \partial \ln R / \partial \varepsilon_2 \sim \partial \ln R / \partial \gamma_{CM}$. Hence it follows that the $\beta$ coefficient can be seen to arise from a modulation in the CM width, caused by a change in the cavity (QW) absorption. This is different to the justifications given earlier when developing the established VCSEL PR model where it was argued that $\beta$ arose from a modulation in the CM depth. [14]
The solid curve in Fig. 5.12 on page 146 shows the fit to the simulated \( \beta \) coefficient at normal incidence using Eq. 5.17. As was the case for the \( \alpha \) coefficient, the fit is of a very high quality, indicating that Eq. 5.17 is appropriate for describing \( \beta \). Comparing Eq. 5.17 with the lineshape used in the established model (Eq. 5.1, p129) we see that the new term again has the raised power on the denominator, making it sharper than the original term. However, the most important difference is the \( \gamma_{\text{CM}}^2 - \Delta_{\text{CM}}^2 \) term in the numerator, since it is this that causes the side-lobes seen in the simulated \( \beta \) coefficients (Fig. 5.12).

Before implementing our new descriptions into a new VCSEL PR lineshape model we must mention one further finding. Recalling the simulated \( R \) spectrum in Fig. 5.8 on page 139, where \( \theta = 40^\circ \), we mentioned that the Lorentzian fit using Eq. 5.7 on page 135 was not as good as in the normal incidence spectrum of Fig. 5.5 (p136). We believe that this is due to the rapidly changing QW absorption that occurs near \( E_{\text{CM}}(40^\circ) \) (see Fig 5.3 on page 134), which creates an energy dependent broadening \( \gamma_{\text{CM}}(E) \), leading to a perturbed CM lineshape. In order to see this effect on the simulated Seraphin coefficients at \( \theta = 40^\circ \) we have plotted them here in figure 5.14.

The filled symbols in Fig. 5.14 show the simulated Seraphin coefficients and the solid curves show the best fits achieved using the new lineshapes (Eqs. 5.14, p144 & 5.17, p148). As expected, since \( R \) has a slightly perturbed shape, (due to the occurrence of the QW absorption edge this energy region) the two Seraphin coefficients also show a similar perturbed behaviour and the fits are not of the highest quality. Fortunately, we find that we can model this effect by introducing a phase mixing term \( \psi \) between the relationships for the Seraphin coefficients. This allows us to incorporate the effect of the form of the QW absorption edge on the Seraphin coefficients. For example, in the case of the \( \alpha \) coefficient we can account for both a change in the CM energy (caused by the modulation induced change to \( \epsilon_1 \)), and also a small change in CM broadening caused as the CM moves to an energy where the QWs within the cavity have a slightly different level of absorption. This latter effect is what we expect to observe from a modulation induced change to \( \epsilon_2 \), normally associated with the \( \beta \) Seraphin coefficient. It is only present here due to the
rapidly changing value of the QW absorption at these energies. Therefore, a slight phase mixing between the two Seraphin coefficient equations can account for such an effect. In order to do this here we may rewrite the Seraphin coefficients to include $\psi$, in the form with which they will appear in the enhanced VCSEL $PR$ model:

$$
\alpha - i\beta = \frac{iC e^{i\psi}}{(\Delta_{CM} - i\gamma_{CM})^2}
$$

(5.18)

To show the improvement of introducing the $\psi$ mixing term into the description of the Seraphin coefficients we display in figure 5.15 a fit using Eq. 5.18 (solid curves) to the simulated 40° data (closed symbols). It is clear from this that by allowing a slight mixing, using a value of $\psi = 352° \equiv -8°$, we are able to achieve fits of a very high quality, similar to the fits achieved for the normal incidence coefficients (Figs. 5.11, p145 & 5.12, p146).

The need for this phase mixing term to describe the VCSEL Seraphin
coefficients may have an important repercussion for the analysis of measured PR lineshapes—in particular, the use of the anti-symmetry theory for determining when VCSELs are tuned. [15] This is because in any VCSEL which demonstrates a clear relation between the CM broadening and the QW absorption (such as this one) the symmetry of the overall lineshape may be distorted by this phase mixing. When attempting to fit our measured PR of the 760 nm VCSEL wafer with the model developed here we shall also investigate the symmetry of the PR lineshape when $E_{CM}=E_{QW}$ to see if it is antisymmetric or not.

**Figure 5.15:** Simulated room-temperature Seraphin coefficients of the VCSEL structure at an angle of incidence of $\theta = 40^\circ$ (filled symbols). The solid curves show the least squares fits using Eq. 5.18, where the phase mixing parameter ($\psi$) has a value of $352^\circ$. 
5.3.2 An enhanced modulated reflectance lineshape model for VCSELs

The PR signal from a single layer in a structure can be written as equation 5.19.

\[ \Delta R/R = \text{Re} \left[ (\alpha - i\beta)(\Delta \varepsilon_1 + i\Delta \varepsilon_2) \right] \]  

(5.19)

Substituting our new model for the VCSEL Seraphin coefficients (Eq. 5.18) into this gives us the new, enhanced model for the PR of a VCSEL:

\[ \frac{\Delta R}{R} = \text{Re} \left[ (\alpha - i\beta)(\Delta \varepsilon_1 + i\Delta \varepsilon_2) \right] 
= \text{Re} \left[ \left( \frac{C}{(\Delta_{CM} - i\gamma_{CM})^2} \right) \left( \frac{e^{i\phi}}{(\Delta_{QW} + i\gamma_{QW})^n} \right) \right] \]  

(5.20)

Here, as in the established model, we have used Aspnes’ TDFF lineshape function [16] to describe the modulated dielectric function of the QW. Note that the amplitude of the TDFF has been absorbed into the amplitude of the Seraphin coefficients, C. Furthermore, the phase of the TDFF has been redefined to include the Seraphin coefficient phase mixing term, \( \psi \), of Eq. 5.18. In order to include multiple QW transitions (i.e. \( e_1hh_1 \) and \( e_1lh_1 \)) the \( \Delta \varepsilon_1 + i\Delta \varepsilon_2 \) term can be modified to include a linear sum of individual TDFF lineshapes.

5.4 Application of the new model: fitting the temperature dependent PR of the 760 nm VCSEL

Now that we have developed a new VCSEL PR model using Seraphin coefficients based on those observed in our simulations of a VCSEL structure very similar to that of the 760 nm VCSEL wafer investigated in chapter 3, we are now in a position to use it to fit those measured PR spectra. In this fitting of the measured PR we shall assume that the three QWs in the sample give the same contribution to the total PR, meaning we can use one single PR equation. We shall focus on fitting the high resolution, temperature dependent PR spectra of section 3.5, as opposed to the convoluted, low resolution angle dependent spectra of section 3.4, since the effects of the convolution
have not been considered in our new PR model.

Our first spectrum fitted with the enhanced lineshape model of Eq. 5.20 is the measurement recorded at a temperature of 150 °C. We showed previously how the established model was unable to reproduce the PR lineshape, especially when we constrained the QW energies to near their known values (Fig. 5.1, p126). Figure 5.16 shows this $T = 150$ °C, normal incidence PR measurement again (closed symbols) along with our earlier, unsuccessful, unconstrained fit using the established model (dashed curve). Also shown is the fit obtained using the new model (solid curve) with two TDFFs representing the QW $e_1hh_1$ and $e_1lh_1$ transitions. In this fit all parameters (except for the exponent $n$, which was fixed at 2.0) were allowed to vary freely. It is clear

![Figure 5.16: Measured normal incidence PR of the 760 nm VCSEL wafer recorded at 150 °C (filled symbols). The $e_1hh_1$ transition region below 1.618 eV has been magnified for clarity. The constrained least squares fit of the established model (Eq. 2.18, p. 37) is shown (dashed curve) as is the unconstrained least squares fit achieved using the enhanced lineshape model of Eq. 5.20 on page 152 (solid curve). The arrows mark the energies of the cavity mode and two quantum well transitions obtained from the enhanced model fit.](image)

from this that the new fit is of a very high quality: in both the magnified
region near the $e_1hh_1$ QW transition, and in the region of the CM, the fit reproduces the lineshape almost perfectly. In particular, the fit is able to reproduce the positions and amplitudes of the three lobes seen near the CM. We believe that it is the presence of the side-lobes in the form of the new $\beta$ coefficient that allows for such a high quality fit. Furthermore our fitted parameters agree well with our findings in section 3.5. The fitted value of the $e_1hh_1$ transition energy is $1.610 \pm 0.001$ eV and this agrees very well with the estimation of $1.613 \pm 0.005$ eV from Fig. 3.14 on page 70. Also, the fitted value of the $e_1lh_1$ transition is $1.624 \pm 0.001$ eV, some 14 meV above the $e_1hh_1$ energy. This energy difference is the same as that observed in the low resolution angle dependent PR spectra shown in Fig. 3.7 on page 59, indicating that the $e_1lh_1$ fitted energy is also at the expected value. Also from Fig. 3.14 we know the expected value for $E_{CM}$ is $1.6267 \pm 0.0002$ eV, which agrees very well with our fitted value of $1.6266 \pm 0.0001$ eV. Therefore it seems that this model, using the new Kramers-Kronig pair Seraphin coefficients, is able to reproduce the complex detail of the PR lineshapes observed for this high-quality 760 nm VCSEL. As we shall shortly demonstrate, similarly successful fits using this model were obtained in the temperature range $T = 100 - 180^\circ$C.

Despite the success of the new model at reproducing the lineshape of the $T = 150^\circ$C measurement, and others too, it is clear from Fig. 3.11 on page 66 that the lower temperature PR measurements ($T < 70^\circ$C) are of a form that cannot be reproduced using Seraphin coefficients whose amplitudes are strictly related via the Kramers-Kronig relations. For example, in the PR spectrum measured at $T = 50^\circ$C, the lineshape is a simple peak near $E_{CM}$. This indicates that here the $\beta$ term dominates over the $\alpha$ term. Furthermore, the PR does not show any side-lobes near $E_{CM}$, indicating that the $\beta$ term is likely to resemble the form of the original coefficient used in the established model discussed in section 2.2.4. In order to discover the reason for this we extended our $R$ simulations to also include the perturbing GaAs cap layer present in the 760 nm VCSEL which was omitted in the process of establishing Eq. 5.20 on page 152. Figure 5.17 shows the resulting simulated Seraphin coefficients for the normal incidence, room temperature condition.
From this we can see that including the GaAs cap layer has indeed had a pronounced effect on the Seraphin coefficients (c.f. Figs. 5.11, p145 & 5.12, p146 which give the same results but with the GaAs cap omitted). Now $\beta$

![Graph showing simulated room temperature normal incidence Seraphin coefficients](image)

**Figure 5.17:** The solid symbols show the Simulated room temperature, normal incidence Seraphin coefficients of the VCSEL structure, now including a GaAs cap layer similar to the one present in the 760 nm VCSEL wafer. The solid curves are a guide to the eye.

is considerably larger in magnitude than $\alpha$ and it has a simple dip shape, with no side-lobes. This is consistent with the observations of the lower temperature PR measurements ($T < 70 \, ^\circ C$) of the 760 nm VCSEL wafer (Fig. 3.11, p66). The $\alpha$ coefficient is relatively unaffected by the inclusion of the GaAs cap layer and its profile remains the same. We find from our simulations at higher angles of incidence, when the CM is closer to the QW transitions, that the effect of the cap layer on the $\beta$ coefficient is much less significant. Therefore, we believe that for the 760 nm VCSEL the Seraphin coefficients are most noticeably perturbed by the presence of the cap layer when the CM energy is in a region of low QW absorption. In order to overcome this complication, which is possibly unique to this sample, we use a 'hybrid' model to describe the PR at the lower temperatures. This hybrid
model contains two terms for each Seraphin coefficient; one from the new, enhanced model of Eq. 5.18 on page 150 \((\alpha_{\text{new}}, \beta_{\text{new}})\) and the other based on the Seraphin coefficients of the established model (Eq. 5.1, p129). However, in order to describe the perturbation of the cap layer we have empirically included an exponent \(m\) in the denominators of these extra terms. The two Seraphin coefficients for this hybrid model are then given by equations 5.21 and 5.22.

\[
\alpha_H = \alpha_{\text{new}} + I_{\alpha} \frac{\Delta_{CM}}{(\Delta_{CM}^2 + \gamma_{CM}^2)^m} \quad (5.21)
\]

\[
\beta_H = \beta_{\text{new}} + I_{\beta} \frac{\gamma'_{CM}}{(\Delta_{CM}^2 + \gamma_{CM}^2)^m} \quad (5.22)
\]

When fitting our measured PR spectra of the 760 nm VCSEL wafer we find that this approach is very successful if we use an empirical value of \(m=1.1\) rather than the value of 1.0 used in Eq. 5.1.

Figure 5.18 shows a fit using this hybrid model (solid curve) to the measured PR at \(T=50\) °C (open symbols). Here the Seraphin coefficients are dominated by the second terms in Eqs. 5.21 and 5.22, with \(C=0.002\) and \(I_{\beta}=0.19\). At this temperature the CM is at a much lower energy than the \(e_1h_1\) transition so does indeed lie in a region of low QW absorption. From Fig. 3.14 on page 70 we estimate their separation to be \(\sim 22\) meV. It is clear from the fit that the hybrid model approach has worked well as a method for describing this PR spectrum. Near the CM the fit reproduces the simple peak shape, while also reproducing the amplitude and shape of the \(e_1h_1\) feature. From the fit we obtain a value of \(E_{CM}=1.6372\) eV and this is very close to the value of 1.6374 eV measured in the \(R\) measurement shown in Fig. 3.13 (p69). For the \(e_1h_1\) transition we obtain a fitted energy of 1.660 eV, in good agreement with the estimated value of 1.659 ± 0.002 eV from Fig. 3.14. In the fit of Fig. 5.18 the \(e_1h_1\) transition, which lies approximately 14 meV above the \(e_1h_1\) transition (see Fig. 3.7, p59), could not be reliably included since its contribution was too small to the overall lineshape (a result of the large separation between it and the CM).

Figure 5.19 shows examples of the fitted PR spectra of the 760 nm VCSEL over the temperature range \(60 \leq T \leq 180\) °C. [17] For clarity, each successive
Figure 5.18: Measured normal incidence PR of the 760 nm VCSEL wafer recorded at a temperature of 50 °C (open symbols). The $e_1 hh_1$ transition region has been magnified for clarity. The least squares fit using the ‘hybrid’ model as described in the text is shown by the solid curve. The arrows mark the energies of the cavity mode and heavy-hole quantum well transition obtained from the fit.

spectrum is vertically offset from the previous one by an amount relative to the corresponding temperature change. Above 100 °C the fits use only the new model, with the KK pair Seraphin coefficients described by Eq. 5.18 on page 150. Below 100 °C the fits required the use of the hybrid model of Eqs. 5.21 and 5.22 on page 156. In all the fits we used a value of 2.0 for the exponent $n$ in the TDFFs (see Eq. 5.20) describing the $\Delta \varepsilon$ terms of the $e_1 hh_1$ and $e_1 lh_1$ transitions. It is clear from Fig. 5.19 that the fits are of a very high quality over the large range of temperatures shown. Before looking at them in detail it is useful to compare the amplitudes obtained from the fits of the newly developed Seraphin coefficients ($C$) with those of the added terms in the hybrid model – $I_\alpha$ and $I_\beta$ in Eqs. 5.21 and 5.22. Each parameter used in the fits of the $T$ dependent $PR$ spectra is listed in table 5.3. These were all free to vary during the least squares fitting of the
5. An enhanced modulated reflectance lineshape theory for vertical-cavity surface-emitting lasers

Figure 5.19: Example 760 nm VCSEL PR spectra measured at normal incidence as a function of temperature, $T$ (shown next to each spectrum). For clarity, baselines of the spectra are offset by amounts relative to the $T$ changes. The solid curves show the least squares fits with the enhanced model of Eq. 5.20 on page 152, except below 100 °C, where the fits use the hybrid Seraphin coefficient model of Eqs. 5.21 and 5.22 on page 156 as explained in the text. The dashed lines indicate the positions of the cavity mode energy and two lowest quantum well transitions determined from the fits. The dotted lines show the extrapolations of the $e_1lh$ energy beyond the range where it could be reliably fitted.
model. It is clear from this that the hybrid model is most influential at lower temperatures, where $I_\beta$ is largest. This corresponds to the conditions where the CM is in a region of low QW absorption, where our simulations indicate that the Seraphin coefficients are influenced by the cap layer (Fig. 5.17, p155). $I_\beta$ quickly reduces in magnitude with increasing temperature as the PR lineshape becomes influenced by the presence of the QWs as the QW-CM detuning is reduced. Then the new form Seraphin coefficients (Eqs. 5.14 and 5.17) begin to dominate over this $I_\beta$ contribution. $I_\alpha$ only ever has a small value and its contribution is minimal compared to the added $\beta$ term (see table 5.3). Figure 5.20 shows $I_\beta$ and $C$ plotted as a function of energy. Close to room temperature $I_\beta$ is particular large and we have to magnify $C$ so that it is visible on the vertical scale used. However, the very rapid decrease of $I_\beta$ is clear and from table 5.3 we can see that the two amplitudes
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Table 5.3: Parameters obtained in the least squares fits of the 760 nm VCSEL PR spectra (Fig 5.19) using the enhanced PR model (Eq. 5.20), except for $T < 100$ °C, where the hybrid model was used (see hybrid parameter columns).
become comparable when $T \approx 80 \, ^\circ\text{C}$. Above this temperature, $C > I_\beta$ and eventually $I_\beta \to 0$ at 100 °C. This smooth transition from the hybrid model, dominated initially by the added term with amplitude $I_\beta$, to exclusively the new model at $T = 100 \, ^\circ\text{C}$, suggests that the use of the hybrid model is acceptable for this sample.

Returning to the example PR spectra in Fig. 5.19 we see that throughout the range of temperatures shown the fits are of a very high quality. For the spectra in which $e_1 hh_1$ is well separated from $E_{CM}$ we have magnified the region of the QW transition. These spectra in particular (ie. at $T = 60, 160, \& 180 \, ^\circ\text{C}$) show how the fits are able to reproduce the lineshapes of both the CM and QW features. It is interesting to note that the PR near the $e_1 hh_1$ feature can be seen to have approximately the same profile in these magnified areas. This is a result of the large separation between the transition and the CM here, so that near the transition the Seraphin coefficients are slowly varying constants (similar to the PR of bulk materials [18]). Therefore, the PR lineshape near these magnified regions (e.g. near 1.655 eV at 60 °C) is virtually a linear combination of $\Delta e_1$ and $\Delta e_2$ for the QW transition.

As the VCSEL sample is heated above 60 °C the $e_1 hh_1$ PR feature can no longer be easily seen due to the interaction with the Seraphin coefficients of the CM feature. At around 80 °C, for example, the two features are separated by an amount ($\sim 14$ meV) comparable to the sum of their HWHMs ($\sim 9$ meV—table 5.3). As the sample is heated further the PR lineshape changes very rapidly as $e_1 hh_1$ is tuned through $E_{CM}$. This apparent 'phase rotation' of the PR near the CM is not actually due to changes in $\phi$, the phase of the $e_1 hh_1$ $\Delta e$ term, which can be seen to be approximately constant from table 5.3. The effect is actually caused by the movement of the multiplicative $e_1 hh_1 \Delta e$ term through the very sharp and detailed CM Seraphin coefficients.

The dashed lines in Fig. 5.19 show the fitted values of $E_{CM}$ and the energies of the two QW transitions. We were only able to reliably fit the $e_1 lh_1$ for a small range of temperatures ($120 \leq T \leq 160 \, ^\circ\text{C}$) where it was close enough to the CM to have a noticeable effect on the overall PR lineshape. For temperatures outside this range we have linearly extrapolated the temperature dependence of $e_1 lh_1$ and this is shown by the dotted lines.
5. An enhanced modulated reflectance lineshape theory for vertical-cavity surface-emitting lasers

Figure 5.21 shows the fitted energies, along with the broadening of the Seraphin coefficients ($\gamma'_{CM}$) obtained from the least squares fits. It is clear that these parameters evolve in a smooth and physically plausible way the expected behaviour from an appropriately applied lineshape model. We see from Fig. 5.21 that $E_{CM}$ and $E_{QW}(e_1lh_1)$ become equal at a temperature of $109 \pm 2$ °C, with the tuned energy equal to $1.6318 \pm 0.0002$ eV. This is close to the temperature and energy determined from Fig. 3.14 on page 70 ($T = 111 \pm 5$ °C, $E = 1.631 \pm 0.002$ eV), where the $E_{CM}$ values were determined directly from the measured $R$ spectra and $E_{QW}$ was linearly interpolated between temperatures at which the $PR$ modulus spectra could yield a value for the QW transition energy. Adding linear trends
to the fitted $E_{CM}$ and $E_{QW}$ values shown in Fig. 5.21 we find respective temperature coefficients of $\Delta E_{CM}/\Delta T = -0.11 \pm 0.01$ meV°C$^{-1}$ and $\Delta E_{QW}/\Delta T = -0.52 \pm 0.01$ meV°C$^{-1}$, which compare very well with the values of $\Delta E_{CM}/\Delta T = -0.11 \pm 0.01$ meV°C$^{-1}$ and $\Delta E_{QW}/\Delta T = -0.50 \pm 0.01$ meV°C$^{-1}$ determined from Fig. 3.14.

The temperature at which we find $E_{CM} = E_{QW}$ in Fig. 5.21 is slightly lower than the value of $T = 113.5 \pm 0.5$ °C, as determined from the evaluation of the lineshape symmetry obtained by fitting the PR with a single empirical TDFF (Fig. 3.17, p75). We believe that this small difference of $\sim 5$ °C is due to a slight distortion of the CM R feature in the present VCSEL caused by the excitonic peaks in the QW absorption spectrum. We saw this effect in our R simulations (Fig. 5.8, p139) and found that we could account for it by incorporating a phase mixing term ($\psi$) into the Seraphin coefficients (see Eq. 5.18 on page 150 and Fig. 5.15 on page 151). As we mentioned previously, the addition of such a term could have implications for the antisymmetry theory of VCSELs. This is because the theory that a VCSEL PR lineshape becomes antisymmetric when $E_{CM} = E_{QW}$ is true for VCSELs with Seraphin coefficients that contain no phase mixing (i.e. of the form of the established model, Eq. 5.1 on page 129). [15] Therefore, our fitted TDFF phase parameter, $\phi$, may contain some small, unknown varying value $\psi$, with the result that the PR lineshape is not quite perfectly antisymmetric when $E_{CM} = E_{QW}$. This effect, however, is only slight and our results confirm that antisymmetry is a good and simple indicator for judging when $E_{CM} = E_{QW}$.

Also shown in Fig. 5.21 is the fitted energy of the $e_1 h h_1$ transition. We were only able to fit this transition with confidence in the range $120 \leq T \leq 160$ °C where it had a noticeable effect on the PR lineshape. We find that it becomes tuned to the CM at an energy of $1.6272 \pm 0.0002$ eV, when $T = 143 \pm 2$ °C.

Looking at Fig. 5.21 we see that the fitted HWHM values of the VCSEL Seraphin coefficients ($\gamma_{CM}$) show two peaks, not dissimilar to the behaviour of $\gamma_{CM}$ measured directly from the R spectra (Fig. 3.24, p84). This is not surprising since we have already shown that there is a relation between $\gamma_{CM}$
and $\gamma_{CM}$ (Eq. 5.12, p143). The main peak in $\gamma_{CM}$ occurs when $T \sim 115$ °C, close to where we find that $E_{CM} = E_{QW}(e_1 \hbar h_1)$. The second, smaller peak, occurs at $T \sim 145$ °C and this coincides with the temperature of $T = 143 \pm 2$ °C at which our fits show $E_{CM} = E_{QW}(e_1 \hbar h_1)$.

5.5 Conclusions

Our simulations of the reflectance of a VCSEL structure chosen to be almost identical to the 760 nm VCSEL sample studied in chapter 3 have shown that the CM $R$ feature can be well modelled using a Lorentzian dip shape (Fig. 5.7, p135). Using the model of Tanguy et al. [4] we have been able to include an appropriate dielectric function for the QWs in the reflectance simulations of this VCSEL structure. By varying the angle of incidence in our simulations we were able to tune the VCSEL CM through the two included QW transitions and, from analysis of the fitted widths of the CM features, we observed a clear maximum in the CM dip broadening when the CM energy was tuned to either of the two QW transitions (Fig. 5.9, p141). This is evidence for the cavity mode broadening effect seen in the 760 nm VCSEL sample (Figs. 3.23 on page 83 & 3.24 on page 84), and implies that the width of the CM feature is indeed proportional to the level of absorption due to the QWs in this VCSEL structure.

We have also used these $R$ calculations to simulate the modulated reflectance Seraphin coefficients of the VCSEL structure. The resulting lineshapes demonstrated attributes that differed from those proposed empirically in the older established model. The $\alpha$ coefficient (Fig. 5.11, p145) appeared sharper than before and $\beta$ in particular was more complex, displaying side-lobes that could not be reproduced using the established model (Fig. 5.12, p146). We were able to write down expressions for the Seraphin coefficients, after finding that the natural log of the simulated reflectance could also be fitted with a Lorentzian dip (Fig. 5.10, p142). For $\alpha$ we used the approximation that $\partial R/\partial \varepsilon_1 \sim \partial R/\partial E_{CM}$, giving us a simple equation for this coefficient (Eq. 5.14, p144). A similar expression for $\beta$ was derived (Eq. 5.17, p148) using the approximation $\partial R/\partial \varepsilon_2 \sim \partial R/\partial \gamma_{CM}$. The reasoning for this ap-
proximation being justified on the basis that the width of the CM reflectance feature is related to the value of the QW $\varepsilon_2$ at the CM energy (Fig. 5.9, p141). Furthermore, we find that the simulated Seraphin coefficients are Kramers-Kronig pairs and we were able to demonstrate analytically why this could be so for a VCSEL (appendix B). We were then able to insert these new lineshapes for the Seraphin coefficients (including a phase mixing term to include the effect of energy dependent CM broadening) into the PR equation to give an enhanced VCSEL PR lineshape fitting model (Eq. 5.20, p152).

Once this new PR model was established we were able to use it to fit the temperature dependent PR spectra measured for the 760 nm VCSEL sample. We found that for temperatures above 100 °C we were able to fit all the PR spectra very successfully (Fig. 5.19, p158), indicating that the new model was very appropriate for the sample. For lower temperatures, however, we found that we had to use a 'hybrid' model to model the measured spectra. This essentially involved adding a simple empirical peak-like term to the new $\beta$ coefficient, somewhat akin to the older empirical form for $\beta$. Our reflectance simulations confirmed that this modification to the model was required only because of the GaAs cap layer present in this 760 nm VCSEL. This suggested that such a hybrid model would only be necessary in samples containing a cap which, like the present one, noticeably altered the profile of the reflectance spectra.

We believe, on the basis of the work carried out in this chapter, the new, more rigorous VCSEL PR model will be most appropriate when applied to VCSELs with sharp CM features, such as the 760 nm VCSEL studied in chapter 3. Furthermore, the side-lobes we see in the $\beta$ coefficient can only be explained if the cavity absorption and CM broadening are related in the fashion that we have established here. Therefore, we believe if a VCSEL sample displays this CM broadening effect, it will also exhibit PR spectra best described using the enhanced model developed here.
5.6 References


6 Mid-infrared photomodulated reflectance of InAs-rich InAsSb and GaInAsPSb alloys

6.1 Introduction

In this chapter we investigate the band structures of a selection of topical narrow gap semiconductors. Unlike the materials studied in the previous chapters, light emitted from narrow gap semiconductors appears in the mid-infrared (MIR) region of the electromagnetic spectrum (2-10 µm). For light to be emitted within the MIR, the band gap of a radiating semiconductor must be of the order of a few hundred meV, compared to semiconductors which emit light in the visible spectrum, which have band gaps of over a thousand meV. This is the reason why MIR emitting semiconductor materials are referred to as narrow gap semiconductors.

The MIR is a topical area of research owing to the number of interesting applications which exist in this part of the electromagnetic spectrum. One such application is gas sensing; many gases appearing in the Earth's atmosphere have strong absorption lines within the MIR and some of these are illustrated in figure 6.1. [1, 2] In this figure the lower axis represents the energy (in meV) of the absorption lines, and the upper axis gives the equivalent wavelength in microns (μm). Developing semiconductors to generate light at the wavelengths of these absorption lines provides potential candidate materials for gas sensing devices. Since the gases shown in Fig. 6.1 play important roles in atmospheric pollution, interest in producing semiconductors emitting light within this 3-5 μm MIR region is high (SO₂ for example is a major cause of acid rain [3] and CO, CO₂ & CH₄ are known to contribute to the atmospheric greenhouse effect [4]).

As well as the gas sensing applications which lie primarily in the 3-5 μm wavelength region, there are other interesting applications which may potentially utilise the wider MIR spectrum. Free space optical (FSO) communication is one such application, involving line of sight communication using lasers or LEDs. FSO communication is already used in both military and commercial contexts (see Ref. [5] for example). These systems currently use
near-infrared technology and their effective ranges are limited to a few kilometers. The MIR spectrum is attractive for FSO communication since at certain MIR wavelengths the atmosphere is > 80% transmissive (compared to just 60% in the visible spectrum (at 610 nm)). [6] These 'optical windows' in the atmosphere are ideal for FSO communication since the low-loss factors gives the potential for networks to span great distances.

To date, the majority of work on narrow gap semiconductors have used conventional techniques such as photoluminescence (PL) spectroscopy to study the properties of the materials. [7, 8, 9, 10] Such studies are useful for determining the fundamental $E_0$ band gap of a material. However, they cannot be used to determine the energies of higher-order transitions and so the level of information that can be determined is limited. As discussed in section 2.2, the technique of modulation spectroscopy allows greater detail regarding a semiconductor's band structure to be determined, making it a very powerful technique for material characterisation. Early electrolytic technique electromodulated reflectance (ER) studies of InAs and InSb yielded
good results. However, these studies were limited to measuring at energies above 1 eV (1.24 μm) due to the transmission properties of the electrolytic solutions used. [11] A more recent ER study in 1992 of InAsSbP grown on InAs using transparent, conductive Cu$_2$S Shottky barriers evaporated onto the sample surface yielded results for both the $E_0$ and $E_0+\Delta_0$ band gaps. [12] These measurements included spectra at energies as low as 500 meV (2.5 μm) demonstrating the viability of ER in the MIR. By requiring a conductive coating to be evaporated onto a sample’s surface such ER measurements involve a certain level of sample preparation work and as a result the measurements are generally considered to be destructive to the sample. In 1997 Lin et al. overcame this problem by demonstrating the first use of photomodulated reflectance (PR) in the MIR, when they reported PR measurements on InAs samples. [13] Our studies follow on from the initial work of Lin et al. and in the next section we describe our MIR PR experimental technique.

### 6.2 Mid-Infrared PR Experimental Technique

Figure 6.2 shows the MIR PR experimental setup developed here. Unlike the step-scan Fourier-transform (FTIR) system developed in our group by Merrick et al., [14, 15] the system used here employs grating spectroscopy. While the FTIR system is particularly suited to measuring in the mid-infrared, it is not so effective at shorter wavelengths, and as such we developed the grating MIR PR system to cover both the near and mid-infrared spectrum. Lin et al. also used a grating spectrometer to measure the first MIR PR results for InAs, proving that grating spectroscopy PR could be conducted at wavelengths as long as 3.5 μm. [13]

In our experimental setup we monochromate light at MIR wavelengths using a Triax 320 spectrometer fitted with a grating blazed at 5 μm. For measurements in the near-infrared (800-2000 nm) we use a grating blazed at 1.5 μm. Unlike Lin et al., who used a ceramic Nernst element as their MIR light source, we use a standard 100 W tungsten element in halogen gas with a quartz glass bulb (QTH source). We found that we could achieve useful light output as far out as ~4.8 μm with the QTH source, which is
Figure 6.2: Mid-infrared photomodulated reflectance experimental setup developed for these studies.

acceptable for these studies. This upper wavelength limit is restricted by the properties of the quartz bulb which stops transmitting near 3.5 μm. We suggest the extended output of the QTH source (to ~4.8 μm) that we see is partly due to infrared blackbody-like emission from the hot source as opposed to photons emitted directly from the tungsten filament and through the glass. Manufacturers of spectroscopic light sources claim that this makes standard QTH bulbs good IR sources. [16] We find the main advantage of using a QTH source rather than a Nernst element is that the visible output of the filament can be used to trace the light path through the experiment. This simplifies the process of optimising the experimental setup, which is crucial in PR spectroscopy since the pump and probe beams must be well-aligned on the sample surface.

Rather than using lenses in the setup we use off-axis 90° parabolic mirrors to collimate and focus the light. Although the experimental setup is slightly
complicated by using mirrors rather than lenses, we find the high collection efficiencies of the reflectors is an advantage. The light path can be seen in Fig. 6.2, where each mirror diverts the light path by 90°. It is important to use the 90° mirrors in this way to minimise any aberration caused by the reflectors.

For our modulation source we use a ~ 10 mW HeNe laser, emitting light at 633 nm, in the same way as in our conventional visible/near-infrared PR experiments. During experiments at low temperatures \((T < 50 \text{ K})\) it is often necessary to use neutral density (ND) filters to reduce the intensity of the modulation laser so that the large background levels can be reduced to manageable levels. These backgrounds are caused by PL emitted from samples, which is strongest, and most detrimental to the PR signals at low temperatures. In order to cool samples below room temperature, and to as low as 10 K, we mounted them in a closed cycle Helium cryostat. The window of the cryostat is made from quartz, which, due to the presence of water within the glass, has poor transmission properties near 2.74 \(\mu\text{m}\). This is illustrated in figure 6.3, where the measured transmission of the cryostat window is plotted. It can be seen that the transmission reduces from greater than 80% to around just 20% as a result of the water in the quartz glass. Although not ideal, luckily this does not particularly effect us here since the poor transmission is confined to just a small wavelength region (2.6-2.9 \(\mu\text{m}\)).

When conducting grating spectroscopy it is necessary to use order-sorting filters so as to cut-out any light diffracted at high-orders. This is particularly important in our MIR studies, since much of the emission from the QTH source appears in the visible spectrum. Sourcing order-sorting filters for the MIR spectrum is difficult since traditional coloured glass filters are not very transmissive at these wavelengths and filters based on interference or scattering principals tend to be costly. Therefore, in terms of this problem, it would have been beneficial to use a cooler Nernst source, which would emit less photons in the visible waveband than a QTH source. However, we opted to use the QTII source to ensure we obtained the best possible optical alignment in our PR experiments.

We use a piece of high-purity epitaxial GaSb on GaAs as an order-sorting
6. Mid-infrared photomodulated reflectance of InAs-rich InAsSb and GaInAsSb alloys

![Graph of measured transmission](image)

**Figure 6.3:** Measured transmission of the quartz cryostat window used in the mid-infrared photomodulated reflectance experimental setup.

During the experiments conducted in this work the piece of GaSb on GaAs was the longest wavelength filter we had at our disposal. Our attempts to use InAs samples as filters were unsuccessful due to the absorption of longer wavelengths in the material caused by the presence of free-carriers. Even in samples with low doping concentrations this free-carrier absorption was found to be a problem. Using a classical description of the free-carrier absorption process it can be shown that the strength of the absorption increases with the second power of the wavelength. This makes it a particularly prominent process in narrow gap semiconductors such as InAs.
In order to detect the MIR reflectance and PR signals we use a Cincinnati Electronics InSb photodiode, cooled using liquid nitrogen to 77 K to improve its performance.

6.3 Sample Details

Before discussing the measured results, we shall first discuss the two series of samples studied here.

6.3.1 InAsSb Samples

The first series of samples studied in detail using our MIR PR setup is a set of seven InAs-rich InAs$_{1-x}$Sb$_x$ samples grown on InAs by Molecular Beam Epitaxy (MBE). The samples were grown by the National Taiwan University and supplied to us by Lancaster University in the UK.
InAs$_{1-x}$Sb$_x$ is an important semiconductor alloy for MIR applications and devices [19, 20, 21] owing to the wide range of band gap energies that can be achieved by varying the Sb content. InAs has a room temperature band gap of 354 meV (3.5 µm) and that of InSb is just 174 meV (7.1 µm) – the smallest band gap (longest wavelength) of all the binary III-V semiconductors. [17] Therefore, both constituent binary semiconductors have their band gaps in the MIR. Furthermore, the strong positive bowing $^1$ observed for the ternary band gap energy means that for certain Sb concentrations the band gap of the alloy is smaller than that of InSb. [22] For example, when $x = 63\%$, InAs$_{1-x}$Sb$_x$ has a room temperature band gap of just 84 meV (14.7 µm). [17]

The first column in table 6.1 on page 185 gives the names of the samples to which we will refer throughout this work. The next two columns give two possible values for the Sb content of each sample, as determined by X-ray diffraction measurements carried out by the National Taiwan University. The reason for quoting two values is related to the possibility of strain within the epilayers which may exist due to the large lattice mismatch between InAs (6.0583 Å) and InSb (6.4794 Å). [17] Note: these are the room temperature lattice constant values. The second column in the table gives the concentrations assuming that the InAs$_{1-x}$Sb$_x$ epilayers are fully-relaxed, whereas the third column gives the concentrations assuming that they are fully-strained. This limitation of the particular X-ray diffraction technique used to characterise the samples is a potential problem since the range of possible Sb concentrations for each sample is large. For example, sample R1966 has a range of concentrations from 11.0% < $x$ < 22.5% and the actual value will depend on the level of strain within the epilayer. Fortunately, the InAs$_{1-x}$Sb$_x$ epilayers in these samples have been grown to 0.5 µm thickness, and layers this thick are likely to be relaxed, with dislocations near the InAs$_{1-x}$Sb$_x$/InAs interface taking up much of the strain. We can make this assumption because the layers are ~ 5 times thicker than the estimated critical thicknesses of the epilayers [23] and for such thick layers one may well expect near full relaxation to occur. [24] Therefore, we shall make the assumption here that

$^1$See appendix C on page 253 for an explanation of the bowing behaviour in ternary semiconductors.
the layers are fully-relaxed and utilise the Sb concentrations in column two of table 6.1. Without meaning to preempt the major findings of this chapter at this early stage we note here that even if the materials were fully strained our key findings would still hold, with any strain-induced effects being less than the alloy-dependent effects of interest in this work. Therefore, our assumption that the layers are fully-relaxed does not pose a significant risk to our findings. We shall return to this point when discussing the results later in the chapter.

The principle reason for studying this series of InAs$_{1-x}$Sb$_x$ samples here is to use MIR PR for the first time to measure both the fundamental band gap energy ($E_0$) and the spin-orbit splitting energy ($\Delta_0$) of these materials. There is a reasonable amount of information regarding $E_0$ in the literature, [22, 25, 26] based on both transmission and PL measurements. The more recent measurements of $E_0$ as a function of Sb content yield similar values to each other for the band gap bowing parameter in InAs$_{1-x}$Sb$_x$, and the review by Vurgaftman et al. recommends using a value of $\gamma(E_0) = +670$ meV. [17] Note: throughout this chapter we shall use $\gamma$ to represent the bowing parameter so as to be consistent with the equations in appendix C.

While much information regarding $E_0$ in InAsSb exists in the literature, the same is not true for the value of $\Delta_0$. The first value for the bowing of the spin-orbit splitting energy ($\gamma(\Delta_0)$) in InAs$_{1-x}$Sb$_x$ was reported by Berolo and Woolley in 1972 [27] and was based on samples grown by the Horizontal Bridgman technique. [22] The authors presented results for the values of $\Delta_0$ based on electroreflectance measurements (although none of their measured spectra were shown) which indicated that the bowing was $\gamma(\Delta_0) = +1170$ meV. This large, positive bowing is the largest of all the ternary alloys [17] and the authors suggested that the bowing (and similar positive bowing observed by them in other ternary alloys) was a result of band mixing effects and disordering within the lattice. [28]

Several authors have since questioned the results of Berolo and Woolley, remarking that a positive bowing (i.e. $\gamma(\Delta_0) > 0$) is not predicted for ordered systems. Siggia notes that his calculations can only demonstrate the bowing observed by Berolo and Woolley if he doubles the value of the Kane-formula.
conduction band effective mass, which would then disagree with the experimentally measured effective mass value. [29] In the early 1980's, as researchers began studying more complex quaternary alloy systems such as InGaAlAs and InGaAsP, authors began reporting values of $\gamma(\Delta_0) < 0$, [30, 31, 32] which did not fit with the findings of Berolo et al. from their earlier measurements on ternary alloys. [27, 28] This prompted Wei and Zunger to conduct self-consistent electronic-structure calculations for ordered ternary alloys, the results of which predicted that $\gamma(\Delta_0) < 0$. [33] For InAs$_{1-x}$Sb$_x$ they were able to show that an unphysically large interband mixing of 48% was required to obtain the large positive bowing reported by Berolo and Woolley. [27] They suggested a possible cause of the strong positive bowing seen by Berolo and Woolley could be sample inhomogeneity and recommended conducting measurements of $\Delta_0$ in homogeneous, epitaxial samples.

By studying the series of high-quality, epitaxial InAs$_{1-x}$Sb$_x$ samples here we hope to determine if the bowing of $\Delta_0$ is large and positive as per Berolo and Woolley [27] or if it is indeed negative as predicted by Wei and Zunger. [33] Within our series of InAs-rich samples the Sb content ranges from 0% to 22.5% and this will hopefully be extensive enough to gain insight into the behaviour of $\Delta_0$ with Sb content in InAs$_{1-x}$Sb$_x$.

Since our focus in this chapter is primarily on the fundamental band structure of the InAs$_{1-x}$Sb$_x$ ternary alloy, and specifically how $\Delta_0$ varies across the alloy range, we choose to restrict our investigations into other interesting phenomenon observed in this work. Such investigations could form part of an extension to this study, and throughout the discussion of the results in this chapter we shall highlight where we feel further investigation may be of scientific interest.

### 6.3.2 GaInAsPSb Samples

As well as studying the series of MBE grown InAs$_{1-x}$Sb$_x$ samples here we shall also study four Ga$_x$In$_{1-x}$As$_{1-y}$P$_y$Sb$_x$ pentenary alloys grown lattice matched to GaSb by Liquid Phase Epitaxy (LPE) at the University of Lancaster. These samples are rich in InAsSb, and should have their fundamental
band gaps in the MIR. These pentenary alloys are particularly interesting since when designing them it is possible to vary say $\Delta_0$ for a given fixed value of $E_0$ or lattice constant. This is due to the high degree of freedom which comes from having five elements within the alloy. [34] This is a useful property in narrow gap semiconductors, which, due to their small band gaps, are particularly affected by non-radiative recombination mechanisms such as Auger recombination and inter-valence band absorption. The ability to control both $E_0$ and $\Delta_0$ in a material means that it is possible to reduce the coefficient of say the conduction, heavy-hole, spin split-off hole, heavy-hole (CIISHI) Auger recombination process, [35] which could result in an improved performance of an optoelectronic device fabricated from the material.

Table 6.3 on page 214 lists the details of the four pentenary samples studied. The names of the samples, to which we will refer, are listed in the first column of the table. The compositions of the samples are also shown, determined from X-ray diffraction measurements carried out at the University of Lancaster. For sample s947 the composition is unknown since no X-ray diffraction measurements were conducted on this sample.

The precise thicknesses of the pentenary epilayers is unknown. However they are known to be between 1.5 $\mu$m and 2.0 $\mu$m thick. From inspection the samples were seen to have mirror-like surfaces. Studies on similar samples grown by the same group have shown strong PL emission indicating the good optical quality of the materials. [36, 37] The epilayers are undoped (n-type), grown on undoped, p-type GaSb buffer layers on p-doped GaSb substrates. The samples were designed to be processed into LEDs. Details of the growth process of these pentenary alloys can be found in Ref. [36].

6.4 Results and discussion

6.4.1 Temperature dependent PR studies of InAsSb

The first sample measured in the series of InAs$_{1-x}$Sb$_x$ samples is R1965. From table 6.1 (p. 185) it can be seen that R1965 contains 0.0% Sb and is therefore equivalent to the binary semiconductor InAs. Figure 6.5 shows the measured PR spectra in the energy region of the $E_0$ feature for R1965.
over the temperature range studied \((10 \leq T \leq 300 \text{ K})\). The solid-vertical curve is a guide to the eye, indicating the approximate position of \(E_0\). It can be seen from this that we have been successful in measuring \(PR\) signals from the fundamental band gap of R1965 from low temperatures up to room temperature. The strength of the signal, especially at room temperature, compared to previous InAs samples measured using this setup\(^2\) [38] indicates that this is a sample of high quality. The measurement at \(T = 10 \text{ K}\) was conducted using a neutral density (ND) filter to reduce the power of the \(\sim 10 \text{ mW}\) modulation laser to \(\sim 1 \text{ mW}\) so that the strong background PL signal could be reduced to give the best possible signal to noise ratio. Above 50 K the measurements were conducted using spectrometer slit widths of 1 mm (corresponds to an instrumental resolution of \(\sim 10 \text{ nm}\)) so that the sharp detail in the spectra could resolved. All other measurements on this sample, and in the remainder of this chapter, were conducted using slit widths of 2 mm (instrumental resolution of \(\sim 20 \text{ nm}\)).

From Fig. 6.5 the red-shift of \(E_0\) to longer wavelengths with increasing temperature is clear. In order to ascertain the band gap energy at each temperature we first attempted to fit the spectra with the appropriate TDFF lineshape fitting function. [39] For some of the spectra this fitting process was straightforward. However, as can be seen from Fig. 6.5, at certain temperatures the spectra become rather complicated (e.g. \(T = 200 \text{ K}\)), making fitting with TDFF functions difficult. We have previously seen similar detail in other InAs samples, [38] and currently we are unable to explain such features. We believe one possible explanation is that they are due to weak Franz-Keldysh oscillations. However, the evidence for this is not strong and it would require further investigation to confirm this. Fortunately, we find that we are able to use the modulus spectrum technique as described in section 2.2.2 (Eq. 2.15, p. 31) to determine the values of \(E_0\). For each of the measured spectra this gives a single clear peak from which we can infer the position of \(E_0\). Figure 6.6 shows an example of the modulus of the \(PR\)

\(^2\)The experimental setup was developed by the author in conjunction with Merrick and Hosea and the first results using the setup were published in the PhD thesis of M.N. Merrick. [38]
6. Mid-infrared photomodulated reflectance of InAs-rich InAsSb and GaInAsPSb alloys

Figure 6.5: Temperature dependent photomodulated reflectance spectra of sample R1965 (InAs$_{1-x}$Sbx, $x = 0\%$) in the energy region of the fundamental band gap, $E_0$. Successive spectra are vertically offset for clarity. The vertical curve is a guide to the eye showing the approximate variation of the $E_0$ energy. The data are plotted as a function of energy and for comparison, the upper axis (not linear) shows the corresponding wavelengths.
spectrum recorded at $T = 10$ K. This shows a clear peak at the position of the critical point transition, giving $E_0 = 414 \pm 1$ meV for R1965 at 10 K. From table 6.1 (p. 185) we see that the value adopted in Ref. [17] for InAs is slightly higher at 417 meV. However, this Ref. quotes a range of values for $E_0$ from 410-420 meV so our measured value falls within this range. Our value also agrees with the 10 K PL measurement conducted at Lancaster university using a high power Ar$^+$ laser (not shown) – the PL peak position for the sample is shown in column five in table 6.1. From Fig. 6.6 we measure the full-width at half-maximum (FWHM) of the $PR$ modulus peak for R1965 at 8 meV. This is around half as broad as the 10 K PL peak (not shown), which had a FWHM of 20 meV (table 6.1). This allows us to determine the value of $E_0$ with greater accuracy than is possible from the broader PL measurement.

Figure 6.7 shows the modulus spectrum of the $T = 300$ K $PR$ measurement of R1965 shown in Fig. 6.5. As in the modulus spectrum at low temperature we see a clear peak. However, it is thermally broadened by the increase in temperature so that $\Gamma_{300K} \sim 11$ meV. From the peak in the modu-
Figure 6.7: PR modulus spectrum of sample R1965 (InAs$_{1-x}$Sb$_x$, $x = 0\%$) at $T = 300$ K. The vertical dashed line marks the energy of the fundamental band gap, $E_0 = 361$ meV. The FWHM ($\Gamma$) of the feature is 11 meV.

In the PR spectrum we find that when $T = 300$ K, $E_0 = 361 \pm 3$ meV, 53 meV lower than the $T = 10$ K value. In order to compare the temperature dependence of R1965 with that reported in the literature for InAs we fit our temperature dependent $E_0$ values as determined from the PR spectra of Fig. 6.5 with a Varshni relationship: [40]

$$E_0(T) = E_0(T = 0\ K) - \frac{\alpha T^2}{\beta + T}$$

(6.1)

Where $\alpha$ and $\beta$ are known as the Varshni parameters.

Figure 6.8 shows the PR modulus values of $E_0$ for R1965 (solid symbols) plotted as a function of temperature. The error bars represent the uncertainty in determining the $E_0$ value from the respective PR modulus spectra. The solid curve in Fig. 6.8 shows the fit of the Varshni equation for our PR determined values of $E_0$ for sample R1965. The quality of the fit is good and from it we obtain values of $\alpha = 0.284$ meV/K and $\beta = 187$ K. These differ to the values listed in Ref. [17], where $\alpha = 0.276$ meV/K and $\beta = 93$ K.
The temperature dependence of $E_0$ using the Ref. [17] Varshni parameters is also displayed in Fig. 6.8, represented by the dashed curve. Comparing the two curves it is clear that we see a slightly different temperature dependence to that given in Ref. [17]. This appears primarily due to us measuring higher values for $E_0$ than are stated in the literature, especially at higher temperatures.

As we mentioned previously, the main reason for studying these InAs$_{1-x}$Sb$_x$ samples is to determine the value for the bowing parameter of the spin-orbit splitting energy ($\gamma(\Delta_0)$). In order to measure the $\Delta_0$ energy in a semiconductor using PR it is necessary to scan in the energy region near $E_0 + \Delta_0$. A critical point occurs in the joint-density of states at this energy, associated with photon absorption promoting electrons in the spin-orbit split-off valence band into the conduction band. This process is illustrated schematically in figure 6.9.

By measuring the PR spectra of both the $E_0$ and $E_0 + \Delta_0$ features one can subtract the two energies once known to reveal the value for $\Delta_0$. Figure 6.10
shows a PR spectrum of sample R1965 in the near infrared $E_0 + \Delta_0$ energy region, measured at $T = 10$ K (filled symbols). The PR spectrum in Fig. 6.10 was recorded using the 1 $\mu$m blazed grating, which is more efficient at these near-infrared wavelengths than the 5 $\mu$m blazed grating used for the MIR PR measurements of the $E_0$ feature. The solid curve shows a TDFF fit to the feature which gives a value of $E_0 + \Delta_0 = 787 \pm 10$ meV. From the aforementioned value for $E_0$ at 10 K of 414 meV this gives us $\Delta_0 = 373 \pm 10$ meV for sample R1965. This is lower than the recommended value in Ref. [17] for InAs, which from table 6.1 (p. 185) can be seen to be 390 meV. However, the range of quoted values for $\Delta_0$ in Ref. [17] is 370-410 meV so our value lies within the low end of this range.

This positive result shows that we are able to measure the feature related to the spin-orbit splitting energy in this sample as required to determine the value of $\Delta_0$. If we are successful in doing this for the other InAs$_{1-x}$Sb$_x$ samples we will be able to examine how $\Delta_0$ varies with Sb content and
compare our results with the results of Berolo and Woolley. [27]

The next sample to be studied in the series is R1968, which has an Sb concentration of 4.3\% (assuming full-relaxation of the epilayer). Figure 6.11 shows the temperature dependent PR spectra in the vicinity of the fundamental band gap feature. As with sample R1965 we are able to observe a PR signal from low temperatures up to room temperature for this sample. At low temperatures \((T < 150 \text{ K})\) we only observe one feature, from the InAs\(_{1-x}\)Sb\(_x\) epilayer. Its approximate position is marked with the first solid vertical curve. However, as the temperature is increased we begin to observe a second feature at higher energies. The intensity of this feature relative to the first increases with temperature and its position is indicated approximately by the second vertical curve. We believe that the feature at higher energies is the \(E_0\) feature of the InAs substrate. One possible explanation for why the substrate \(E_0\) feature is not visible at low temperatures could be that
### Table 6.1: Details of the MBE grown InAs$_{1-x}$Sb$_x$ samples studied in this work.

The Sb concentrations have been determined from X-ray diffraction measurement, giving two possible values for each sample; one assumes the sample is fully-relaxed (f.r.) and the other, fully-strained (f.s.). Data in the columns with headings showing the superscript $^1$ have been interpolated from the data in Ref. [17] (assuming full-relaxation in all samples). The experimentally determined data measured using both PL and PR are also shown. $E_0$ is the fundamental band gap energy at 10 K and $\Gamma$ is the FWHM broadening of the transition. $\Delta_0$ is the spin-orbit splitting energy, and $\alpha$ and $\beta$ are the Varshni coefficients (Eq. 6.1, p. 181).

| Sample name | Sb conc. % (f.r.) | Sb conc. % (f.s.) | $E_0^1$ (meV) | $E_0^{PL}$ (meV) | $E_0^{PR}$ (meV) | $\Gamma^{PL}$ (meV) | $\Gamma^{PR}$ (meV) | $\Delta_0^1$ (meV) | $\Delta_0^{PR}$ (meV) | $\alpha^1$ (meV/K) | $\beta^1$ (K) | $\alpha^{PR}$ (meV/K) | $\beta^{PR}$ (K) |
|-------------|------------------|------------------|--------------|-----------------|-----------------|-----------------|-----------------|----------------|-----------------|----------------|$\alpha^{PR}$ | $\beta^{PR}$ |
| R1965       | 0.0              | 0.0              | 417          | 414 ± 2         | 414 ± 1         | 20              | 8               | 390            | 373 ± 10        | 0.276          | 93             | 0.284         | 187           |
| R1968       | 4.3              | 2.1              | 382          | 397 ± 3         | 395 ± 1         | 27              | 8               | 359            | 398 ± 10        | 0.278          | 96             | 0.302         | 180           |
| R1970       | 6.9              | 3.3              | 361          | 383 ± 2         | 384 ± 2         | 22              | 10              | 342            | 417 ± 15        | 0.279          | 98             | 0.510         | 547           |
| R1971       | 9.0              | 4.3              | 346          | 369 ± 4         | 365 ± 3         | 27              | 12              | 330            | 429 ± 15        | 0.280          | 100            | -             | -             |
| R1967       | 15.5             | 7.3              | 301          | 333 ± 5         | 327 ± 4         | 32              | 10              | 298            | 459 ± 20        | 0.283          | 105            | -             | -             |
| R1972       | 16.0             | 7.5              | 298          | 317 ± 4         | 319 ± 3         | 29              | 11              | 296            | -               | 0.283          | 105            | -             | -             |
| R1966       | 22.5             | 11.0             | 259          | 268 ± 4         | 261 ± 4         | 28              | 20              | 275            | -               | 0.286          | 110            | -             | -             |
Figure 6.11: Temperature dependent PR spectra of sample R1968 (\(\text{InAs}_{1-x}\text{Sb}_x\), \(x = 4.3\%\)) in the energy region of the fundamental band gap, \(E_0\). Successive spectra are vertically offset for clarity. The vertical curve extending to the lowest temperatures is a guide to the eye showing the approximate variation of \(E_0\) for the InAsSb epilayer. The second vertical curve, beginning at \(T = 150\) K, marks the fundamental band gap of the InAs substrate, whose PR signal becomes discernible above this temperature.
the HeNe laser and/or monochromated probe light is more strongly absorbed within the InAs$_{1-x}$Sb$_x$ epilayer at low $T$. If either were completely absorbed within the epilayer then no PR signal would be produced from the substrate layer. For this reason one might expect to observe an $E_0$ PR signal from the substrate as well as the epilayer as the temperature was increased if the thermal broadening of the epilayer absorption edge reduced the absorption coefficient for photons of energy equal to $E_0$ of the substrate.

Calculating the modulus of each of the PR spectra in Fig. 6.11 enables us to determine the values of $E_0$ as was done for sample R1965. Figure 6.12 shows the resulting values of $E_0$, fitted with a Varshni relationship (solid curve – Eq. 6.1). Also shown (dashed curve) is the literature expected behaviour, interpolated from the parameters in Ref. [17]. From this it is clear that our measured temperature dependence of R1968 is very similar to that of the literature expected behaviour. However, at all temperatures there is an almost constant energy difference of $\sim 10$ meV between the two values of $E_0$. This difference could potentially be caused by the presence of strain in the InAs$_{1-x}$Sb$_x$ epilayers, which we presumed to be unstrained. Using strain

![Figure 6.12: Varshni fit (solid curve) of the temperature dependence of $E_0$ (solid symbols) for sample R1968 (InAs$_{1-x}$Sb$_x$, $x = 4.3\%$) determined from the PR spectra in Fig. 6.11. The dashed curve displays the literature expected behaviour. [17]](image)
calculations [41] and parameters in Ref. [17] we find that if the InAs\(_{1-x}\)Sb\(_x\) layer of R1968 was fully strained the band gap would increase by around 5 meV. This is not enough to explain the difference between our measured \(E_0\) values and the literature values and, furthermore, a fully strained 0.5 \(\mu\)m epilayer is highly unlikely since it is considerably larger than the critical thickness. [23] Therefore, we do not believe strain is causing the energy difference seen in Fig. 6.12. As we shall see in section 6.4.3, when we compare our low temperature measurements and the results of other authors with the values predicted using the literature bowing of \(\gamma(E_0) = +670\) meV, we find it is common that the measured values of \(E_0\) lie several meV above the predicted values.

Figure 6.13 shows the measured \(PR\) spectra of sample R1968 in the region of the \(E_0 + \Delta_0\) transition for the range of temperatures in which we could observe a \(PR\) feature. For R1968 we are able to measure the \(E_0 + \Delta_0\) feature up to \(T = 175\) K. The solid curves through the data show the TDDF fits used to determine the values of \(E_0 + \Delta_0\). The vertical curve is a guide to the eye, indicating the approximate position of the transition energy with temperature. Subtracting the values of \(E_0\) as determined from the spectra in Fig. 6.11 gives us the values of \(\Delta_0\) at the four temperatures. When \(T = 10\) K we find that \(\Delta_0 = 398 \pm 10\) meV, some 40 meV greater than the value obtained through interpolation of the literature values [17] and using the bowing parameter of Berolo and Woolley [27], which gives a value of 359 meV (see table 6.1 on page 185). In section 6.4.3 we shall discuss this difference in more detail.

Table 6.2 lists the measured values of \(E_0\), \(E_0 + \Delta_0\) and the resulting \(\Delta_0\) values for sample R1968. It is clear from this that the value of splitting energy is constant to within a few meV over the temperature range 10 K \(\leq T \leq 175\) K. It is expected that \(\Delta_0\) is independent of temperature since the spin-orbit splitting is an atomic process, not dominated by thermal effects [42] and our results appear to be consistent with this.

For these InAs\(_{1-x}\)Sb\(_x\) epilayers grown on InAs there is a possibility that we may observe \(PR\) features from both the \(E_0\) and \(E_0 + \Delta_0\) transitions of the InAs substrate as well as the epilayers in which we are interested. Indeed we
Figure 6.13: Temperature dependent photomodulated reflectance spectra of sample R1968 (InAs$_{1-x}$Sb$_x$, $x = 4.3\%$) in the region of the $E_0 + \Delta_0$ transition (filled symbols). The solid curves show TDFF fits to the data and the vertical curve indicates the approximate variation of the fitted $E_0 + \Delta_0$ energies with temperature.
have already seen in Fig. 6.11 (p. 186) that for temperatures above 150 K we observe a PR feature from the $E_0$ transition of the substrate layer in R1968. The existence of a discernible feature from the fundamental band gap of the substrate in a sample is not a problem since it is well separated from the $E_0$ feature of the epilayer, due to the Sb content. More of a problem could be a PR signal from the $E_0 + \Delta_0$ transition of the substrate since the bowing of the spin-orbit splitting energy is under investigation in this work and there is a possibility that we might mistake a PR feature as being from the epilayer when in reality it is wholly or partly from the substrate. To ensure we do not mistake any PR features in each sample we shall be careful to investigate each spectrum in detail. If we take the PR spectrum of the $E_0$ feature in R1968 measured at $T = 10$ K as an example (Fig. 6.11) we see no PR feature from $E_0$ of the substrate at this temperature ($E \sim 415$ meV). Since we see no PR feature from the fundamental band gap of the substrate, the likelihood of observing a feature from the spin split-off transition must be very small since a PR feature from this transition is always considerably weaker than that of the $E_0$ transition. [11, 13] Therefore, if the $E_0$ substrate signal is so weak that it cannot be discerned then the same must be true for the $E_0 + \Delta_0$ feature. Furthermore, the InAs$_{1-x}$Sb$_x$ epilayer will tend to filter out short wavelength light at energies greater than its $E_0$ band gap so that photons with such energy will be strongly absorbed before reaching the InAs substrate. In order to observe a PR feature from the $E_0 + \Delta_0$ feature of the substrate, light from the spectrometer would need to travel through the 500 nm thick InAs$_{1-x}$Sb$_x$ epilayer (and back) and the penetration depth of the light through the epilayer at the wavelength of the $E_0 + \Delta_0$ transition.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$E_0$ (meV)</th>
<th>$E_0 + \Delta_0$ (meV)</th>
<th>$\Delta_0$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>395 ± 1</td>
<td>793 ± 10</td>
<td>398 ± 10</td>
</tr>
<tr>
<td>77</td>
<td>391 ± 1</td>
<td>790 ± 10</td>
<td>399 ± 10</td>
</tr>
<tr>
<td>125</td>
<td>382 ± 1</td>
<td>781 ± 12</td>
<td>399 ± 12</td>
</tr>
<tr>
<td>175</td>
<td>370 ± 2</td>
<td>767 ± 15</td>
<td>397 ± 15</td>
</tr>
</tbody>
</table>

Table 6.2: Temperature dependence of our measured values of $E_0$ and $E_0 + \Delta_0$ for sample R1968.
of the substrate is approximately half that of light at the wavelength of the $E_0$ gap of the substrate. Therefore, if we do not detect a feature from the substrate $E_0$ transition there is a very much reduced possibility of detecting the higher-energy $E_0 + \Delta_0$ substrate feature.

The arguments outlined above can be repeated here in the following list so that they can be referred to quickly in the discussions of the other samples studied in this work:

*At a given temperature, if the $E_0$ InAs substrate PR signal is too weak to be discerned, it follows that the $E_0 + \Delta_0$ feature will also be undetectable since*

- $E_0 + \Delta_0$ PR features are, by their nature, considerably weaker than those of $E_0$ features.

- the absorption coefficient in an InAsSb epilayer will be greater at the higher energy of an $E_0 + \Delta_0$ substrate feature than at the energy of an $E_0$ substrate feature. The extra attenuation of light at the higher energy will thus reduce the relative strength of an $E_0 + \Delta_0$ substrate feature compared to a lower energy $E_0$ feature.

The next sample of the series to be studied is R1970, which, as can be seen from table 6.1, contains 6.9% Sb. Figure 6.14 shows our measured PR spectra for this sample in the region of the $E_0$ transition. As for the previous two samples studied we were able to measure PR signals for R1970 from low temperature up to room temperature. The first of the two vertical, solid curves (at lower energy) marks the approximate movement of the fundamental band gap of the epilayer. The spectra are comparatively as well defined as in the samples with lower Sb content, indicating that the optical quality of the sample has not been compromised by increasing the Sb content. We measure the FWHM of the PR feature at 10 K to be 10 meV – only 2 meV broader than the equivalent feature in sample R1965.

Similar to R1968 (Fig. 6.11, p. 186), we see a second feature in the PR spectra as the temperature is increased from the $E_0$ gap of the InAs substrate. In R1970 this becomes noticeably visible only when $T > 10$ K. The movement
Figure 6.14: Temperature dependent PR spectra of sample R1970 (InAs_{1-x}Sb_x, x = 6.9%) in the region of the $E_0$ transition. The solid vertical curve at lower energy is a guide to the eye indicating the position of $E_0$ for the InAsSb epilayer. The second vertical curve, at a higher energy, marks the position of the InAs substrate $E_0$ energy.
of this feature is marked approximately with the second, vertical solid curve. The difference between the energies of the two features (illustrated by the separation between the two vertical curves in Fig. 6.14) is larger than the energy difference seen in R1968 due to the increased Sb content in R1970. This red-shifts the epilayer band gap further from the InAs band gap than in R1968.

We determine the values of $E_0$ from the epilayer by the $PR$ modulus method and these are shown as a function of temperature in figure 6.15. As can be seen in Fig. 6.14 some of the $PR$ spectra exhibit a rather unconventional form, most notably when $77 \text{ K} < T < 175 \text{ K}$. For these spectra, we are still able to determine a value for $E_0$ using the modulus technique. However, the uncertainties in the obtained values is large—reflected by the error bars in Fig. 6.15. We are unsure of the reason for the unusual lineshapes seen at certain temperatures in this sample; it even appears as if there is a third $PR$ feature between the signals from the epilayer and substrate at certain temperatures (i.e. at $T = 125 \text{ K}$). We do not believe that this is related to strain within the epilayer giving rise to separate light-hole and heavy-hole to conduction band transition $PR$ features since this should be apparent at all temperatures. In order to remain focussed on studying $E_0$ and $\Delta_0$ in this material we shall not investigate the cause of the unusual $PR$ lineshapes further. However, it may be interesting to look at the effect further in a separate study.

The solid curve in Fig. 6.15 shows a fit using the Varshni relationship of Eq. 6.1 (p. 181). The fit is of a good quality and yields the parameters $\alpha = 0.510 \text{ meV/K}$ and $\beta = 547 \text{ K}$. The literature values, interpolated from the binary values for InAs and InSb in Ref. [17], are quite different at $\alpha = 0.279 \text{ meV/K}$ and $\beta = 98 \text{ K}$. The temperature dependence of $E_0$ using these literature values and the literature value for $E_0(T = 0 \text{ K})$ is displayed in Fig. 6.15 by the dashed curve. As in sample R1968 (Fig. 6.12) there is a notable disagreement between our measured value of $E_0$ and the literature interpolated value. We find the value to be $E_0 = 384\pm 1 \text{ meV}$ when $T = 10 \text{ K}$, which is in agreement with the data from the PL measured at Lancaster (see table 6.1), whereas the literature value is 361 meV; a difference of over
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20 meV. As mentioned in the discussion of R1968 we shall return to this difference in section 6.4.3.

While the absolute values of the measured $E_0$ energies and the literature interpolated $E_0$ energies differ, the temperature dependence which is represented by the curvature of the two lines in Fig. 6.15 is broadly similar. This is in spite of the fact that our fitted Varshni parameters do not agree too closely with the literature interpolated values, highlighting a particular problem in using the Varshni relationship – it is often possible to achieve similar forms for the temperature dependence of a semiconductor using quite different values of the Varshni parameters. This is caused by a notable covariance between the parameters in Eq. 6.1 (p. 181) and is an inherent problem with the relationship. There are other relationships which can be used to model the temperature dependence, such as that based on a Bose-Einstein relationship. [43] However, there is less information in the literature on the fitted parameters of these models with which to compare our results. Therefore,
we use the more popular Varshni model here since it allows easier comparison with results reported by other authors.

Sample R1970 is the highest Sb content InAsSb sample for which we are able to measure the PR at high temperatures, enabling comparisons of the temperature dependence in these samples with the expected behaviour obtained by interpolating the literature dependencies for InAs and InSb. To illustrate that the overall temperature dependencies seen in our measurements are not dissimilar to the literature expected dependencies we plot the $T$ dependent $E_0$ data for the three InAsSb samples discussed so far in figure 6.16. Also shown is the temperature dependence of $E_0$ for sample s922—one of the pentenary alloys discussed in full in the next section.

The solid curves in Fig. 6.16 represent the $T$-dependence of $E_0$ obtained using the literature expected values for the Varshni $\alpha$ and $\beta$ parameters. However, unlike in the individual sample $T$ dependence figures (e.g. Fig. 6.12, p. 187), we have not used the literature expected values for $E_0(T = 0 \text{ K})$ here since we know that our measured values for this parameter vary by as much as 20 meV compared to the literature values (see offset between curves, in say Fig. 6.15). Rather, we have allowed this parameter to vary so that the curves may overlay our measured $E_0$ data points. This allows a simple comparison between our measured $E_0$ $T$-dependence and the dependence expected from the literature information.

It is clear from Fig. 6.16 that our measured $E_0$ data generally follow the solid curves for each of the samples shown—illustrating that our observed temperature dependence is broadly similar to that expected from the literature published behaviour for InAs and InSb [17] (note: for the pentenary sample (s922) the predicted behaviour is dependent on the Varshni parameters of a further four binary semiconductors). It does appear however that at low temperatures ($T < 50 \text{ K}$) the agreement is not as good, with our data exhibiting a somewhat 'flatter' temperature dependence than that of the expected behaviour. Deviation from Varshni behaviour at low temperatures is often seen in samples containing inhomogeneities and is a result of carrier localisation effects. This is particularly pronounced in dilute nitride semiconductors, and gives rise to an 's-shaped' temperature dependence. [44] We
do not believe that there is significant evidence in our data to indicate any deviation from a standard Varshni-like temperature dependence. While the low temperature deviation appears clear in Fig. 6.16 it is important to stress what the curves in this figure represent. They are generated by simple linear interpolation of the recommended Varshni parameters for InAs and InSb [17] (and other binaries in the case of sample s922). This has two limitations: firstly, in the review of Ref. [17] it is stated that there is a wide range of published Varshni parameters for both InAs and InSb. This creates uncertainty in which Varshni parameters should be used for each of the binary alloys.

Figure 6.16: Summary of the temperature dependencies of the InAsSb samples studied in this work (R1965-Sb=0.0%, R1968-Sb=4.3%, R1970-Sb=6.9%). Also plotted is the temperature dependence of sample s922—a GaInAsPSb pentenary alloy studied in the next section. The solid and dashed curves are explained in the text.
Secondly, it is not known if a linear interpolation between binary Varshni parameters is appropriate for describing the $E_0$ temperature dependence in the InAsSb alloy. This means that the curves in Fig. 6.16, whilst being the best currently available to us, are not, by any means, definitive descriptions for the $E_0$ temperature dependence in these alloys. Therefore, since we are not comparing our data directly with other published temperature dependencies for InAsSb it is not possible to draw strong conclusions based on the observed differences in Fig. 6.16. Furthermore, since our best fits achieved (using the Varshni equation) of our $E_0(T)$ data were very successful at reproducing our measured temperature variation (see Fig. 6.12 on page 187 for example) we do not believe that these samples are exhibiting non-Varshni temperature dependencies. Rather, we conclude that they are exhibiting a slightly different dependence (accounted for by using different Varshni parameters only) compared to that expected by simply considering the temperature dependence of the binary alloys as recommended by Ref. [17].

Also plotted in Fig. 6.16 is our measured $E_0 + \Delta_0$ values for R1968 (note the broken scale on the energy axis). Here the apparent temperature dependence is due to the variation in $E_0(T)$ since $\Delta_0$ is not a function of $T$. The dashed curve is a simple replica of the curve through the $E_0(T)$ data for R1968 in this graph, vertically shifted to overlay these $E_0 + \Delta_0$ values.

Returning to the analysis of the PR results of R1970, figure 6.17 shows a spectrum for the $E_0 + \Delta_0$ feature at $T = 10$ K (the final spectrum for this sample). The solid curve through the data shows a TDFF fit to the feature which gives the $E_0 + \Delta_0$ energy as $801 \pm 15$ meV. Subtracting the $E_0$ energy determined from the PR spectrum at 10 K (Fig. 6.14) gives a value for the spin-orbit splitting energy of $\Delta_0 = 417 \pm 15$ meV. The expected literature value is 342 meV using the bowing of Berolo and Woolley (discussed later). [27]

For the argument outlined in the discussion of the PR spectra of R1968 (see page 191) we can be confident that the feature in Fig. 6.17 is not an $E_0 + \Delta_0$ feature from the InAs substrate in this sample since at 10 K we observed no clear $E_0$ substrate feature (see bottom spectrum in Fig. 6.14, p. 192 in the 414 meV InAs $E_0$ region).
Figure 6.17: PR spectrum measured for sample R1970 (InAs$_{1-x}$Sb$_x$, $x = 6.9\%$) at $T = 10$ K (closed symbols) in the energy region of the conduction to spin-orbit split-off valence band transition ($E_0 + \Delta_0$). The solid curve shows a TDFF fit to the data and the arrow indicates the fitted value of $E_0 + \Delta_0 = 801$ meV.

The next InAs$_{1-x}$Sb$_x$ sample studied is R1971, which contains 9.0% Sb. Unfortunately we were only able to record spectra at low temperatures for this sample and the PR spectrum measured at $T = 10$ K is shown in figure 6.18 (a). The solid curve shows our best fit achieved using a single TDFF function, giving a fundamental band gap energy of $E_0 = 367 \pm 3$ meV. This fit, however, is not completely satisfactory, leading to uncertainty in the value of $E_0$. We made an attempt to fit the spectrum using two TDFFs. However, we found this was still unable to replicate the PR lineshape, mainly due to the broad extent of the feature at low energies. Also, the oscillatory nature of the lineshape at higher energies (above 380 meV) may indicate the presence of Franz-Keldysh oscillations in the PR of this sample. Unfortunately the weak signal level of these oscillations makes it difficult to conduct a detailed
Figure 6.18: (a) Solid symbols show the measured PR spectrum of sample R1971 (InAs$_{1-x}$Sb$_x$, $x = 9.0\%$) at $T = 10$ K near $E_0$. The solid curve shows the best fit achieved using a single TDFF, yielding a value of $E_0 = 367$ meV. (b) Shows the modulus spectrum of the PR measurement in (a), which peaks at 365 meV and has a FWHM of $\Gamma = 12$ meV.
study into their nature. If the signal to noise level of the experiment could be improved in the future it may be possible to explore this further. As we show in our discussion of the PR modulus method, the technique may still yield a peak at the critical point energy, even if the original PR data cannot be fitted with a standard low-field limit TDFF (see page 32). Figure 6.18 (b) shows the calculated modulus of the PR spectrum in (a). The peak in the modulus spectrum implies that $E_0 = 365 \pm 3$ meV, 2 meV lower than the value obtained from the fit to the PR spectrum. Due to the relatively poor quality of the PR fit in (a) we believe the correct band gap energy for R1971 is $E_0 = 365 \pm 3$ meV determined from the modulus spectrum in (b). This agrees reasonably well with the data from the PL measured by Lancaster University (not shown), where the PL peak position was determined to be $369 \pm 4$ meV (table 6.1, p. 185). However, it is nearly 20 meV greater than the recommended literature value. [17]

Figure 6.19 shows the PR spectrum of R1971 in the near-infrared region of the $E_0 + \Delta_0$ transition, measured at a temperature of 10 K. The solid curve shows the fitted TDFF function, which unlike the fit to the $E_0$ feature illustrated in Fig. 6.18 (a), is of a good quality. From the fit we obtain a value of $E_0 + \Delta_0 = 794 \pm 15$ meV. This gives a value for the spin-orbit splitting energy of $\Delta_0 = 429 \pm 15$ meV, nearly 100 meV greater than the value interpolated using Berolo and Woolley's bowing parameter (table 6.1, p. 185). Once again, using the argument on page 191, we can be confident that the $E_0 + \Delta_0$ feature in Fig. 6.19 is from the epilayer since there is no discernible $E_0$ feature from the InAs substrate ($E_0$(InAs) ~ 414 meV) in Fig. 6.18(a) (p. 199).

Figure 6.20 (a) shows the $T = 10$ K PR spectrum of sample R1967, the next sample studied, which contains 15.5% antimony. As with the previous sample we were only able to measure low temperature spectra for this sample since the signals were too weak at higher temperatures. The solid curve in Fig. 6.20 (a) shows the fit to the data achieved using two TDFF functions. We find that in order to achieve an acceptable fit it is necessary to include a second TDFF, which has an intensity around 40% that of the main feature attributable to $E_0$. We refer to the energy of this second feature as $E'$. From
the fit we obtain $E_0 = 327$ meV and $E' = 339$ meV. The precise reason for requiring this second TDFF to describe the shape of the measured PR is unknown; it is unlikely to be defect related since it occurs at a higher energy than that of the $E_0$ feature. It is possible that the PR of this sample is in a hybrid state, i.e. between one being correctly described by a TDFF (low-field regime) and another demonstrating Franz-Keldysh Oscillations (FKOs) synonymous with the intermediate regime. [39, 45] Such lineshapes are particularly difficult to describe and fitting them with an appropriate model is difficult. We attempted to fit the spectra using an Airy function (standard model used to describe FKO's [45]), but this was unsuccessful here. Estrera et al. have been successful in fitting PR spectra similar in form to that shown in Fig. 6.20 (a). [46] In their approach they fit such PR features using two Airy functions to account for both the light and heavy hole valence bands. Furthermore, they modify their Airy functions to include an energy

Figure 6.19: $PR$ spectrum measured for sample R1971 (InAs$_{1-x}$Sb$_x$, $x = 9.0\%$) at $T = 10$ K, (closed symbols) in the energy region of the conduction to spin-orbit split-off valence band transition ($E_0 + \Delta_0$). The solid curve shows a TDFF fit to the data and the arrow indicates the fitted value of $E_0 + \Delta_0 = 794$ meV.
Figure 6.20: (a) PR spectrum of sample R1967 (InAs$_{1-x}$Sb$_x$, $x = 15.5\%$) at $T = 10$ K in the region of the fundamental band gap (solid symbols). The solid curve shows a fit to the data, where, in order to achieve a reasonable fit, two TDFFs were used. From this we obtain a value of $E_0 = 327$ meV, and $E' = 339$ meV (for the second, weaker TDFF). (b) Shows the modulus spectrum of the PR measurement in (a), which has a main peak at 326 meV, with a FWHM of $\Gamma = 10$ meV.
dependent broadening allowing them to describe the effects of electric field gradients within samples, and modulation between two finite fields – effects which complicate the form of modulated reflectance lineshapes. [46] We do not carry out such a detailed approach to fitting the PR spectrum of sample R1967 here, although a successful attempt using the method of Estrera et al. may result in an improved value for \( E_0 \).

Figure 6.20 (b) shows the modulus of the measured PR spectrum shown in Fig. 6.20 (a). This shows two clearly discernible peaks and from these we can infer values for \( E_0 \) and \( E' \) of 326 meV and 341 meV, which agree closely with the values obtained from the fit using the two TDFFs to the PR spectrum. Since the modulus peaks and TDFF fit parameters give similar results we are confident that \( E_0 = 327 \pm 4 \) meV for R1967. The FWHM of the main peak in the modulus spectrum is 10 meV, close to the value of 11 meV obtained from the FWIIM of the TDFF used to fit the \( E_0 \) feature in Fig. 6.20 (a). This broadening is only a few meV larger than the FWIIM of the PR feature in the InAs sample (R1965), indicating that the sample still has high optical quality.

Figure 6.21 shows the PR spectrum of the \( E_0 + \Delta_0 \) feature of R1967, measured at \( T = 10 \) K, where the solid curve shows the best fit achieved using a TDFF function. From this we find the spin-orbit splitting in R1967 to be \( \Delta_0 = 459 \pm 20 \) meV. As for the other samples studied so far, this is quite different to the literature value of 298 meV obtained from interpolation using the bowing of Berolo and Woolley \((\gamma(\Delta_0) = +1170 \) meV\). [27] We shall discuss this in depth in the review of the low temperature PR results in section 6.4.3. We saw no \( E_0 \) substrate PR signal in this sample at 10 K so we can be confident that the \( E_0 + \Delta_0 \) feature in Fig. 6.21 is from the InAsSb epilayer, not the substrate (see page 191).

It is clear from the spectrum in Fig. 6.21 that the PR signal from the spin split-off band is very weak in this sample, with a maximum intensity of just \( \Delta R/R \approx 2.5 \times 10^{-6} \). Indeed this is the sample with the highest Sb concentration (15.5%) in which we have been able to observe a feature from the \( E_0 + \Delta_0 \) transition. In the remaining two samples, with higher concentrations of Sb, the signals were too weak to be used for determining
values for $\Delta_0$.

Figure 6.22 (a) shows the low temperature PR spectrum of sample R1972 in the region of the $E_0$ transition. This sample has a similar concentration of Sb (16.0%) to that of R1967, which contained 15.5%. The spectrum shown here was recorded at a temperature of 50 K since the signal to noise ratio of the spectrum at $T = 10$ K is very poor due to the relatively strong PL background compared to the weak PR signal of this sample. The magnitude of the PR signal is less than $2 \times 10^{-6}$ and in order to reduce the noise levels to those shown in Fig. 6.22(a) it was necessary to run the experiment for a period of several hours.

The solid curve in Fig. 6.22 (a) shows a TDDFF fit of reasonable quality to the PR measurement, which gives an energy for the feature of $318 \pm 3$ meV. Figure 6.22 (b) shows the calculated modulus of the spectrum in (a). The modulus peak occurs at an energy of $319 \pm 3$ meV, just 1 meV different to
Figure 6.22: (a) The solid symbols show the PR spectrum of sample R1972 (InAs$_{1-x}$Sb$_x$, $x = 16.0\%$) at $T = 50$ K, where the signal to noise ratio is improved upon that at $T = 10$ K. The solid curve shows a TDFF fit to the data and from this we obtain a value of $E_0 = 318$ meV. (b) Shows the modulus spectrum of the PR measurement in (a), which peaks at 319 meV and has a FWHM of $\Gamma = 11$ meV.
the value obtained from the fit. We adopt a value of $E_0 = 319 \pm 3$ meV for R1972 – the average of the two values when rounded to the nearest meV. The modulus peak has a FWHM of 11 meV – nearly 40% greater than the FWHM of sample R1965 (InAs). This, and the much reduced PR intensity is an indication that the inclusion of 16% Sb does have a noticeable impact on the optical quality of the material.

The final sample in the series of InAs$_{1-x}$Sb$_x$ materials studied is R1966, which has the largest Sb concentration of 22.5%. Figure 6.23 (a) shows the PR for this sample in the region of the $E_0$ transition. A sizeable, sloping background present in the measured PR of this sample has been removed in the figure to make the analysis of the data more straightforward. We believe that this spurious background was caused by problems with the filter in the helium compressor of the cryostat during the experiment on this sample and that it is correct to subtract it from the PR spectrum. The precise cause of the background is unknown, but it could have been related to scattering from contaminants present in the cryochamber due to the failure of the filter. Unfortunately time did not allow for the measurement to be repeated once the filter had been replaced.

The TDFF fit to the spectrum (solid curve) gives a value of $E_0 = 261 \pm 4$ meV for R1966. The same value is found from the peak of the PR modulus spectrum shown in Fig. 6.23 (b). The FWHM of the modulus peak is found to be twice as broad as the $E_0$ feature for the InAs sample (R1965), having a value of 20 meV. However, this is still lower than the FWHM of the PL peak measured for this sample (not shown), which is 28 meV (see table 6.1 on page 185).

The measurement in Fig. 6.23 (a), displaying a feature at 261 meV (4.75 µm), represents our longest wavelength PR measurement to date using the grating spectroscopy system, and to the best of our knowledge it represents the longest such measurement in the literature.

After discussing the temperature dependent measurements recorded for the GaInAsPSb pentenary alloys in the next section we shall look in detail at the low temperature results for each of the narrow-gap samples studied in this work in order to examine the behaviour of both $E_0$ and $\Delta_0$ with Sb.
Figure 6.23: (a) Measured PR spectrum of sample R1966 (InAs$_{1-x}$Sb$_x$, $x = 22.5\%$) at $T = 10$ K in the region of the fundamental band gap (solid symbols). The solid curve shows a TDF fit to the data and from this we obtain a value of $E_0 = 261$ meV. (b) Shows the modulus spectrum of the PR measurement in (a), which peaks at 261 meV and has a FWHM of $\Gamma = 20$ meV.
6.4.2 Temperature dependent studies of GaInAsPSb samples

Figure 6.24 shows the temperature dependent $PR$ results of sample s922, the first of the LPE grown Ga$_{1-y}$In$_{y}$As$_{1-x}$P$_x$Sb$_x$ samples to be studied here. This represents the first $PR$ results on this pentenary alloy system. As can be seen from the figure, we were able to measure $PR$ for s922 up to a temperature of 200 K, where the signal thereafter became too weak to be discernible from the noise. From Table 6.3 on page 214 we see that s922 contains 4% Ga, 4% P, and 13% Sb (determined from x-ray diffraction measurements conducted by Lancaster University). In terms of Sb content, the closest sample to this in the series of InAs$_{1-x}$Sb$_x$ samples is R1967, which contains 15.5% Sb. For that particular ternary alloy we are only able to measure $PR$ up to temperatures of $\sim$ 100 K. Therefore, the ability to measure $PR$ for this pentenary alloy up to 200 K indicates that despite the complexity of the material, it is of a good quality. Furthermore, if we compare the intensity of the 10 K measurement of s922 with that of R1967 (Fig. 6.20, p. 202) we see that the $PR$ of s922 is around four times more intense. This could potentially be related to the electronic properties of the sample, and not be a direct indication of the quality of the material. A better measure of quality is the broadening of the $PR$ features and the measured FWHM of the s922 $PR$ feature at $T = 10$ K is 12 meV, comparable to the broadening of 10 meV seen for R1967.

The $T = 10$ K spectrum of s922 is a relatively simple spectrum and from the modulus peak we obtain a value for $E_0 = 342 \pm 2$ meV. This is some 26 meV greater than the value obtained by interpolating$^3$ the literature parameters in Ref. [17]. In the measurements on the InAs$_{1-x}$Sb$_x$ samples we also saw similar differences between the literature values and our measurements. For these samples we suggested that strain within the epilayers, caused by the lattice mismatch with the InAs substrates, could cause part of the differences. However, strain cannot be the cause in the case of these pentenary samples since they are lattice matched to their GaSb substrates.

$^3$The interpolation procedure developed here for pentenary alloys is discussed in detail in appendix C
Figure 6.24: Temperature dependent PR spectra of sample s922 \((\text{Ga}_{x}\text{In}_{1-x-\frac{y}{2}}\text{As}_{1-x-\frac{y}{2}}\text{P}_{y}\text{Sb}_{z})\), \(x = 13\%, y = 4\%, z = 4\%) in the energy region of the fundamental band gap, \(E_0\). Successive spectra are vertically offset for clarity. The vertical curve is a guide to the eye showing the approximate variation of \(E_0\) for the GaInAsPSb epilayer.
This will be discussed further in the next section.

It can be seen from Fig. 6.24 that as $T$ increases an extra feature appears on the low energy side of the main PR lineshape (see $T=125$ K spectrum for example). Fortunately for this sample the extra feature is relatively weak and it does not significantly complicate our analysis of these spectra. Since it is weak, and only present in a few spectra, we shall not speculate as to the cause of the feature here.

The vertical curve in Fig. 6.24 indicates the approximate position of the $E_0$ transition with increasing temperature. The energies, determined from the peaks in the modulus of the PR spectra (not shown) are plotted in figure 6.25 and fitted with a Varshni relationship (Eq. 6.1, p. 181). From this fit

(solid curve) we obtain the following Varshni parameters: $\alpha = 0.20$ meV/K and $\beta = 90$ K. These are quite different to the values interpolated from Ref. [17], which give $\alpha = 0.29$ meV/K and $\beta = 109$ K and the different temperature dependencies can be seen in Fig. 6.25, where the literature in-
terpolated behaviour is illustrated by the dashed curve. Although there is a noticeable difference in the slope of the two curves, much of the disagreement is due to the difference in $E_0$ as measured and as interpolated from literature values. In Fig. 6.16 shown earlier (p. 196) the temperature dependence in Fig. 6.25 is displayed again, however, only the literature values for $\alpha$ and $\beta$ are used to generate the curve – the $E_0(T = 0)$ K value is varied so that the curve overlays the data points. From this it can be seen that the general temperature dependence is not dissimilar to that expected from linear interpolation of the literature binary Varshni parameters.

The growers of these pentenary alloys have also reported Varshni parameters for a sample with a similar composition (Ga=3%, P=6%, Sb=13%) to s922. From their PL measurements (4 K < $T$ < 240 K) they obtained the values $E_0(0 \text{ K})=348$ meV, $\alpha = 0.12$ meV/K and $\beta = 100$ K. [36] This $\beta$ parameter is relatively close to our measured value for sample s922. However, their value for $\alpha$ is nearly half our measured value. In Fig. 6.25 we also plot this reported temperature dependence (dotted curve). Comparing this with our measurements for s922 we find that the $T = 0$ K band gap values are different by 3 meV. This is most likely due to the different compositions of the two samples. At higher temperatures it is clear that the temperature dependence reported in Ref. [36] is apparently weaker than we see for s922. This may be due to their analysis of their temperature dependent PL measurements – if the authors did not remove a factor of $k_B T/2$ from their PL peak energies when determining $E_0(T)$ their values may be overestimated (more so at higher temperature). Such a $k_B T/2$ correction (valid for parabolic bands) is required in the analysis of PL spectra due to the dependence of the emission peak energy on the occupation function and density of states within the conduction band. If we assume this correction was not made in Ref. [36] we can examine the impact of excluding it here. Take $T = 250$ K for example: here the difference between our Varshni curve and that of Ref. [36] is 18.3 meV. However, if we subtract $k_B T/2 = 10.8$ meV from the Ref. [36] energy for $E_0(T=250 \text{ K})$, i.e. 326.6 meV, we get a reduced value of 315.8 meV. This is now only 7.6 meV different to the value obtained from our Varshni fit for s922. If we now remove a further 3 meV from this
difference (the difference between the 0 K band gaps of the two samples), we find the adjusted variance to be just 4.6 meV – comparable to the uncertainty in our $E_0(T)$ values. This would suggest that the temperature dependencies are actually similar for the two samples. Therefore, we believe the $\alpha$ parameter reported in Ref. [36] may be underestimated because it would appear that a $k_B T/2$ factor has not been accounted for in their analysis.

Figure 6.26 (a) shows the $T=10$ K $PR$ spectrum of sample s922 in the region of the $E_0 + \Delta_0$ transition. The TDFF fit to the data (solid curve) indicates that the transition energy is $798 \pm 10$ meV. Since the fit is not of the highest quality, we show in Fig. 6.26 (b) the calculated modulus of the $PR$ spectrum in (a). This peaks at a slightly lower energy of $795 \pm 10$ meV. Taking the average of these two values we obtain the value $E_0 + \Delta_0 = 797 \pm 10$ meV for sample s922. Subtracting the value for $E_0 = 342 \pm 2$ meV at $T = 10$ K, determined from the $PR$ spectrum in Fig. 6.24, we find $\Delta_0 = 455 \pm 10$ meV.

With these pentenary alloys, grown lattice-matched to their GaSb substrates, there is a possibility that we observe $PR$ features from the substrate layers. This could potentially lead to a misidentification of the epilayer $E_0 + \Delta_0$ signal since the fundamental band gap of GaSb is 812 meV, [17] which is relatively close to the value of $E_0 + \Delta_0 = 798$ meV of sample s922. Fortunately, due to the thickness of the pentenary epilayers (1.5-2 μm), we are confident that there is very little possibility of observing a $PR$ signal from the substrate. This is because the penetration depth of the HeNe laser modulation source (633 nm) is estimated to be just $\sim 0.3$ μm in the epilayer and as such the substrate reflectance will not be significantly modulated by the strongly attenuated laser. Also, the penetration depth of the monochromated probe light at $\sim 800$ meV is estimated to be $\sim 0.7$ μm. To see a $PR$ signal in this energy region from the substrate, photons of energy $\sim 800$ meV must travel through the epilayer and back. This corresponds to a distance of 3-4 μm, around five times larger than penetration depth. Therefore we can be confident that any signals seen in the 800 meV near-infrared region must arise from the $E_0 + \Delta_0$ transition of the pentenary epilayer material. Note: the estimated penetration depths here are calculated using the absorption coefficient data (extrapolated to high energy) published in Ref. [47] for InAs,
Figure 6.26: (a) The solid symbols show the PR spectrum of sample s922 (Ga$_x$In$_{1-x}$As$_{1-y}$P$_y$Sb$_z$, $x = 13\%$, $y = 4\%$, $z = 4\%$) at $T = 10$ K in the energy region of the $E_0 + \Delta_0$ spin split-off transition. The solid curve shows a TDFF fit to the data and from this we obtain a value of $E_0 + \Delta_0 = 798$ meV. (b) Shows the modulus spectrum of the PR measurement in (a), which peaks at 795 meV and has a FWHM of $\Gamma = 60$ meV.
Table 6.3: Details of the LPE grown Ga$_{x}$In$_{1-x}$As$_{y}$P$_{1-y}$Sb$_{z}$ samples studied in this work. Data in the columns with headings showing the superscript$^1$ have been interpolated from the binary data and ternary bowing parameters in Ref. [17] using Eq. C.8 (p. 260). The experimentally determined data measured here using PR are also shown. $E_0$ and $\Gamma$ refer to the fundamental band gap energy and broadening at a temperature of 10 K. $\Delta_0$ is the spin-orbit splitting energy.

where we have assumed the epilayers to have similar optical properties to the binary semiconductor.

The next pentenary alloy studied here is sample s923, which contains 7% Ga, 3% P, and 15% Sb. Figure 6.27 shows the temperature dependent PR spectra measured for this sample. The spectrum recorded at a temperature of 10 K is similar in its form to that observed for s922 (Fig. 6.24). However, the low-energy feature seen in the spectra of s922 was very weak at 10 K, but a similar low-energy feature is clearly discernible at 10 K for s923. From the modulus of this spectrum (not shown) we find that $E_0 = 340 \pm 3$ meV, equal to that of s922 (within experimental uncertainty).

At higher temperatures the low-energy feature seen at 10 K quickly increases in size and the PR takes on an oscillatory-like form, making it difficult to obtain useful information. For example, the spectrum recorded at $T = 60$ K has six, clearly discernible lobes. These oscillations appear to persist at energies below that of the fundamental band gap of the sample and therefore we believe them to be Low Energy Interference Oscillations (LEIOs). [48] These LEIOs are caused when there is strong interference of the light within a layer of a sample and this is a definite possibility in these LPE grown samples since the epilayers are between 1.5–2 $\mu$m thick. This is because the optical thickness of these layers (thickness $\times$ refractive index) will be $\sim 5 \mu$m – close to the wavelengths being measured here. We did not observe clear interference features in the $R$ spectra of this sample. How-
Figure 6.27: Temperature dependent PR spectra of sample s923 (Ga$_{0.65}$In$_{0.35}$As$_{1-x-y}$P$_x$Sb$_y$, $x = 15\%$, $y = 3\%$, $z = 7\%$) in the energy region of the fundamental band gap, $E_0$. Successive spectra are vertically offset for clarity. The vertical curve is a guide to the eye showing the approximate variation of $E_0$ for the GaInAsPSb epilayer.
ever, the sensitivity of the PR mechanism can enhance such features, yielding oscillations in the PR spectra. [48]

Figure 6.28 shows the $T = 10$ K PR spectrum of the spin split-off feature of s923. From the least squares fit to the data using a TDFF function we find $E_0 + \Delta_0 = 816 \pm 10$ meV. Subtracting the value of the fundamental band gap energy as determined from the 10 K PR spectrum in Fig. 6.27 we obtain a value of \( \Delta_0 = 476 \pm 10 \) meV. Using this result we can highlight the advantage of these pentenary alloys since this splitting energy is \( \sim 20 \) meV greater than that of sample s922, while their fundamental band gaps are only 2 meV different. Therefore, although these two materials could be used to fabricate devices operating at essentially the same wavelength, their non-radiative losses due to say CHSH Auger recombination would be different due to their different spin-orbit splitting energies. [35]

Figure 6.29 shows the temperature dependent PR spectra in the region of
the \( E_0 \) transition measured for sample s924, which contains 6% Ga, 4% P, and 14% Sb. The \( PR \) spectrum measured at a temperature of 10 K demonstrates a strange 'dip-like' feature near 340 meV, which reduces in intensity as the temperature is increased. The origin of this feature is unknown, although we believe that it is not related to the band gap of the sample since it does not persist at higher temperatures. As the feature occurs at a lower energy than \( E_0 \) it could be from an excitonic, or defect state. Excitonic features can be observed in \( PR \) spectra (see Ref. [46] for example) and they appear at an energy below the fundamental band gap equal to the exciton binding energy. In InAs the exciton binding energy is just \( \sim 1 \) meV [49] and therefore we would expect a similar value to this for sample s924. However, this is much smaller than the energy separation between the 'dip-like' feature and the \( E_0 \) feature seen in the \( T = 10 \) K \( PR \) spectrum in Fig. 6.29 (\( \sim 20 \) meV) so we can discount the possibility that this \( PR \) signal is from an excitonic transition.

The solid vertical curve marks the approximate movement of \( E_0 \) with temperature. At \( T = 10 \) K we determine the band gap to be \( E_0 = 343 \pm 5 \) meV (from the peak in the modulus spectrum—not shown). This is similar to the band gaps of s922 and s923 (see table 6.3, p. 214) and is nearly 30 meV greater than the value of 371 meV obtained by interpolation (Eq. C.8, p. C.8) of the literature values for the binary semiconductor band gaps. [17]

Unfortunately we were unable to observe a clear feature from the spin split-off feature in this sample.

The final sample of this study is sample s947. No X-ray diffraction measurements were conducted on this sample so its composition is unknown. We include the measurements here so that they may be referred to if any future study is conducted on the sample. Figure 6.30 (a) shows the 10 K \( PR \) spectrum of this sample. A meaningful fit to the data was not achievable, and so in Fig. 6.30 (b) we plot the modulus of the \( PR \) spectrum, which shows a clear peak (with FWHM of 40 meV) at an energy of 408 meV. Since the composition of the sample is unknown we cannot draw many conclusion regarding this result. However, it appears that the band gap of this sample is slightly larger than that of the other pentenary samples studied here, possibly indicating a lower Sb and/or higher Ga content compared to the other
Figure 6.29: Temperature dependent PR spectra of sample s924 (Ga$_x$In$_{1-x}$As$_{1-y}$P$_y$Sb$_z$, $x = 14\%$, $y = 4\%$, $z = 6\%$) in the energy region of the fundamental band gap, $E_0$. Successive spectra are vertically offset for clarity. The vertical curve is a guide to the eye showing the approximate variation of $E_0$ for the GaInAsPSb epilayer.
Figure 6.30: (a) Measured PR spectrum of sample s947 (Ga$_{x}$In$_{1-x}$As$_{1-y}$P$_y$Sb$_x$ - composition not measured) at $T = 10$ K in the energy region of the $E_0$ transition. (b) Calculated modulus spectrum of the PR measurement in (a), which peaks at 408 meV and has a FWHM of $\Gamma = 40$ meV.
samples. As for sample s924, we were unable to observe a PR feature from the $E_0 + \Delta_0$ transition in this sample.

6.4.3 Analysis of the low temperature measurements

In this section we investigate the low temperature results obtained for the MIR samples studied in this work. A publication of these studies can be found in Ref. [50]. Figure 6.31 shows the low temperature PR spectra measured for all the InAs$_{1-z}$Sb$_z$ samples studied in section 6.4.1. The spectra are vertically offset for clarity, and are ordered in terms of the Sb content within each sample (listed next to each spectrum). As well as displaying the PR of the InAs$_{1-z}$Sb$_z$ samples, we also show the spectra for samples s922 and s923 – the two pentenary alloys for which we were able to measure both the fundamental band gap and spin split-off features. These are also plotted in the order determined by their respective Sb concentrations.

The energy axis is broken in Fig. 6.31, enabling us to plot both the $E_0$ and $E_0 + \Delta_0$ features of each sample (where measured). For clarity, we show the spectrum of the particularly weak $E_0 + \Delta_0$ feature of sample R1967 (15.5% Sb) using solid symbols and the TDFF fit to the data. We shall focus firstly on the $E_0$ features of each sample, before looking in detail at the spin split-off features.

It is clear from figure 6.31 that as the Sb content is increased $E_0$ decreases in a steady fashion. With 0% Sb the value for $E_0 = 414$ meV and this decreases to 261 meV for the sample with the highest Sb content of 22.5%. In terms of wavelength this represents a shift from 3.0 µm to 4.75 µm. Recalling the figure shown at the start of this chapter, which illustrated the positions of various gas absorption lines (Fig. 6.1, p. 168) we see that this wavelength range is extensive enough to cover the absorption lines of all these gases (although these samples are cooled to 10 K). This illustrates why InAs$_{1-z}$Sb$_z$ is such an important material for MIR applications.

In order to compare our results for $E_0$ with those of other authors studying InAs$_{1-z}$Sb$_z$ we plot the values as a function of Sb content in figure 6.32. Here the closed symbols represent our data, taken from the MIR PR results.
Figure 6.31: Low temperature spectra of the $E_0$ and $E_0 + \Delta_0$ PR features of the InAsSb samples studied here, and samples s922 and s923 (two of the pentenary GaInAsPSb samples studied). [50] The spectra are vertically offset with increasing Sb content, which is shown next to each spectrum. The baseline for each spectrum is indicated by the tick marks on the vertical axis. For the weakest observed $E_0 + \Delta_0$ PR feature, data points with a least-squares fit are shown for clarity. The corresponding InAsSb sample names can be found in table 6.1 (p. 185) by looking up the Sb concentrations (fully relaxed).
Figure 6.32: Low temperature fundamental band gap ($E_0$) as a function of Sb composition for InAs$_{1-x}$Sb$_x$. The filled circles (●) show the results determined from the PR measurements of this work. The crosses (×) mark the results from Ref. [22]; the diamonds (○) show the results from Ref. [25]; and the open squares (□) show the results from Ref. [26]. The open circles represent our data again, but now assuming that the layers are fully-strained. The solid curve represents the accepted bowing of the fundamental band gap (+670 meV). [17]
of this work. The remaining symbols represent the results of other authors as detailed in the figure caption. The solid curve illustrates the recommended bowing of the fundamental band gap, taken from Ref. [17] as +670 meV. It is clear that for the results of each author there is a certain level of scatter between the data points and the bowing curve. At a first glance this scatter looks rather insignificant and the bowing curve appears to give a good representation of the variation of the band gap. For example, our data (solid symbols), which sits largely in the left hand side of the figure since our study focussed on InAs-rich samples, appears to agree reasonably well with the recommended literature values (curve). However, as we saw in section 6.4.1 our values for $E_0$ differ from the literature values by as much as 23 meV (see table 6.1, p. 185). While this disagreement is relatively large and would suggest that our measured values do not agree with the literature values, when viewed in Fig. 6.32 they tell a different story. For the Sb concentrations in which our measurements yield higher values for $E_0$ than the literature accepted values ($x < 16\%$) it can be seen that the results of other authors show a similar trend and that our results agree well with their measurements. Therefore it is our belief that the literature bowing curve, using $\gamma(\Delta_0) = +670$ meV, does a reasonable job of describing the behaviour of $E_0$ across the whole alloy composition range but that at a given composition it may over- or under-estimate the true band gap of the alloy. This is an important point to consider when designing materials for use in specific applications since the actual band gap of a sample may be significantly different to that predicted by the curve in Fig. 6.32. To illustrate this point we take sample R1970 as an example. This sample, containing 6.9% Sb, has a measured value of $E_0 = 384$ meV compared to the value of 361 meV interpolated using the bowing curve. Therefore if R1970 was fabricated for use in say an LED one would predict it to operate at $\sim 3.4 \mu$m. However, it would actually output light at around 3.2 $\mu$m and this large difference could render the material inappropriate for the purpose it was grown.

As we discussed in section 6.3.1 we believe that the InAsSb epilayers are fully-relaxed since they are $\sim 5$ times thicker than the estimated critical thicknesses of the layers. [23] Therefore, we used the Sb contents determined

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from x-ray diffraction measurements assuming full relaxation to describe the sample compositions (column two of table 6.1, p. 185). It is worth considering here what effect there would be on our data in Fig. 6.32 by assuming full strain in the epilayers. We can do this by using instead the Sb concentrations in the third column of table 6.1. The open circles in Fig. 6.32 show our $E_0$ values plotted using these alternative Sb concentrations (except for the samples containing the lowest concentrations of Sb, where the difference is small). The data points are shifted towards the left compared to our data plotted assuming full-relaxation (solid circles), since the Sb concentrations assuming no relaxation are lower than when assuming full relaxation. It is clear from this that these points do not lie near the bowing curve, and unlike our data plotted assuming full-relaxation, this data is in poor agreement with the results published by other authors. We therefore believe that this is strong evidence that the samples are not fully strained, and that our assumption that the epilayers are relaxed is reasonable. Furthermore, if the samples were strained we would also need to adjust our $E_0$ values to account for this so we could compare the values to the literature data on unstrained samples. Strain will increase the $E_0$ band gap and so we would need to reduce the energies of the points represented by the open circles by the relevant amounts. Therefore, the agreement between this data and the literature published data would be worse still, again indicating the epilayers are not fully-strained.

If we now consider the pentenary samples studied in this work, looking at the data in table 6.3 on page 214 we see that for the these we see large differences between our measured values of $E_0$ and the values interpolated using the literature recommended parameters in Ref. [17] - which includes the bowing in InAsSb ($\gamma(E_0) = +670$ meV). This is similar to the differences seen in the InAsSb ternary samples (compare closed circles with bowing curve in Fig. 6.32). The pentenary alloy interpolation procedure used here was developed for the analysis of these results and is described in appendix C. In light of the differences between our measured $E_0$ values and the literature accepted values for InAs$_{1-x}$Sb$_x$ it is not surprising that we see similar differences in these pentenary samples, especially since the value $E_0$ in Ga$_x$In$_{1-x}$As$_{1-y-z}$P$_y$Sb$_z$ is dependent on the bowing of $E_0$ in InAs$_{1-x}$Sb$_x$.
(see Eq. C.8 on page 260).

Before examining the behaviour of the spin-orbit splitting energy with alloy composition we shall briefly look at the broadening of the $E_0$ transition by studying the FWHM of the $PR$ features obtained from the modulus peaks. Figure 6.33 shows the FWHM of the low temperature features for the InAsSb samples (solid symbols), and the pentenaries s922 and s923 (open symbols). The solid curve is a simple guide to the eye through the data points illustrating the general trend of the increasing FWHM with increasing Sb content. We believe that this increased broadening is partly related to a decrease in optical quality of the materials as the Sb content is increased. The broadening will also be increased in materials with higher Sb concentrations since, generally speaking, non-radiative recombination rates will be faster in samples with smaller band gaps. The associated reduction in the lifetimes of excited states in the materials is then translated into an increased linewidth of the transition energies.

When compared to the $PR$ results of other, near-infrared samples, Fig. 6.33

![Figure 6.33: Variation of the full width at half maximum (FWHM) broadening of the 10 K fundamental band gap $PR$ modulus feature for each of the InAsSb samples studied here, plotted as a function of antimony content (solid symbols). The open symbols show the FWHM for two of the pentenary alloys, s922 and s923. The solid curve is a guide to the eye through the data points.](image-url)
appears to illustrate the high quality of the samples studied here. For example, low-T measurements on GaSb give a reported FWHM of 10.4 meV; [43] greater than our measured value of 8 meV for sample R1965 (InAs). In the same study a quaternary alloy (GaInAsSb) with $E_0 = 645$ meV was found to have $\Gamma = 16.3$ meV – broader than for all the samples shown in Fig. 6.33, except the one with highest Sb content. It is perhaps fairer, however, to compare the ratios $\Gamma/E_0$ in order to account for the wider band gap in these other samples. Such a comparison would reveal that the linewidths of the mid-infrared semiconductors are relatively broader than those with the wider bandgaps. This may be, for example, due to the increased non-radiative recombination rates in the narrow gap materials, and/or due to non-uniformities in the samples.

Figure 6.34 shows our measured spin-orbit splitting energy values for the InAs$_{1-x}$Sb$_x$ samples studied here (closed symbols). Also shown are the results of Berolo and Woolley (×) measured using electroreflectance on samples grown by the Horizontal Bridgman (HB) technique. [27] The HB technique used to grow these samples produced an ingot of varying material composition along the crystal by drawing it through a furnace with a steep temperature gradient at a rate of ~0.5 cm per day. [22] Ideally a cross-section of such an ingot will be homogenous, having a single material composition. In reality, the HB technique used at this time would have been unable to produce InAsSb samples of the quality studied here, which are grown using MBE.

The downwards bowing curve in Fig. 6.34 through the data points of Berolo and Woolley represents the large, positive bowing value ($\gamma(\Delta_0) = +1170$ meV) reported by the authors, [27] which describes well the behaviour observed by them. It is immediately evident from this figure that our data for $\Delta_0$ shows a very different behaviour with varying Sb content to that of the only other published results on this alloy. Indeed, our data almost sit on the straight line between the InAs and InSb $\Delta_0$ endpoints, which represents the zero bowing behaviour expected in the virtual crystal approximation. [51] A fit to our data using Eq. C.1 (p. 254) suggests that the bowing is $\gamma(\Delta_0) \approx -165$ meV, which is much smaller and of a different sign than
Figure 6.34: Low temperature spin-orbit split-off band gap energy ($\Delta_0$) as a function of Sb composition for InAs$_{1-x}$Sb$_x$. The filled circles (●) show the results determined from the PR measurements of this work. The crosses (×) mark the results of Berolo and Woolley and the solid curve through these points represents their fitted bowing of $+1170$ meV. [27] The straight line indicates the zero bowing behaviour consistent with the virtual crystal approximation, [51] and the upward bowing curve represents the best fit to our measured data ($-165$ meV). The open square represents the $\Delta_0$ energy for sample R1967, if it were fully-strained as opposed to fully-relaxed. Under these conditions the antimony concentration would be just 11% instead of 22.5%. We have also reduced the measured $\Delta_0$ value here by 20 meV in order to account for the increase in spin-orbit splitting due to strain.

The bowing reported by Berolo and Woolley. [27] Since we have only studied InAs-rich samples here it is not possible for us to conclude with certainty that the bowing is indeed $-165$ meV. However, we are confident that the bowing in these high quality epitaxial samples is very different to that of the HB grown samples studied in the early 1970’s by Berolo and Woolley. Our results, showing negligible bowing compared to these only other published results, [27] are in line with the theoretical predictions of Siggia, [29] and Wei and Zunger [33] for homogenous, ternary alloys as discussed earlier in section 6.3.1 and this gives us confidence in our result. Wei and Zunger suggested that the large positive bowing observed in the first study of $\Delta_0$ in

\[ \gamma(\Delta_0) = -230 \text{ meV} \quad \text{for InAsSb. However, an improved fit of the data indicates that} \gamma(\Delta_0) = -165 \pm 30 \text{ meV} \]
InAsSb was caused by sample inhomogeniety. [33] We conclude this to be true here since our high-quality, epitaxial samples show no such bowing.

It is also interesting to consider the impact of strain on our interpretation of the data in Fig. 6.34. If we assume for a minute that the layers are fully-strained as opposed to being fully-relaxed our data points would be shifted leftwards since the Sb concentrations obtained from x-ray diffraction measurements are lower if we assume strain is present (table 6.1, p. 185). This would cause the data to exhibit an even more strongly negative bowing, pushing the data points further from those using the bowing of Berolo and Woolley. [27] However, If the InAsSb was fully-strained we should also account for the shift in $\Delta_0$ due to the strain before comparing to the literature values for unstrained material. Consider sample R1967 (the highest Sb containing sample for which we could measure an $E_0 + \Delta_0$ transition): if it is fully-strained it should contain 7.3% Sb. We calculate that $\Delta_0$ for this material would increase due to strain by approximately 20 meV. [41, 17] Therefore, to compare our data to the literature accepted values we should subtract this amount to remove the effect of strain. The open square in Fig. 6.34 represents the position on the graph of this strain-corrected $\Delta_0$ value for sample R1967. It is clear that if the sample was fully-strained its spin-orbit splitting would still follow a negative bowing curve, rather than the strong, positive bowing of Berolo and Woolley. Therefore, it appears that we are in the fortunate position that our main result (i.e. that the bowing of $\Delta_0$ in these samples is very different to that previously published) is not at risk due to our assumption that the epilayers are fully-relaxed.

To highlight the potential impact that our results in Fig. 6.34 may have we consider here a hypothetical semiconductor device designed to detect the presence of CO$_2$ gas at 4.25 $\mu$m ($E_0 \approx 290$ meV). Such a device, if cryogenically cooled, could be based on InAs$_{1-x}$Sb$_x$, with $x \sim 17$ % since the band gap at this concentration would coincide with selected CO$_2$ absorption lines. At this concentration, and using the bowing parameter of Berolo and Woolley ($\gamma(\Delta_0) = +1170$ meV), this alloy would have a spin-orbit splitting energy of $\Delta_0 \sim 295$ meV - just 5 meV different to the $E_0$ band gap. However, if we calculate the value of $\Delta_0$ for this alloy using our measured bowing value
(-165 meV) we obtain a value of $\Delta_0 \sim 485$ meV. This is now 195 meV greater than the fundamental band gap energy.

To illustrate how these two different scenarios would lead to quite different non-radiative recombination properties we illustrate the CHSH Auger recombination process schematically in Fig. 6.35: The left hand figure shows the situation where $E_0 \sim \Delta_0$ (such as that obtained above for the hypothetical device using Berolo and Woolley's $\gamma (\Delta_0)$ value). The right hand figure shows the situation where $E_0 < \Delta_0$ (as obtained using our $\gamma (\Delta_0)$ value). From Fig. 6.35 it can be seen that when $E_0 \sim \Delta_0$ states close to the band edge (where carrier concentrations are large) can contribute to the recombination process, and as such, the recombination rate will be high (involving near-vertical transitions). [35] However, when $E_0 < \Delta_0$ (right hand side) an electron near the band edge, recombining with a heavy-hole, will not release sufficient energy to promote an electron in the spin split-off valence band into the heavy-hole band (the solid symbol with the dotted outline represents the required electron state for the CHSH process in Fig. 6.35 to occur
- however, there is no available state with this energy and momentum). In this situation only energetic carriers, far from the band edges (where carrier concentrations are low), may contribute to CIISH recombination and so the rates are significantly lower in this scenario.

On this basis we would expect the rate of CIISH recombination to be much reduced in our hypothetical CO$_2$ gas detector if we used our $\gamma(\Delta_0)$ value instead of Berolo and Woolley's. This indicates how the calculated performance of a device could be very different to that of the actual performance, simply as a result of using a different value for the splitting energy in the prediction.

We hope that our new result for the bowing of the spin-orbit splitting energy in InAsSb will be of use to researchers working with MIR semiconductors, and that our measured value of $\gamma(\Delta_0)$ will enable future MIR devices based on InAsSb to be designed with lower non-radiative losses.

We can put our slightly tentative suggestion that the bowing of the spin-orbit splitting energy in InAs$_{1-x}$Sb$_x$ is $\gamma(\Delta_0) = -165$ meV to the test, by attempting to use it to interpret our results for the two pentenary alloys in which we were able to measure $\Delta_0$ (i.e. s922 and s923). Since these two samples consist of predominantly InAs$_{1-x}$Sb$_x$ (see table 6.3 on page 214) their $\Delta_0$ value will depend heavily on the bowing exhibited in InAs$_{1-x}$Sb$_x$. This can be seen in our interpolation scheme for these pentenary alloys which is described in appendix C (Eq. C.8). Table 6.4 lists various values of $\Delta_0$ for s922 and s923. The second column of this table lists our measured value of $\Delta_0$ in these two pentenary alloys – taken from the results in section 6.4.2. The third column shows the interpolated values of $\Delta_0$ using the bowing parameter reported by Berolo and Woolley ($\gamma(\Delta_0) = +1170$ meV). [27] The fourth column shows the value calculated using zero bowing for the InAs$_x$Sb$_{1-x}$ spin-orbit splitting energy, and the final column shows the value obtained using our tentative value of ($\gamma(\Delta_0) = -165$ meV). The binary alloy parameters and bowing values for the other ternary alloys required for the interpolation have been taken from Ref. [17]. We have also listed uncertainties in these interpolated values, which are representative of the uncertainty in the compositions of the two samples. This arises since the X-ray diffraction measurements

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Table 6.4: Comparison of our measured spin-orbit splitting energy ($\Delta_0^{\text{meas}}$) for the two pentenary alloys (s922 and s923) with values obtained from interpolating binary literature values and ternary bowing parameters. Three interpolated values are shown, using differing bowing values for $\Delta_0$ in InAsSb. The first shows the value of Berolo & Woolley (1170 meV) [27], the second is for zero bowing (0 eV) and the third uses our tentative result from the studies on InAsSb (−165 meV). Other parameters are taken from Ref. [17].

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$\Delta_0^{\text{meas}}$ (meV)</th>
<th>$\Delta_0(\gamma = +1170 \text{ meV})$ (meV)</th>
<th>$\Delta_0(\gamma = 0 \text{ meV})$ (meV)</th>
<th>$\Delta_0(\gamma = -165 \text{ meV})$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s922</td>
<td>455 ± 10</td>
<td>293 ± 20</td>
<td>415 ± 20</td>
<td>432 ± 20</td>
</tr>
<tr>
<td>s923</td>
<td>476 ± 10</td>
<td>286 ± 20</td>
<td>420 ± 20</td>
<td>439 ± 20</td>
</tr>
</tbody>
</table>

conducted on the samples gave alloy concentrations which are only accurate to the nearest 1%. It is interesting to note that the resulting uncertainties are greater than the experimental uncertainties of our measured values.

It is clear from table 6.4 that our measured values of $\Delta_0$ for these two pentenary alloys bear no resemblance to the values obtained for the interpolation using Berolo and Woolley’s bowing parameter. For s922 the interpolated energy is 162 meV smaller than the measured value and for s923 the difference is 190 meV. This is in line with our studies on InAs$_{1-x}$Sb$_x$ and indicates that the bowing of $\gamma(\Delta_0) = +1170$ meV is not incorrect for these homogeneous, epitaxial samples. Furthermore, our measured splitting energy is larger in sample s923 than that of s922, the opposing trend to that given by the interpolated values for $\Delta_0$ using Berolo and Woolley’s bowing parameter.

Comparing our measured splitting energies with the interpolated values using zero bowing for $\Delta_0$ in InAs$_{1-x}$Sb$_x$ we see that the agreement is much improved – indicating that the bowing is closer to zero than +1170 meV. Now the differences between the $\Delta_0$ values are just 40 and 50 meV for s922 and s923 respectively. Also, this interpolated result predicts a higher splitting in s923 than s922, as is seen in our experimental results.

The agreement between our measurements and the interpolated literature values is closer still if we use a value of $\gamma(\Delta_0) = -165$ meV for InAs$_{1-x}$Sb$_x$ as determined from our data in Fig. 6.34. For sample s922 the difference between the two $\Delta_0$ values is just 23 meV – comparable to the uncertainty in the interpolated result due to the uncertainty in the sample composition.
The agreement for sample s923 is not quite as good as this (37 meV). However, it is clear that the agreement is far better than that achieved using the large, positive bowing reported by Berolo and Woolley. This provides strong evidence to support our claim that the bowing of the spin-orbit splitting energy in InAs$_{1-x}$Sb$_x$ is close to zero. Our tentative suggestion that $\gamma(\Delta_0) = -165$ meV is also consistent with our MIR PR measurements on the Ga$_x$In$_{1-x}$As$_{1-y-z}$P$_y$Sb$_z$ pentenary alloys.

6.5 Conclusions

We have been successful in developing a mid-infrared grating spectroscopy PR system capable of measuring signals up to 4.75 $\mu$m. This has allowed us to conduct extensive studies on a series of InAs-rich InAs$_{1-x}$Sb$_x$ samples. From these studies our data for the Sb dependence of the fundamental band gap agrees with the literature behaviour (Fig. 6.32, p. 222). We have also been able to measure the temperature dependence of the fundamental band gap in some of the samples studied and we have compared this to the expected behaviour.

For all but two of the InAs$_{1-x}$Sb$_x$ samples we have been able to measure the spin-orbit splitting energy. To the best of our knowledge this is the first measurement of this energy in InAs$_{1-x}$Sb$_x$ since Berolo and Woolley published data in 1972 indicating that the bowing of $\Delta_0$ was +1170 meV. [27] Our results are in disagreement with this result and we observe almost no bowing for $\Delta_0$ (Fig. 6.34, p. 227). A best fit of our results indicates that the bowing is actually slightly negative, giving a value of $-165$ meV. This result is in line with the theoretical predictions of Wei and Zunger whose calculations indicate that the bowing of the splitting energy in InAs$_{1-x}$Sb$_x$ should be slightly negative. [33] It is our belief that Wei and Zunger's suggestion that sample inhomogeneity is the cause of the positive bowing observed in Ref. [27] is plausible since our measurements on homogenous epitaxial samples show no such bowing.

We have also been successful in measuring the first PR measurements of the pentenary alloy Ga$_x$In$_{1-x}$As$_{1-y-z}$P$_y$Sb$_z$. From these studies we were
able to determine the spin-orbit splitting energy in this material system for the first time. We were then able to use these values to show that our measured bowing for $\Delta_0$ in InAs$_{1-x}$Sb$_x$ gave a far better agreement with these measurements compared to that obtained using the bowing of Berolo and Woolley.

6.6 References


6. Mid-infrared photomodulated reflectance of InAs-rich InAsSb and GaInAsSb alloys


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6. Mid-infrared photomodulated reflectance of InAs-rich InAsSb and GaInAsPSb alloys


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7 Conclusions and future work

Within this work we have reported results on a number of studies on semiconductor materials and devices and here we aim to give a brief summary of these. As well as reviewing our conclusions we shall also discuss the possible implications of the results, and the future prospects within each area.

In chapter 3 we reported on photomodulated reflectance (PR) studies of an unprocessed vertical-cavity surface-emitting laser (VCSEL) wafer designed to be a high-temperature oxygen gas sensor, emitting at 760 nm. Initial conventional reflectance measurements of the sample indicated that the VCSEL was of a very high finesse, with a cavity mode (CM) FWHM of just 0.19 nm (see Fig. 3.4 on page 53). In both the low resolution angle dependent PR studies and the high-resolution temperature dependent PR studies we were able to determine the conditions at which the VCSEL CM energy \( E_{CM} \) was tuned to the ground state energy of the quantum well transition \( E_{QW} \) by observing the symmetry of the PR lineshapes. It is known that in VCSELS which have quantum well (QW) PR features broader than that of the CM (such as in this sample) the PR spectrum becomes antisymmetric when the VCSEL is tuned \( E_{QW} = E_{CM} \). [1] Here we saw that the lineshapes became almost perfectly antisymmetric at room temperature and an angle of 45° (Fig. 3.10, p. 63) and the temperature dependent studies (at normal incidence) returned an antisymmetric lineshape at a temperature of 114 °C(Fig. 3.17, p. 75). At this temperature, when the VCSEL was tuned, the CM wavelength was found to be \( \sim 760 \) nm, indicating that sample was, as desired, suitable for the production of high temperature oxygen gas sensors.

On analysis of the high-resolution reflectance measurements of the 760 nm VCSEL wafer we noticed an interesting effect regarding the shape of the CM feature as we changed either the angle of incidence, or the temperature of the sample. We observed that the FWHM of the CM in the reflectance spectrum was dependent on the energy separation between the CM and the QW transitions, and that the broadening became maximised when the CM was tuned to the ground state transition energy (see Fig. 3.23, p. 83 &
Fig. 3.24, p. 84). We suggested that this 'cavity mode broadening effect' would be prominent in high finesse VCSELs such as the 760 nm sample studied here, and that the technique could be used as a verification of PR results, or an alternative technique if PR was not possible for some reason.

In order to learn more about the possible performance of a VCSEL oxygen gas sensor based on the material system of the sample studied in chapter 3 we examined the carrier recombination mechanisms in two 760 nm edge-emitting lasers (EELs) containing similar active regions to the 760 nm VCSEL wafer. By studying the variation of the threshold current of the EELs as a function of temperature in chapter 4 we concluded that the devices suffered from thermally activated leakage of electrons from the active regions. Using a simple model to describe the leakage process we were able to determine the activation energy of the leakage process in each device, the values for which indicated the electrons were escaping into the X-minima of the barrier and/or cladding layers. By applying hydrostatic pressure on the devices we were able to vary the activation energy of the leakage process in the EELs and using the known pressure coefficients of the different energy bands in the materials were were able to determine that the carrier leakage did indeed involve the X-minima in the barrier/cladding layers. Although we did not conduct studies of the threshold current in a processed 760 nm VCSEL (which would depend on both the carrier leakage, and the extent of the gain-cavity de-tuning) we were able to indicate the possible effects of the carrier leakage in a VCSEL operating at high temperatures \((T \sim 110 \, ^\circ\text{C})\). At similar temperatures we found that \(\sim 85\%\) of the threshold current in the EELs was due to carrier leakage. Such high levels of leakage would reduce the thermal stability of a VCSEL, which would be detrimental for a gas sensing device, and it would also lead to high carrier densities in the distributed Bragg reflectors, which would reduce the reflectance and, in turn, the efficiency of a laser. Unfortunately, choices of materials for use in devices operating near 760 nm are rather limited so overcoming the problems caused by the carrier leakage is not a simple task. The best solution would be to improve the radiative efficiency of the lasers by optimising factors such as the strain within the active region. This may then help to reduce the impact caused by the non-radiative
7. Conclusions and future work

In chapter 5 we returned to investigate the measured PR spectra of the 760 nm VCSEL wafer. Although we were successful in determining when $E_{CM} = E_{QW}$ in the sample by examining the symmetry of the PR lineshapes, we were unable to fit the measured spectra using the existing lineshape model. We reasoned that we were unable to achieve fits of the low resolution, angle dependent spectra since these were not fully resolved, and thus exhibited convoluted features not described by the existing model. However, we also found that our high-resolution temperature dependent PR measurements, which displayed some very intricate detail, could not be described by the existing model (see Fig. 5.1, p. 126). We believed that this may be due to the very high finesse of the VCSEL CM feature, which caused the PR lineshapes to exhibit these intricate details. In order to investigate this further we calculated the reflectance of the VCSEL structure using transfer matrices, including a detailed model for the dielectric function of the QWs in the structure. We were able to calculate the reflectance of the VCSEL at different angles of incidence allowing us to monitor the changes as the CM was tuned through the QW transition energies. The first finding from this study was that the reflectance simulations reproduced the cavity mode broadening effect which we had observed in our measured reflectance spectra of the 760 nm VCSEL wafer. We demonstrated that the FWHM of the CM reflectance feature was directly proportional to the absorption of the QWs as our earlier experimental results had suggested (Fig. 5.9, p. 141). By also calculating the Seraphin coefficients of the QW layers in the VCSEL structure we were able to develop a new model which could describe the intricate lineshapes in the region of the sharp CM feature. Analysis of the simulations revealed that in the vicinity of the CM the Seraphin coefficients were Kramers-Kronig pairs. From a detailed mathematical analysis of the problem, we were able to prove that such a relationship could indeed occur for the Seraphin coefficients of a VCSEL CM. This relationship forced a new constraint on our model, but with it came the advantage of a reduced number of parameters required to fit the spectra. Using the information gained from the reflectance simulations and our newly developed VCSEL PR model we were successful in fitting our
measured \( PR \) spectra of the 760 nm VCSEL (Fig. 5.19, p. 158). This indicated that the new model, with the enhanced Seraphin coefficient lineshapes, was appropriate for describing the \( PR \) spectra of high-finesse VCSELs such as the 760 nm sample studied in this work.

While the model was successful at fitting the measured \( PR \) spectra of the VCSEL studied in this work it would be interesting to test its effectiveness on other samples. Our work suggests that the model should be appropriate for high-finesse VCSELs, whose CM features are influenced by the QWs within the structure, and not unduly spoilt by say absorption within the Bragg mirrors. Any future studies on such VCSELs will hopefully help to verify the validity of the new model.

In chapter 6, the final chapter of results in this work, we discussed our mid-infrared (MIR) \( PR \) studies of narrow gap semiconductors including a series of InAs\( _{1-x} \)Sb\( _x \) samples, and four Ga\(_{0.2} \)In\(_{1-x} \)As\(_{1-y} \)P\(_y \)Sb\( _x \) pentenary alloys. Using our newly developed MIR \( PR \) setup we were able to measure the fundamental band gap energy \( (E_0) \) in all of the samples studied, and the spin-orbit splitting-energy \( (\Delta_0) \) in the majority of samples. Also, for the samples with lower Sb concentrations we were successful in measuring the temperature dependence of \( E_0 \) up to room temperature. The measured values of \( E_0 \) in InAs\(_{1-x} \)Sb\( _x \) were seen to be in reasonably good agreement with the literature values (Fig. 6.32, p. 222). However, for our measured values of \( \Delta_0 \) we obtained a quite different finding – our splitting energies tentatively suggested a bowing of \( \gamma(\Delta_0) = -165 \) meV in InAs\(_{1-x} \)Sb\( _x \), compared to the only other reported value in the literature of \(+1170 \) meV. [2] Although this strong, positive bowing seen in Ref. [2] was the only recorded value in the literature of the \( \Delta_0 \) bowing in InAs\(_{1-x} \)Sb\( _x \), several authors had since reported theoretical studies which indicated that the expected bowing should actually be negative, consistent with our tentative result (see for example Ref. [3]). We suggested that we did not see a positive bowing in our studies since the InAs\(_{1-x} \)Sb\( _x \) samples we investigated were of a good quality, and homogenous. It has been mentioned previously that sample inhomogeneity could cause an apparent positive bowing of \( \Delta_0 \) in ternary alloys. [3]

Analysis of our measured \( \Delta_0 \) values in the pentenary alloys showed that
the results were in line with our findings for the bowing of $\Delta_0$ in InAs$_{1-x}$Sb$_x$. The expected values for $\Delta_0$, obtained by interpolating the binary semiconductor values and ternary bowing parameters of the constituent alloys, were very different to our measured values when we used the literature reported bowing in InAsSb of $\gamma(\Delta_0) = +1170$ meV. However, when we used our measured value of $\gamma(\Delta_0) = -165$ meV, as determined from the studies of the InAs$_{1-x}$Sb$_x$ samples, we obtained a much better agreement with our measurements. This was a strong indication that our measured value for $\gamma(\Delta_0)$ in InAs$_{1-x}$Sb$_x$ was indeed correct.

It is possible that our findings may encourage the future development of materials used in MIR semiconductor devices due to the importance of the InAs$_{1-x}$Sb$_x$ alloy for MIR applications, and the spin-orbit splitting energy in non-radiative loss processes. It is our hope that these results will add to the body of work on InAs$_{1-x}$Sb$_x$, enabling a better understanding of the material and others based upon the alloy.

With the strong level of interest in the MIR, there is a wide range of topical semiconductor material systems designed to operate in the 3–5 µm region which could be studied using the current $PR$ setup. As an example of this we have conducted some initial $PR$ studies on an interesting lead salt semiconductor sample. These results are shown in figure 7.1. This sample contains PbSe/EuSe superlattices grown on BaF$_2$ and was grown at the University of Linz, Austria. Lead salt semiconductors have quite different band structures to their III-V counterparts and the combination of PbSe (a narrow gap semiconductor) and EuSe (a relatively wide gap semiconductor) in a superlattice arrangement has not previously been studied. Our early results show that we have been successful in measuring $PR$ from this sample and the solid vertical line in Fig. 7.1 shows the variation of the energy of the calculated $PR$ modulus peaks. What is interesting is that these energies are $\sim 95$ meV higher than those obtained from the peaks of the photoluminescence spectra (not shown) measured at Linz (see the dashed vertical line in Fig. 7.1). The reason for this difference is unknown at this stage and future studies on this and similar samples may help to increase the knowledge of these interesting lead salt material systems.
Having demonstrated the viability of the MIR PR system we believe there are future improvements which can be made to the setup which should improve the capability and range of the system. These include the incorporation of dedicated order sorting filters to cut out high-order light more effectively, using an IR transmissive cryostat window, and using a Nernst source in place of the QTH source to produce more output at longer wavelengths. This could make possible studies on samples deeper into the MIR than we have measured in this work, and thus open up the potential for studying an even greater range of interesting materials.

References

7. Conclusions and future work


APPENDIX

A Multi-band envelope function $k \cdot p$ method for calculating quantum well confined states

Here we discuss the method used for calculating the confined state energies in the quantum wells (QWs) studied in this work. The method, known as the multi-band envelope function technique, follows that described by Ikonin in Ref. [1] and Chen et al. in Ref. [2]. It allows us to find the eigenstates in a QW, accounting for both interband interactions and strain, using $k \cdot p$ theory; effects ignored in the single band approximation described briefly in section 2.1.3. We limit our discussion of the technique to the $6 \times 6$ Hamiltonian of the valence band (VB) since for larger systems spurious solutions are known to occur, [2] which must be removed in order to obtain meaningful results (beyond the scope of this work). For our purposes this is adequate since the QWs studied in this thesis have relatively wide band gaps (i.e. not like the bulk, narrow gap semiconductors studied in chapter 6). For the conduction band (CB) we use the simple, single band theory, with the assumption that it is well separated from the VB that the confined states in the CB are not significantly influenced by the confined states in the VB.

Since we are only interested in the confined state energies at the $\Gamma$-point in this work, and not the dispersion of the confined state bands, we do not consider finite values of the in-plane wavevector here ($k_x = k_y = k_{||} = 0$) – where $z$ is the growth direction. Therefore, certain terms (mostly off-diagonal, coupling terms) which appear in the standard $6 \times 6$ Luttinger-Kohn valence band Hamiltonian [3] are zero here.

The first step required to solve for the allowed state of a QW is to write out the Hamiltonian as a sum of components, which are coefficients of $k_z$ (the wavevector in the growth direction):

$$[H] = [H_2k_z^2 + H_1k_z + H_0] \quad (A.1)$$

Where $H_2$, $H_1$ and $H_0$ are all matrices.
As explained in Ref. [1] it is possible to reduce the size of the Hamiltonian $H$ to $3 \times 3$ by block-diagonalising the original $6 \times 6$ matrix. The three components of the $3 \times 3$ block-diagonalised Hamiltonian in Eq. A.1 are given by the three matrices below:

\[ H_0 = \begin{bmatrix} P_e + Q_e + V & 0 & 0 \\ 0 & P_e - Q_e + V & \sqrt{2}Q_e \\ 0 & \sqrt{2}Q_e & P_e + \Delta_0 + V \end{bmatrix} \] (A.2)

\[ H_1 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \] (A.3)

\[ H_2 = \begin{bmatrix} (\gamma_1 - 2\gamma_2) & 0 & 0 \\ 0 & (\gamma_1 + 2\gamma_2) & -2\sqrt{2}\gamma_2 \\ 0 & -2\sqrt{2}\gamma_2 & \gamma_1 \end{bmatrix} \] (A.4)

The $H_1$ matrix is zero here because we are only considering the case where $k_{||} = 0$. In our calculations we use atomic units for simplicity, so that $\hbar^2/m = 1$. The atomic units of energy are Hartrees (1 Hartree $\approx 27.211$ eV) and the units of length are Bohrs (1 Bohr $\approx 0.52918$ Å). [4]

In these three matrices the first (last) columns and rows correspond to the heavy-hole (spin split-off hole) band and the second columns and rows represent the light-hole band. These matrices describe the bands at the $\Gamma$-point in bulk materials and in this technique they are used to describe the envelope wavefunctions for each state in the wells and barriers, allowing the quantum confined states to be described. [1] The well and barrier bulk material parameters can be entered into Eqs. A.2–A.4 to describe the wavefunctions in both materials. The term $V$ is the potential energy and is zero in the well (assuming no electrostatic field is applied across it). In the barriers $V$ is equal to the valence band offset between the well and barrier materials. We take the zero energy to be the valence band edge in the well and use positive energies to describe points lying deeper in the valence band (inverted energy picture). Therefore $V$ will be positive in the barriers of a QW such as the
Appendix A. Multi-band envelope function $k \cdot p$ method for calculating quantum well confined states

type shown in Fig. 2.5 (p. 20). $\Delta_0$ is the spin-orbit splitting energy, and the $P_\epsilon$ and $Q_\epsilon$ terms are given by Eqs. A.5 and A.6, which incorporate the effects of strain into the calculations (resulting from a lattice mismatch between the well and substrate materials):

$$P_\epsilon = -a_v (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})$$  \hspace{1cm} (A.5)

$$Q_\epsilon = -\frac{b}{2} (\epsilon_{xx} + \epsilon_{yy} - 2\epsilon_{zz})$$  \hspace{1cm} (A.6)

Here $a_v$ and $b$ are the material dependent Pikus-Bir hydrostatic and uniaxial strain deformation potentials respectively and the $\epsilon$ terms are the strains given by the following equations (for growth of a layer in the $z$ direction on a $[001]$ oriented substrate): [1]

$$\epsilon_{xx} = \epsilon_{yy} = \frac{a_0 - a_{latt}}{a_{latt}}$$  \hspace{1cm} (A.7)

$$\epsilon_{zz} = -\frac{2C_{12}}{C_{11}} \epsilon_{xx}$$  \hspace{1cm} (A.8)

$C_{12}$ and $C_{11}$ are the material stiffness constants, which like $a_v$ and $b$, can be obtained from the literature. [5] $a_0$ is the lattice constant of the substrate (to which the barrier layers are assumed to be latticed matched here) and $a_{latt}$ is the unstrained lattice constant of the well material. These strain terms are required for calculating the confinement energies in QWs such as those in the edge-emitting laser containing compressively strained InGaAlAs QWs studied in chapter 4. Their presence in the diagonal terms of the $H_0$ matrix in Eq. A.2 shifts the relative positions of the three valence bands at the $\Gamma$-point. The off-diagonal $\sqrt{2}Q_\epsilon$ strain terms in $H_0$ couple the light-hole and spin split-off hole bands, even when the wavevector is zero.

From Eq. A.1 it follows that the complex wavevector $k_z$ is an eigenvalue of the $3 \times 3$ non-linear eigenvalue problem $[H(k_z) - E] [F] = 0$, where $[F]$ is an eigenvector of length three. To solve the non-linear problem it can be
Appendix A. Multi-band envelope function k·p method for calculating quantum well confined states

converted into a $6 \times 6$ linear problem, given by equation A.9: [1, 2]

\[
\begin{bmatrix}
0 & 1 \\
-H_2^{-1}(H_0 - E) & -H_2^{-1}H_1
\end{bmatrix}
\begin{bmatrix}
u \\
kzu
\end{bmatrix}
= k_z
\begin{bmatrix}
u \\
kzu
\end{bmatrix}
\]  
(A.9)

Here $0$ and $1$ are $3 \times 3$ null and unit matrices. This eigenvalue problem yields six, generally complex valued $k_z$ wavevectors and six corresponding eigenstates, $[u]$. In order to solve Eq. A.9 we used a freely available add-in tool written for MS Excel, capable of solving complex-eigenvalue problems. [6]

The eigenstates behave as plane waves in a layer and are expressed in the basis $[F]$ so that $[u]$ is a particular linear combination of $F_1 - F_3$ at energy $E$. The first three components of $[u]$ are amplitudes, the remaining three (multiplied by $i$) are derivatives ($k_z$ is replaced with the operator $i\partial/\partial z$ in a QW system grown along the $z$ direction). [1, 2] A state with purely real $k_z$ is denoted a forward-going state if $k_x > 0$, and backward-going otherwise. If $k_z$ is complex, or purely imaginary, a state is classified as forward (backward) if the wavefunction decays to the right (left). In a layer there are three forward, and three backward states, and any wavefunction can be expressed as a linear sum of these. The vector containing the coefficients of the three forward (backward) states in layer $j$ is denoted as $[a_j]$ ($[b_j]$).

Now we may discuss how a wavefunction at the beginning of layer $j$ may be transferred through the layer and across the interface into the $(j + 1)$th layer. By left multiplying a state vector with the diagonal matrix $D_j = diag(..., \exp(ik_zd_j), ...)$, it may be transferred from the beginning to the end of the $j$th layer, where $d_j$ is the width of the layer. Then, by applying the boundary conditions (i.e. that $\psi$ and $(1/m_{eff})\partial\psi/\partial z$ are continuous, where $m_{eff}$ is the effective mass) in the form of an interface matching matrix, the wavefunction $\psi$ can be transferred across into the next layer. This interface matrix $I_j$ is given by the matrix in the relationship of equation A.10, where again $0$ and $1$ are the $3 \times 3$ null and unit matrices respectively, and $H_2$ is the matrix appearing in Eq. A.4:

\[
\begin{bmatrix}
1 & 0 \\
0 & H_2
\end{bmatrix}
\begin{bmatrix}
F \\
F'
\end{bmatrix}
= \text{const}  
(A.10)
\]
Appendix A. Multi-band envelope function k·p method for calculating quantum well confined states

The 6 x 1 vector $[F \ F']^T$ contains the amplitudes (first three terms) and derivatives of a wavefunction expressed in the $F$-basis.

Since Eq. A.10 is constant, we can state the following for two adjoining layers in a QW heterojunction:

$$ [I_{j+1}] \begin{bmatrix} F \\ F' \end{bmatrix}_{j+1} = [I_j] \begin{bmatrix} F \\ F' \end{bmatrix}_j $$ (A.11)

This leads directly to the matrix $I_{j+1}^{-1}I_j$, which transfers a state in the $F$-basis from the end of layer $j$, across the interface, and into layer $j+1$.

A wavefunction obtained from Eq. A.9 is expressed in the $u$-basis and must be re-expressed in the $F$-basis so that it can be transferred across an interface using the matrix $I_{j+1}^{-1}I_j$. This can be done by multiplying vector $[u]$ with the matrix $U$ – constructed by stacking the states $[u_1] - [u_6]$ side by side:

$$ U = [u_1|u_2|...|u_6], \ [F] = U [u], \ [u] = U^{-1} [F] $$ (A.12)

Putting all this together, we can define the transfer matrix $T^{j,j+1}$ (a matrix of 3 x 3 component matrices), which transfers a wavefunction at the beginning of layer $j$ to the beginning of layer $j+1$, as Eq. A.13 below:

$$ T^{j,j+1} = U_{j+1}^{-1}I_{j+1}^{-1}I_jU_jD_j $$ (A.13)

Equation A.14 shows how the layer transfer matrix relates the forward (a) and backward (b) travelling states in two adjoining layers:

$$ \begin{bmatrix} a_{j+1} \\ b_{j+1} \end{bmatrix} = T^{j,j+1} \begin{bmatrix} a_j \\ b_j \end{bmatrix} $$ (A.14)

In a structure of $N$ layers, the total transfer matrix is given by the product:

$$ T^{0,N} = \prod_{j=0}^{N-1} T^{j,j+1} $$ (A.15)

This allows us to reveal how the states in the final layer of a structure
Appendix A. Multi-band envelope function \( k \cdot p \) method for calculating quantum well confined states

\([a_N \ b_N]^T\) are related to the states in the first \([a_0 \ b_0]^T\):

\[
\begin{bmatrix}
a_N \\
b_N
\end{bmatrix} =
\begin{bmatrix}
T_{11} & T_{12} \\
T_{21} & T_{22}
\end{bmatrix}
\begin{bmatrix}
a_0 \\
b_0
\end{bmatrix}
\]  \hspace{1cm} (A.16)

We know that, for bound states, the forward-going elements must be zero in the first layer (i.e. \( a_0 = 0 \)) so that the wavefunction decays to the left (i.e. \( \psi_{x=-\infty} \to 0 \)). Similarly, the backward-going element of a bound state in the final layer must also be zero (\( a_N = 0 \)) so that the wavefunction decays to the right and \( \psi_{x=\infty} \to 0 \). Therefore, from Eq. A.16, we find that the following must be true for bound states in a QW:

\[
T_{22}b_0 = 0 \]  \hspace{1cm} (A.17)

Equation A.17 is only satisfied for bound states and so by varying the energy \( E \) and searching for states which satisfy \( \det |T_{22}(E)| = 0 \) we can find the allowed confined states of a QW. Once a confined state energy is found it is then possible to find the wavefunction of the state using the determined \( b_0 \) vector. \[1\]

As an example of the process described above, figure A.1 shows a plot of \( \ln(\det |T_{22}(E)|) \) versus energy, obtained by us here for a single, 8 nm \( Al_{0.135}Ga_{0.865}As / Al_{0.386}Ga_{0.614}As \) QW such as the QWs in the unstrained edge-emitting laser studied in chapter 4. The material parameters required for this calculation were obtained from Ref. \[5\], and the value for \( V \) in the barriers is 100.0 meV at room temperature (using the conduction band offset \( Q_c = 68\% \) used in chapter 4). Each of the minima in Fig. A.1 corresponds to a confined state at that particular energy, and each is labelled accordingly.

The advantage of the technique outlined here is that it can be easily used to calculate the confined states in more complex structures such as multiple-QWs, or superlattices, simply by adding the appropriate transfer matrices to Eq. A.15. It can also be used with Hamiltonians other than the \( 6 \times 6 \) Luttinger-Kohn VB matrix discussed here, thus allowing the effects of other bands, such as the CB, to be included explicitly.

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Appendix A. Multi-band envelope function $k \cdot p$ method for calculating quantum well confined states

Figure A.1: Plot of the natural log of $\det |T_{22}(E)|$ versus confinement energy for a quantum well in the unstrained $\text{Al}_{0.135}\text{Ga}_{0.865}\text{As} / \text{Al}_{0.386}\text{Ga}_{0.614}\text{As}$ 760 nm edge-emitting laser studied in chapter 4. The minima occur at the energies of the confined states in the well as per Eq. A.17. Each minimum is labelled in terms of the state to which it is associated ($hh=$ heavy-hole, $lh=$ light-hole). The depth of the well, $V$, is 100.0 meV.

References

[1] P. Harrison, Quantum wells wires and dots, 2nd ed, Ch. 10 (Z. Ikonic), Wiley, UK (2005) p345


Appendix B. Kramers-Kronig analysis of the Seraphin coefficients of VCSELs

Here we use the theory of Complex Analysis to provide a mathematical explanation as to why the Seraphin coefficients of a VCSEL could be a Kramers-Kronig pair in the vicinity of the cavity mode energy. Equations B.1 and B.2 give the relations determined from our Seraphin coefficient simulations (see Fig. 5.13 on page 147), where $\text{KK}_{r-i}$ implies that the transform used is of the form that converts a real component into an imaginary one.

\[ \text{KK}_{r-i}[\alpha] = -\beta \quad \text{(B.1)} \]

\[ \text{KK}_{r-i}[\beta] = \alpha \quad \text{(B.2)} \]

The KK transform of the $\alpha$ Seraphin coefficient can be written explicitly using the following relation:

\[ \text{KK}_{r-i}[\alpha] = -\frac{2\omega}{\pi} \int_{0}^{\infty} \frac{\partial \ln R(\omega)}{\omega^2 - \omega'} d\omega' \quad \text{(B.3)} \]

The term inside the integral can be converted to a form more useful for our purpose by using the quotient rule of differentiation. This is shown here by equation B.4.

\[ \frac{\partial}{\partial \varepsilon_1} \left( \frac{\ln R}{\omega'^2 - \omega^2} \right) = \frac{\partial (\ln R)/\partial \varepsilon_1}{\omega'^2 - \omega^2} - \frac{\ln R \partial (\omega'^2 - \omega^2)/\partial \varepsilon_1}{(\omega'^2 - \omega^2)^2} \quad \text{(B.4)} \]

The term on the left hand side is of a form that will allow us to take the differential ($\partial/\partial \varepsilon_1$) outside of the integral in Eq. B.3. The first term on the right hand side of Eq. B.4 is the term appearing in the integral of the KK transform. The second term on the right contains $\partial (\omega'^2 - \omega^2)/\partial \varepsilon_1$; if, over the energy range where $\alpha$ extends, the energy dispersion of $\varepsilon_1$ is negligible (or constant), then this term can be assumed to be insignificant. Over such a limited energy range (i.e. the CM region) such a condition is approximately valid and thus we can neglect this term. This argument then allows us to
write the KK transform of $\alpha$ as Eq. B.5.

$$KK_{\text{r-i}}[\alpha] \approx \frac{\partial}{\partial \xi_1} (KK_{\text{r-i}}[\ln R]) \quad (B.5)$$

It is important to highlight that this is only true if the second term on the right of Eq. B.4 can be approximated as zero over the energy range where $\ln R$ is significantly varying (i.e., in the energy region of the CM). Therefore, Eq. B.5 is unique to the situation of a VCSEL CM feature.

The desired KK transform of $\ln R$ in Eq. B.5 can be derived from the relationship of the complex amplitude of the reflectance, $r = a + ib = \sqrt{R}e^{i\theta}$. Here $\theta$ is the phase of the reflectance, $\theta = \tan^{-1}(b/a)$. Taking the natural log of $r$ we obtain equation B.6, containing $\ln R$.

$$\ln r = \frac{1}{2} \ln R + i\theta \quad (B.6)$$

Since $\ln r$ in Eq. B.6 is subject to causality, its real and imaginary parts must be a KK pair. Therefore, $KK_{\text{r-i}}[\ln R] = 2\theta$. We can substitute this result into Eq. B.5, giving equation B.7 for the KK transform of $\alpha$.

$$KK_{\text{r-i}}[\alpha] \approx 2 \frac{\partial \theta}{\partial \xi_1} \quad (B.7)$$

Equation B.7 gives the KK transform of $\alpha$ in terms of the phase of the reflectance, $\theta$. However, such a relationship is of little use in this form since $\theta$ is not directly measurable using conventional $R$ or PR experiments. Fortunately, in the theory of Complex Analysis, there exists a mathematical relationship useful in this situation. Consider a complex variable, $z = x + iy$: a function, $f(z)$ dependent on $z$ may be written as $f(z) = u(z) + iv(z)$. The derivative of $f$ with respect to $z$ can then be written as equation B.8. [1]

$$\frac{df}{dz} = \frac{\partial u}{\partial x} + i \frac{\partial v}{\partial x} = \frac{\partial v}{\partial y} - i \frac{\partial u}{\partial y} \quad (B.8)$$

This leads directly to the Cauchy-Riemann equations (Eq. B.9), which relates
Appendix B. Kramers-Kronig analysis of the Seraphin coefficients of VCSELs

the derivatives of the real and imaginary parts of \( f(z) \).

\[
\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y} \quad \text{and} \quad \frac{\partial v}{\partial x} = -\frac{\partial u}{\partial y} \quad (B.9)
\]

In order for us to use the Cauchy-Riemann relations of Eq. B.9 we make the following correspondences: \( z = x + iy \equiv \varepsilon = \varepsilon_1 + i\varepsilon_2 \) and \( f(z) \equiv \ln r \) so that \( u = 1/2 \ln R \) and \( v = \vartheta \). Therefore, we can rewrite the derivative \( \partial \vartheta / \partial \varepsilon_1 \) in Eq. B.7 using Eq. B.10.

\[
\frac{\partial \vartheta}{\partial \varepsilon_1} = -\frac{1}{2} \frac{\partial (\ln R)}{\partial \varepsilon_2} = -\frac{1}{2} \beta \quad (B.10)
\]

This gives us the final step for showing how \( \alpha \) and \( \beta \) for a VCSEL can be related by the KK relations. Substituting Eq. B.10 into Eq. B.7 gives the relationship found from the numerically calculated KK transforms between \( \alpha \) and \( \beta \) given in Eq. B.1. A similar analytical approach can be used to prove the result of Eq. B.2.

References

Appendix C. Interpolation formulae for ternary, quaternary and pentenary semiconductor alloys

C Interpolation formulae for ternary, quaternary and pentenary semiconductor alloys

Here we discuss the interpolation formulae used to describe how the parameters of the semiconductor alloys studied in this work depend upon the composition of the materials. While the standard interpolation formula used to describe ternary alloys is well established and straightforward to understand, the formulae for higher-order alloys are more complex. In chapter 6 we study alloys containing five different elements - so called pentenary alloys. In order to interpret the measurements of these samples it is necessary to develop an interpolation formula for pentenary alloys as no equivalent could be found in the literature. For interested readers the process of developing our pentenary interpolation formula is described here.

Consider first a ternary alloy such as \( \text{Al}_x\text{Ga}_{1-x}\text{As} \), composing of the two binary semiconductors, GaAs and AlAs. Under the virtual-crystal approximation (VCA) a given property of the ternary alloy, say the band gap, is simply a weighted average between the two binary endpoint values. For example, if we have \( x \) % of AlAs and \( (1 - x) \) % of GaAs, the ternary band gap would be simply \( E_0(\text{Al}_x\text{Ga}_{1-x}\text{As}) = xE_0(\text{AlAs}) + (1-x)E_0(\text{GaAs}) \). This linear interpolation between the binary endpoints is known as Vegard's law. [1]

The VCA assumes that a ternary alloy forms with a perfect lattice, having an averaged atomic potential at each lattice site. [2] However, when ternary alloys are formed the resulting crystal is, in reality, imperfect and deviations from the VCA cause certain properties of the alloy to be either reduced or increased from their expected weighted average value. This effect is known as bowing and is demonstrated in figure C.1 for a general ternary alloy \( \text{A}_x\text{B}_{1-x}\text{C} \), where \( \text{C} \) is the common element and \( \text{AC} \) and \( \text{BC} \) are the two constituent binary alloys. \( T \) is the value of the ternary parameter under consideration (e.g. the band gap). The dashed line in Fig. C.1 linking the two binary endpoint values of the parameter in question shows the linear, weighted average relation consistent with the VCA. The solid curve, clearly demonstrating a bowing away from the straight line, represents the typical behaviour of \( T \) as a function of alloy composition \( x \) when the ternary alloy does not adhere to the
Appendix C. Interpolation formulae for ternary, quaternary and pentenary semiconductor alloys

Figure C.1: Representation of the interpolation between two binary endpoints (BC and AC) to give the ternary alloy \( A_xB_{1-x}C \) property, \( T \). The dashed line shows the linear interpolation as per Vegard's law and the solid curve shows the bowing due to deviations from the virtual crystal approximation.

VCA. This behaviour can be described using the standard alloy interpolation formula of Eq. C.1, where the first two terms give the linear interpolation of Vegard's law and the third term \( -x(1-x)\gamma \) describes the bowing seen in Fig. C.1.

\[
T = xAC + (1-x)BC - x(1-x)\gamma \quad \text{(C.1)}
\]

In Eq. C.1 \( \gamma \) is known as the bowing term and is dependent on both the parameter in question (i.e. band gap, spin-orbit splitting, effective mass) and the two binary semiconductors involved. Eq. C.1 is written in such a way that a positive value of \( \gamma \) results in an downward bowing, meaning that \( T \) is reduced below the linearly interpolated VCA value. In the example shown in Fig. C.1 \( T \) demonstrates an upward bowing, consistent with a negative value for \( \gamma \).

In order to develop an equivalent to Eq. C.1 for pentenary alloys it is necessary to first consider quaternary alloys, which consist of four different elements. Quaternary alloys can be classified into two distinct types: type-I and type-II alloys. Type-I quaternary alloys, an example of which is
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Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$, have two group III elements and two group V elements (in the case of III-V semiconductors). Type-II quaternary alloys on the other hand contain one element from group III and three elements from group V, or alternatively, one element from group V and three from group III. An example of a type-II quaternary alloy would be InAs$_x$P$_y$Sb$_{2z}$, where $z = 1 - x - y$.

Quaternary alloys have been studied for a number of years and the work of Glisson and Williams et al. [3, 4] is among the earliest to establish interpolation schemes for both type-I and type-II quaternaries. While these equations appear often in the literature, alternate schemes can be found; in particular, Krijn uses a different scheme for type-II quaternary alloys. [5] We shall look here at how the interpolation scheme for type-I quaternaries is derived and also discuss how the two main type-II alloy schemes present in the literature gives rise to uncertainty in the interpolated quaternary parameter values.

Figure C.2 shows a representation in compositional space of a type-I quaternary alloy (A$_x$B$_{1-x}$C$_y$D$_{1-y}$), which we call $Q_I$. The $x$ and $y$ axes represent the alloy composition, with the four possible binary endpoints fixed at the corresponding locations on the $xy$ plane. For example, when $x = 1$ and $y = 0$ $Q_I = AD$ and the binary endpoint AD can be seen in Fig. C.2, lying on the $x$ axis (since $y = 0$) at $x = 1$. The vertical axis in Fig. C.2 represents the value of the quaternary parameter which is being interpolated; here we have labelled it $E$ for energy. The solid circles which represent the binary endpoints lie above the $xy$ plane, where the height above the plane represents the value of the binary parameter.

Between the four binary endpoints there are four possible ternary alloys which can be produced (A$_x$B$_{1-x}$D, AC$_y$D$_{1-y}$, A$_x$B$_{1-x}$C, & BC$_y$D$_{1-y}$). These appear on curves between the four binary endpoints, where the curvatures represent the bowing for each ternary alloy (see Eq. C.1). These four curves form the perimeter of a mesh, which represents the values that the quaternary parameter $Q_I$ can take on. At a given point the mesh has a specific curvature, which depends on the four curvatures of the outer edges, defined by the ternary bowing parameters. The quaternary alloy parameter $Q_I$ lies at a point on this mesh as shown in Fig. C.2. Two dashed curves, parallel to
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Figure C.2: Representation of a type-I quaternary alloy in compositional space (the $x-y$ plane). The vertical axis (labelled $E$ for energy gap) represents the values of the parameters of the various semiconductors being interpolated. The four binary semiconductors are located at the corners of the mesh shown, with the ternary alloys existing along the mesh boundary. The quaternary alloy parameter $Q_I$ is located on the mesh surface.

either the $x$ or $y$ axis, extend to the mesh perimeter where the positions of four ternaries are marked with open circles. These curves demonstrate how the value of $Q_I$ can be found by two routes, interpolating between either pair of ternary endpoints. It can be shown that both routes give the same result as required. If we consider the route between $BC_yD_{1-y}$ and $AC_yD_{1-y}$ we can express $Q_I$ using Eq. C.2

$$Q_I = xAC_yD_{1-y} + (1 - x)BC_yD_{1-y} - x(1 - x)y' \quad \text{(C.2)}$$

Here $y'$ is the bowing of the curve on which $Q_I$ lies and which links the two ternary endpoints. It can be represented as a linear interpolation of the bowing of ternary $A_xB_{1-x}D$ and $A_xB_{1-x}C$ which is given by Eq. C.3

$$y' = y\gamma^{A_xB_{1-x}C} + (1 - y)\gamma^{A_xB_{1-x}D} \quad \text{(C.3)}$$

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Combining Eqs. C.1 – C.3 gives us Eq. C.4, the interpolation formula for a type-I quaternary alloy $A_xB_{1-x}C_yD_{1-y}$. This is the same as the equation that appears in the literature, [3] except here we represent it in terms of the binary values and the ternary bowing parameters, which are readily found in the literature for a wide range of semiconductor materials.

\[
Q_I = BD + x[AD - BD] + y[BC - BD] + xy[AC + BD - BC - AD] - xy(1 - y)\gamma^{AC_yD_{1-y}} - (1 - x)(1 - y)\gamma^{BC_yD_{1-y}} \tag{C.4}
\]

Turning our attention to type-II quaternaries, Eq. C.5 gives the interpolation formula developed by Williams et al. [4] for the alloy $AB_zC_yD_{1-x-y}$.

\[
Q_{II}^{(Williams)} = \frac{yx[uAC + (1 - u)AB - u(1 - u)\gamma^{AB_zD_{1-x}}]}{xy + y(1 - x - y) + x(1 - x - y)} + \frac{y(1 - x - y)[vAD + (1 - v)AC - v(1 - v)\gamma^{AC_yD_{1-z}}]}{xy + y(1 - x - y) + x(1 - x - y)} + \frac{x(1 - x - y)[wAD + (1 - w)AB - w(1 - w)\gamma^{AB_zD_{1-w}}]}{xy + y(1 - x - y) + x(1 - x - y)} \tag{C.5}
\]

Here $u, v & w$ are given by Eq. C.6:

\[
u = \frac{1 - x + y}{2} \quad v = \frac{2 - 2y - x}{2} \quad w = \frac{2 - 2x - y}{2} \tag{C.6}
\]

Eq. C.5 is often used in the literature [6, 7, 8] indicating support for this interpolation scheme. However, as we mentioned previously, there is another interpolation equation for type-II quaternary alloys. Used by Krijn, [5] the
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formula in Eq. C.7 differs from that of Williams et al. [4]:

$$Q_{II}^{(Krijn)} = xAB + yAC + (1 - x - y)AD$$

$$- xy\gamma^{AB}_{C_{1-x}} - x(1 - x - y)\gamma^{AB}_{D_{1-x}}$$

$$- y(1 - x - y)\gamma^{AC}_{P_{1-y}}$$  (C.7)

Krijn's interpolation scheme is notably simpler in its form to that of Eq. C.5. It has also been independently derived by Hosea [9] suggesting that it is a valid interpolation scheme.

In order to observe any differences that arise from using the two interpolation schemes of Eqs. C.5 and C.7, and as a method for deciding which is best suited for our work, we shall use both to calculate the band gap of the alloy InAs$_{1-x-y}$P$_x$Sb$_y$ for varying antimony concentrations (0 < x < 1 - y%). Fixing the phosphorous concentration at y = 5% and using binary alloy and ternary bowing parameters from Ref. [8] gives us all the required inputs for Eqs. C.5 and C.7 to conduct the calculations. For simplicity we have opted to exclude the effects of strain caused by the differing lattice constants of InAs and InSb here. [8]

Figure C.3 shows the results of the calculations. The solid curve shows the InAs$_{1-x-y}$P$_x$Sb$_y$ band gap obtained using Eq. C.5 while the dashed curve shows the result using Krijn's formula (Eq. C.7).

It is clear from Fig. C.3 that when the antimony content is low (x < 10%) the two interpolation formulae yield very similar results. However, as x increases the bowing of the two lines differ resulting in large differences between the interpolated band gap energies in the range 20% < x < 90%. Also clear from Fig. C.3 is the fact that the curvature of the solid line changes sharply as x > 90%, and when the antimony reaches 95% (the maximum concentration possible since the phosphorous concentration is fixed at 5%) both interpolation methods tend towards the same result. This sudden change in curvature appears to be somewhat un-physical and is a possible indication that Krijn's formula, which gives the smooth varying result is the more appropriate interpolation equation.

We also note that the denominator in Eq. C.5 means that Williams et
Figure C.3: Band gap (at $T = 0$ K) of the type-II quaternary alloy $\text{InAs}_{1-x-y} \text{P}_x \text{Sb}_y$ ($y = 5\%$) calculated using parameters from Ref. [8] and the interpolation scheme of Williams et al. [4] given by Eq. C.5 (solid curve). The dashed curve shows the equivalent calculation using the interpolation scheme of Krijn. [5] given by Eq. C.7. The effects of strain have been omitted in both cases for simplicity.

al.'s approach cannot be used when both $x$ and $y$ are set to zero. For this particular example it means that their interpolation scheme cannot return the band gap for InAs.

Given both the fact that Eq. C.5 breaks down when $x = y = 0\%$, and that it gives rise to the unusual bowing profile of the solid curve seen in Fig. C.3 we recommend using Eq. C.7 for determining the interpolated parameters of type-II quaternaries. For these reasons we also use this equation as our base for developing an interpolation scheme for pentenary alloys of the form $A_xB_{1-x}C_{1-y-z}D_yE_x$. For this, we take the view that such an alloy is a simple mixture of two type-II quaternaries (i.e. $zAC_{1-y-z}D_yE_x$ and $(1 - z)BC_{1-y-z}D_yE_x$). This allows us to write an interpolation formula for
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a pentenary alloy $P$ as:

$$P = z\{(1 - y - x)AC + yAD + xAE - y(1 - y - x)\gamma_{C,1-y-x}D_{y+z} - z(1 - y - x)\gamma_{C,1-y-x}E_{y+z} - yx\gamma_{D,yE,1-y}\}$$

$$+ (1 - z)\{(1 - y - x)BC + yBD + xBE - y(1 - y - x)\gamma_{C,1-y-x}D_{y+z} - z(1 - y - x)\gamma_{C,1-y-x}E_{y+z} - yx\gamma_{D,yE,1-y}\}$$

(C.8)

This is the interpolation formula we use in chapter 6 for interpreting our mid-infrared photomodulated reflectance results of the liquid phase epitaxial grown pentenary alloy Ga$_z$In$_{1-z}$As$_{1-y-x}$P$_y$Sb$_x$.

References

[1] L. Vegard, Z. Phys. 5 17 (1921)


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