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Photoreflectance of Layered SiGe and III-V Semiconductors

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Abstract

Room temperature photoreflectance (PR) is shown to be influenced by optical interference between Si/SiGe/Si layers. The PR changes with wafer position due to a variation of Si cap thickness. By comparing the phase found from experiment with the theoretical phase calculated from the Séraphin coefficients, the thickness of the Si cap layer is determined across the wafer.

Energies of the SiGe $E_4$ and $E_4+\Delta_4$ critical point transitions found from room temperature PR measurements of thin strained SiGe layers are greater than expected. It is known that the SiGe interfaces are graded in composition, but this does not fully explain the energies found from the PR. Therefore, a simple square quantum well model is compared with experiment. It is likely that both composition grading and quantum confinement contribute to the energy shifts.

Franz-Keldysh oscillations (FKO) are observed in room temperature PR spectra of InGaAsP and InP layers. Electro-modulation theory has been developed to fit the FKO. It is found that the InGaAsP spectra are best fitted when considering light and heavy holes. This is applied to the FKO from the InP layers, and a good match between experiment and theory is achieved.

Energy transitions between electron and hole confined states in strained InGaAs quantum wells have been measured using room temperature PR and photoluminescence. The transition energies found from the PR have been compared with a theoretical quantum well model, and the band offsets found from the comparison. The agreement between experiment and theory is good for tensile strained InGaAs/InGaAsP quantum wells, and the band offset appears to vary little with tensile strain. A low energy feature in the PR spectra of InGaAs/InP quantum wells with compressive and tensile strain is attributed to a Zn impurity state. Despite difficulties in matching experiment with theory, the band offsets are also found for these structures.
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Publications

R. T. Carline, C. Pickering, T. J. C. Hosea and D. J. Hall, "Photoreflectance Spectroscopy of Pseudomorphic Si$_{1-x}$Ge$_x$ (100) Structures (x<0.26)", Mat. Sci. and Technol. 11, 416 (1995).

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D. J. Hall and R. T. Carline, "Photoreflectance of Thin Strained Si$_{1-x}$Ge$_x$ Layers (0.17<x<0.23)", in preparation
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Chapter 1

Introduction

1.1 Thesis Overview

The work undertaken during this PhD has included several material systems at the forefront of semiconductor research. The materials studied are SiGe and III-V alloys, both of which are important components in modern day semiconductor devices. The principle aims of this work have been to further understanding of the mechanisms contributing to photoreflectance (PR) spectra in these materials, and to use PR as a tool to investigate the properties of layered structures. The former aim is fulfilled in chapters 3 and 5, where a theoretical study of PR is compared with experiment. The latter aim is realised in chapters 4 and 6, where both SiGe and III-V quantum wells are investigated.

The properties of the semiconductor materials examined in this work are introduced in this chapter. These are InGaAs/InP, InGaAs/InGaAsP and Si/SiGe layers. As an introduction to the reader, early work on the theory of electroreflectance (ER) is presented, where much of the theoretical work done for ER can be directly applied to PR. Least squares fitting is essential in all PR work, and so this chapter is concluded with a brief description of the least squares fitting routine used to fit the PR spectra.

In chapter 2, the experimental arrangements for measuring infrared and ultra violet PR are described. The infrared system at the University of Surrey was set up at the outset of this work, and so is described in detail. In contrast, the ultra violet system was established before this work was begun, so only the refinements for which the author has been responsible are described in detail.

In chapter 3, theoretical work on the effect of optical interference on PR spectra of layered structures is presented. The terms in PR theory which are influenced by optical interference are the Seraphin coefficients. These are calculated using a method not previously applied to Seraphin coefficients. Comparing these calculations with room temperature ultra violet measurements of samples comprising of Si/SiGe/Si layers allows PR to be used for the first time to determine the thickness of the Si cap layer in such structures.

Room temperature and low temperature ultra violet PR measurements of thin SiGe layers grown on Si are shown in chapter 4. Anomalies in the critical point energies found from least squares fits to the spectra are investigated in terms of quantum confinement in the SiGe layer, and composition grading at the SiGe interfaces. Although no definite conclusions as to the origin of the systematic shift in critical point energies can be drawn from this work, there is strong evidence that quantum confinement occurs at the L point in Si/SiGe structures.

In chapter 5, Franz-Keldysh (FKO) oscillations in the room temperature PR spectra of InGaAsP and InP barriers in quantum well structures are observed. A method of fitting the
oscillations, based on expressions containing Airy functions, is developed. This is then successfully applied to the FKO in the experimental spectra by assuming that spectral features originate from contributions of light and heavy holes, and in the case of InP, split-off holes also.

Transitions between confined electron and hole states in InGaAs/InGaAsP and InGaAs/InP quantum wells are measured using room temperature PR and photoluminescence for wells of varying strain in chapter 6. The transition energies deduced from least squares fits to the PR are compared with a quantum well model. The band offsets are determined from this comparison.

1.2 Introduction to Semiconductors

This section is intended to be a brief introduction to the crystal and electronic structure of the semiconductors investigated in this thesis. This is followed by a description of quantum wells, and an overview of some applications of the materials and structures studied in this work. An interested reader requiring more detailed information may refer to the references herein.

1.2.1 Crystal and Electronic Structures

At room temperature and pressure, the semiconductors studied in this work have either diamond or zincblende crystal lattice structures. The tetrahedral bonding between atoms in such structures is shown in figure 1.1. In the figure, each atom is surrounded by four equidistant nearest neighbours which lie at the corners of a tetrahedron, and the covalent bond between two nearest neighbours is formed by two electrons with opposite spins. Both crystal structures can be considered in terms of two interpenetrating face-centred cubic lattices, that are displaced relative to one another along the main diagonal. For a diamond lattice, such as Si, all the atoms are the same, whereas in a zincblende lattice, such as GaAs, one sublattice is Ga and the other As. Most III-V materials crystallise into the zincblende structure.

![Figure 1.1 The unit cells of a diamond (Si) and zincblende (GaAs) lattice (Kelly (1995)).](image-url)
When considering the electronic structure of covalently bonded diamond and zincblende semiconductors, it is informative to begin with a single free atom made up of s and p electronic orbitals. When forming crystals, many atoms are brought into proximity and the outermost s and p electrons of the atoms interact with their nearest neighbours to form bonding and anti-bonding states. This electron interaction is repeated throughout the crystal, and the states consist of a linear combination of the s and p orbital states of the single atoms. All of the bonding states form what is known as a valence energy band, and the anti-bonding states form a conduction energy band. When these states are formed, there is a distinct gap in energy between electrons in the conduction and valence bands, and the difference in energy between the lowest point of the conduction band and the highest point of the valence band is called the bandgap. The number of electrons in the conduction band is largely controlled by the ratio of the bandgap and the temperature, such that at absolute zero a perfect semiconductor would be an insulator with all electrons in the valence band.

Brillouin described energy band theory in terms of a reciprocal lattice Brillouin zone, or Wigner-Seitz cell. This zone represents the different interactions of the atomic orbitals for electrons with different velocities, and is the unit cell of the reciprocal lattice. It is constructed by drawing perpendicular bisector planes in the reciprocal lattice from the centre to the nearest reciprocal lattice sites. These planes are important in the theory of wave propagation in crystals, because a wave whose wave-vector drawn from the origin terminating on any of these planes will satisfy the condition for diffraction. The central cell in the reciprocal lattice is important in the theory of solids, and is called the first Brillouin zone. The first Brillouin zone of diamond and zincblende crystal structures is shown in figure 1.2.

![Figure 1.2 The first Brillouin zone of diamond and zincblende structures (Kelly (1995)).](image)

The relation between the crystal momentum \( \mathbf{k} \), represented by a point in the first Brillouin zone, and energy is given by the band structure. This band structure represents electronic states in the conduction and valence bands. The band structure of GaAs is shown in figure 1.3. In general, the valence band in the zincblende crystal structure consists of four subbands. At \( \mathbf{k}=0 \) (\( \Gamma \) point), three of the four bands are degenerate, but spin-orbit interaction causes one of these to split, leaving two degenerate bands. Similarly, the conduction band is made up of subbands. It is important to realise that for some materials, notably Si, the bottom of the conduction band does not necessarily occur at \( \mathbf{k}=0 \).
Chapter 1

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Figure 1.3 Simple energy band structure of GaAs (Kelly (1995)).

An photon with momentum q can stimulate an electron from a state in the valence band with momentum k to a state in the conduction band with momentum k'. Creating an electron-hole pair has little effect on the overall electronic state of the crystal because the electron wave functions are spread through large regions of it. If the wave function representing the single electron is a Bloch function (found from solutions of Schrodinger's equation), then the probability of finding an electron in the excited state is zero unless k-k'+q=0. If the momentum of the photon is small compared with k and k', then the absorption of a photon connects states in the conduction and valence bands with the same momentum. That is, within the one electron approximation, an optical photon with an energy larger than the bandgap will promote electrons vertically in the band structure.

At points in the band structure corresponding to particular points on the Brillouin zone surface, the curvature of the conduction and valence bands are highly symmetrical and the probability of an electron interacting with a photon at these points is greater than elsewhere. This occurs at the \( \Gamma \), K, L and X points, and these are known as critical points. There are four types of critical points, defined by the signs of the effective masses in the three dimensions of reciprocal space. The \( M_0 \) and \( M_2 \) critical points can be described as parabolic, and the \( M_1 \) and \( M_3 \) critical points as hyperbolic or saddle point. For a detailed description of critical points, see Séraphin (1972). If the effective mass in one direction of reciprocal space is infinite then the critical point is two dimensional, otherwise it is three dimensional.

For a comprehensive explanation of crystal and band structures, the author recommends the book by Kittel (1986).

1.2.2 Quantum Wells

If two semiconductors with different bandgaps are brought together, then the valence and conduction bands of the two materials line up in a certain way at a certain critical point. This band alignment can be classified into two types, shown schematically in figure 1.4. For a type I interface, the smaller bandgap lies entirely inside the larger bandgap. For a type II interface, the bandgaps are staggered, or totally misaligned.
If the material with the smaller bandgap is sandwiched between two layers with a larger bandgap (as in figure 1.4), then a quantum well can be formed. For this to occur, the thickness of the quantum well layer must be sufficiently small, so that the free movement of electrons and holes in the growth direction (across the page) is suppressed and they are confined quantum mechanically. Discrete energy states are formed in such a structure, given by solutions of Schrödinger's equation. A schematic diagram of the energy states in a type I quantum well is shown in figure 1.5. The most common study of quantum wells concerns the $E_0$ critical point transition at the $I$ point. In this work, however, confinement of the $E_1$ and $E_1 + A_1$ transitions at the $L$ point is also considered. A more detailed description of quantum wells and their applications can be found in the book by Kelly (1995).
1.2.3 III-V Alloy Materials

This section is intended to give the reader an idea of the development and applications of the III-V alloys studied in this work. It is not intended to be a comprehensive review, but an illustration of the importance of these materials.

The development of low loss optical fibres in the 1950s initiated a communication revolution that demanded improved optoelectronic devices. Some of the most important gains in device performance stemmed from the development of III-V alloy growth technology. These alloys showed much promise, but suffered from a significant drawback: the relationship between the bandgap and lattice constant shown in figure 1.6. From this figure, it is obvious that there lies enormous potential for engineering the bandgap by changing alloy compositions. Few compositions could be grown, however, as they had to be lattice matched to available substrates. Despite this limitation, it is clear from figure 1.6 that the III(Ga,Al) - V(P,As,Sb) alloys can be formed with varying bandgaps at almost constant lattice parameter. Since GaAs technology was well developed, the most popular of these alloys was AlGaAs, and the first devices were comprised of GaAs/AlGaAs structures. The most prominent of these devices was the AlGaAs heterojunction laser.

![Figure 1.6 Variation of the lattice constant with bandgap (Antypas (1982)).](image)

Although AlGaAs was sufficient for optoelectronic applications over certain energy ranges, there was an increasing demand for alloys with bandgaps lower in energy than GaAs. To this end, research was expanded to other III-V ternary alloys such as InGaAs, GaAsSb and InAsP. It was discovered that the bandgap and lattice constant could be adjusted independently by incorporating a fourth component to the alloy. Such a material is InGaAsP, and in figure 1.6, this system is bounded by the InGaAs, InAsP and GaAsP alloy lines. The advantage of these quaternary alloys was that they could be grown on commercially available substrates, such as InP.

A more recent development in bandgap engineering has stemmed from the ability to grow strained layers. This has opened a whole new realm of device design. The effects of strain are briefly discussed later in this chapter.
Since the development of III-V alloys, many important devices have been fabricated from them. A few of these devices, relevant to the materials studied in this work, are described below.

InGaAs/InGaAsP/InP heterojunction bipolar transistors (HBTs) (Tsang et. al. (1988)) are attractive for microwave and high speed switching applications, particularly for optoelectronic integrated circuits. Not only are they compatible with long wavelength sources and detectors, but a superior high frequency performance is expected compared with GaAs based HBTs due to the higher electron mobility of InGaAs, and a greater drift velocity of InP at high fields.

InGaAs/InP structures have been used to construct long wavelength photodiodes. In conventional pin photodiodes, there is a trade off between quantum efficiency and bandwidth. This problem can be overcome by using a microcavity photodiode. Using a series of InP/InGaAsP layers as a Bragg reflector, the incoming light bounces off the reflectors, leading to a buildup of the optical field at the resonant wavelength. For a further explanation of this, see Dentai et. al. (1991).

Probably the most important application of III-V alloys has been in the area of quantum well lasers. Strained-layer InGaAs/InGaAsP lasers at 1.5µm wavelength for fibre communication systems are of particular interest. The introduction of strain to these devices has several advantages. The effect of compressive strain is to reduce the in-plane effective mass in the quantum well, and so reduce the threshold current of the laser. In addition, strain induced band structure modifications result in a reduced magnitude of harmful loss mechanisms like Auger recombination and intervalence band absorption. For a detailed description of strained InGaAs/InGaAsP quantum well lasers, see Thijs et. al. (1991).

1.2.4 Si/SiGe Alloy Materials

In contrast to the recent developments in III-V materials, Si has been the major material used in the semiconductor industry since the invention of the bipolar transistor by Bardeen and Brattain (1948). The recent advancements in Si technology, coupled with its high mechanical strength and insulating oxide, ensure the future of Si devices. The main drawback of Si based materials when compared with III-V materials is that the fundamental bandgap in the band structure is indirect. This means that they are unsuitable for optoelectronic applications. This deficiency has been the main stimulus for research into III-V materials. There have been several attempts to integrate III-V alloys with existing Si devices, but this has proved difficult.

Bandgap engineering of Si has recently been achieved by incorporating Ge into Si structures. If strained SiGe alloys are used, greater flexibility can be achieved when designing devices. In the following paragraphs, some current device structures that utilise SiGe layers grown on Si are described.

The Ge p-i-n photodetector was first proposed by Luryi et. al. (1984), and consisted of a p-n Ge junction diode with an intrinsic doped region at the junction where light is absorbed. This comprised of a Si substrate, a graded SiGe alloy buffer and a series of Ge layers. The device performance was improved by incorporating a SiGe superlattice in the buffer region.

An optical device making use of the fact that the bandgaps of SiGe alloys are smaller than those of Si is the multi-quantum well photodetector. This was reported by Temkin et.
al. (1986), who fabricated a structure with SiGe quantum wells. The effect of using quantum wells, as opposed to simple alloy layers, is to shift the response of the absorption to shorter wavelengths. The absorption of light in such structures is still indirect, however, and so only a small amount of light is absorbed.

The first transport devices that utilised SiGe structures were based on buried channel Field Effect Transistors (FETs). In such structures, the different bandgaps and different band alignments between the alloy and bulk Si were used to confine carriers in a channel (People (1985)).

By growing alternate Si and SiGe alloy layers with short periods, band theory predicts that the atomic potentials of this superlattice modify the bulk crystal properties. This changes the bandstructure in such a way that the fundamental bandgap changes from being indirect to direct.

1.2.5 Strain Effects

Strained layer semiconductors were initially developed for the convenience of bandgap engineering, but it was subsequently realised that strain incorporated during growth can also be used to engineer the band structure as a whole, as is the case with the laser devices described earlier.

Any sufficiently thin semiconductor overlayer will be strained if the bulk lattice constant of the overlayer differs slightly from that of the substrate. For small differences in the lattice constants, the overlayer will distort. If the lattice constant of the overlayer is larger than the substrate, the unit cell of the strained layer is compressed in the growth plane, as in figure 1.7a. If the lattice constant is smaller than that of the substrate, however, the overlayer has tensile strain, as in figure 1.7b.

![Figure 1.7](image)

**Figure 1.7** A schematic diagram showing overlayers with (a) compressive strain and (b) tensile strain.

Strained layers can be successfully grown to thicknesses up to a critical thickness, above which it is energetically favourable to relieve the strain via dislocations. A good description of the critical thickness of different materials has been published by O'Reilly (1989).

The total strain in an overlayer can be resolved into two distinct components, hydrostatic and axial. The hydrostatic component changes the crystal unit volume, but not the crystal symmetry. The effect of this is to change the bandgap of the material. As a result of the axial component, however, the symmetry of the crystal is changed. This in turn removes the degeneracy of the light and heavy holes in the valence band at the $\Gamma$ point. For a detailed
explanation of the effects of strain, see O'Reilly (1989).

1.3 Electroreflectance and Photoreflectance of Bulk and Layered Materials

It is appropriate at this point to introduce the concept of electroreflectance (ER) and photoreflectance (PR), and to describe the principles behind the measurements. Surface states in bulk semiconductors, and interface states in layered structures, trap charge near the surface or interface. In ER, the ensuing built-in field is modulated periodically by applying an ac voltage across the material. This modulation changes the optical properties of the material, and the ER is given by the resulting change in reflectance from the sample.

The main disadvantage of ER is that contacts must be formed on the surface and underside of the sample in order to apply the voltage. Not only are these contacts difficult to form, but they often damage the sample. PR however, provides a non-destructive method of probing the built-in fields. The underlying mechanisms of PR are similar to those of ER, which means that much of the theory derived for ER can be applied to PR.

A schematic diagram of the built-in electric field at the surface of a bulk material is shown in figure 1.8a. If the surface is illuminated with light of energy greater than the bandgap of the material, electron-hole pairs are formed. The photogenerated electrons or holes migrate to the surface, and reduce or eliminate the electric field. In the case of PR, laser light is used to form the electron-hole pairs. The chopped laser provides periodic illumination, resulting in a periodic suppression of the electric field, leading to a periodic change in the optical properties. The application of laser light is shown schematically in figure 1.8b.

The main disadvantage of PR is that it relies solely on the built-in fields. If these fields are weak, then they cannot easily be varied.

![Diagram of built-in electric field](image)

Figure 1.8 A schematic representation of (a) the electric field due to surface or interface states and (b) the effect of laser light on the field.

1.4 The History of Electroreflectance

The author endeavours in this section to plot the historical development of electroreflectance (ER), and to present the theory from it that is most relevant to this thesis. Since the conception of quantum mechanics, investigations of the effect of an electric field on crystalline solids has been a great challenge to many scientists. The first
investigations concentrated on transport in conducting solids, and the first quantum mechanical treatment of the problem of conduction was given by Bloch (1928). It was not until 1958 that the effect of an electric field on the optical properties of solids was considered.

1.4.1 Early Optical Absorption and Modulation Spectroscopy

The absorption properties of the Mg fundamental edge were investigated independently by Franz (1958) and Keldysh (1958). They found that for an electron in the periodic electric field present in a crystal, the low energy edge of the absorption profile was sharp. If, however, they considered an electron in a uniform electric field as well as the periodic field, they found that the absorption edge consisted of an exponential tail extending into the forbidden gap.

Bulyanitsa (1960), Tharmalingham (1963) and Callaway (1963, 1964) extended the theoretical work of Franz and Keldysh to include absorption for energies greater than the bandgap, and experimental measurements of this were performed by Frova and Handler (1965) and by Handler (1965). Both of these authors showed that the Franz-Keldysh theory described the observed electro-absorption, and that the absorption was dependent on the magnitude of the electric field.

Séraphin (1964) was the first to realise that the electric field at the surface of Ge was strong enough to observe the Franz-Keldysh effect at the fundamental edge in reflectance spectra. The reflectance study was then extended into the energy region above the fundamental edge (Séraphin and Hess (1965a)). They found that by modulating the surface electric field externally, the normalised change in reflectance $\Delta R/R$ due to the modulation yielded sharper structure than that observed in reflectance spectra. Séraphin and Bottka (1965b) later showed that the Franz-Keldysh effect could be observed in refractive index measurements.

Following the ER observations of Séraphin, Séraphin and Bottka (1965b) showed that ER spectra depend on the change in refractive index due to the electric field modulation. Aspnes (1966) explained ER in terms of the effect of the electric field on the absorption coefficient, and then in terms of the dielectric constant (Aspnes (1967)).

Rees (1968) and Aspnes et al. (1968) showed that the effect of an electric field on the dielectric properties in the one electron approximation could be represented by a convolution which gave a broadening of the zero field dielectric function. As a result of this, the theory was no longer restricted to the region close to the critical points in the Brillouin zone.

The important mathematical conclusions of the above pioneers of modulation spectroscopy are presented in the following sections.

1.4.2 The Theory of Electroreflectance

Following the first experimental observation of ER, Séraphin and Bottka (1965b) proposed that the normalised change in reflectance $\Delta R/R$ could be expressed in terms of the change in refractive index due to modulation. They then proposed that ER could be expressed in terms of the change in dielectric function due to modulation (Séraphin and Bottka (1966)).
\[
\frac{\Delta R}{R} = \alpha (\varepsilon_1, \varepsilon_2) \Delta \varepsilon_1 + \beta (\varepsilon_1, \varepsilon_2) \Delta \varepsilon_2
\]  

(1.1)

where \(\Delta \varepsilon_1\) and \(\Delta \varepsilon_2\) are the changes in the real and imaginary parts of the dielectric function respectively, and \(\alpha\) and \(\beta\) are called Séraphin coefficients. The Séraphin coefficients are described in more detail in chapter 3. Aspnes and Frova (1969) showed that if the electric field is not uniform, then mixing of the real and imaginary parts of the dielectric function occurs and the ER lineshapes change. Rowe and Aspnes (1970) also examined the effect of excitons on electric field modulation spectra, and deduced that an additional term should be included in equation 1.1 to account for this.

If the two observations of field non-uniformity and exciton effects mentioned above are included, equation 1.1 becomes,

\[
\frac{\Delta R}{R} = \text{Re} \left( C_x C_z C_i \Delta \varepsilon \right)
\]  

(1.2)

where \(\Delta \varepsilon = \Delta \varepsilon_1 + i \Delta \varepsilon_2\), \(C_x = \alpha - i \beta\), \(C_z\) is the exciton term and \(C_i\) is the field non-uniformity term.

1.4.3 Importance of the Magnitude of the Electric Field

Electroreflectance (ER) can be classified into three distinct regimes, depending on the strength of the electric field. The first of these is the high field regime, where the energy gained by an electron across the unit cell of the crystal due to the field approaches the energy of the bandgap. Fields that are this strong change the band structure, and these effects are observed experimentally as Stark shifts.

If the energy gained by an electron across a unit cell is significantly less than the bandgap energy, the bandgap is not changed and the ER is classified into two additional field regimes. These two regimes depend on the relative magnitude of two characteristic energies; the collision broadening, \(\Gamma\), and the electro-optic energy \(\hbar \Theta\) (defined by equation 1.8). In the intermediate regime, the acceleration of electrons due to the field dominates the effects of collision broadening \(\Gamma\geq \hbar \Theta\). This regime is characterised in ER spectra by Franz-Keldysh oscillations above the bandgap energy. In the low field regime, where collision broadening is the dominant mechanism \(\Gamma>\hbar \Theta\), spectra do not contain Franz-Keldysh oscillations.

Only the intermediate and low field regimes are described by the theory in the next section.

1.4.4 The Effect of an Electric Field on the Dielectric Function

The two-particle Schrodinger equation for electrons and holes, with \(r\) as the relative coordinate of the electron-hole pair is,

\[
-\frac{\hbar^2}{2\mu} \nabla^2 \psi (r) = V \psi (r)
\]  

(1.3)
where $\hbar$ is the Planck constant, $V$ the sum of the electron and hole energies measured from the respective band edges and $\mu$ the reduced mass given by,

$$\mu = \frac{m_e m_h}{m_e + m_h}$$

(1.4)

where $m_e$ and $m_h$ are the electron and hole masses respectively. The solutions for the wave function from equation 1.3 are of the form,

$$\psi(x) = A e^{ikx}$$

(1.5)

where $A$ is a constant.

In the presence of a uniform electric field $E$, the wave function is given by the Schrödinger equation,

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi(x) = (eE + V) \psi(x)$$

(1.6)

The solutions to this equation are of the form (Tharmalingham (1963)),

$$\psi = CA_i \left( \frac{-eE + V}{\hbar \theta} \right)^{\frac{1}{3}}$$

(1.7)

where $C$ is a constant, $A_i$ is an Airy function, and the electro-optic energy $\hbar \theta$ is given by,

$$\hbar \theta = \left( \frac{e^2 \varepsilon_0 \hbar^2}{2\mu} \right)^{\frac{1}{3}}$$

(1.8)

Aspnes (1967) derived the imaginary part of the dielectric function $\varepsilon_2$ in terms of the wavefunction $\Psi$. More important than this, he derived the change in dielectric function due to the field modulation in terms of the wavefunction. The details of this derivation are beyond the scope of this thesis, but the final conclusion of Aspnes is important. That is, the change in the real and imaginary parts of the dielectric function due to modulation for an $M_0$ critical point with energy gap $E_g$ are given by,

$$\Delta \varepsilon_1 = -\frac{2\hbar^2}{\omega^2} \varepsilon \left( \frac{E_g - \hbar \omega}{\hbar \theta} \right)$$

(1.9)

$$\Delta \varepsilon_2 = -\frac{2\hbar^2}{\omega^2} \varepsilon \left( \frac{E_g - \hbar \omega}{\hbar \theta} \right)$$

(1.10)

where,
\[ G(x) = \frac{N^2}{\pi} \left[ A_1(x) B_1(x) - x A_2(x) B_2(x) \right] + \frac{1}{3} u(x) \]

and,

\[ F(x) = \frac{N^2}{\pi} \left[ A_1^2(x) - x A_2^2(x) \right] - \frac{1}{3} u(-x) \]

and B is an amplitude term, \( \hbar \omega \) is the energy, N is a normalisation constant, \( u(x) \) is the unit step function (zero for negative argument and one for positive argument), \( A_i \) and \( B_i \) are Airy functions (Abramowitz and Stegun (1965)) and \( A_i' \) and \( B_i' \) are derivatives of the Airy functions. Collision broadening can be included in the model by using a Lorentzian broadening term \( \Gamma \). In this case, the change in dielectric function due to modulation is given by (Aspnes 1972a),

\[ \Delta \varepsilon_1 = \frac{B \theta}{\omega^2} G \left( \frac{E_g - \hbar \omega}{\hbar \theta} + \frac{i \Gamma}{\hbar \theta} \right) \]

\[ \Delta \varepsilon_2 = \frac{B \theta}{\omega^2} F \left( \frac{E_g - \hbar \omega}{\hbar \theta} + \frac{i \Gamma}{\hbar \theta} \right) \]

1.4.5 Aspnes' Third Derivative Functional Form (TDFF)

Although the details of the derivation of Aspnes' third derivative functional form are beyond the scope of this thesis, the important conclusions from his work are presented here. If the energy bands are assumed to be parabolic, and the field is sufficiently small, then the modulated dielectric function can be expressed as (Aspnes and Rowe (1970, 1972b)),

\[ \Delta \varepsilon = \frac{n e^2 \hbar^2 P_{ve} P_{ov}}{m^2 E^2} \left( \frac{2}{(2\pi)^3} \right) \int d^3 k \left( \frac{\hbar \theta}{E_g - E - i \Gamma} \right)^3 \]

where \( e \) is the electronic charge, \( P_{ve} \) and \( P_{ov} \) are momentum matrix elements, \( m \) is the electron mass, \( E \) is the energy, \( k \) is the momentum, \( E_g \) is the energy gap, \( \hbar \theta \) is the electrooptic energy and \( \Gamma \) is the broadness. This was shown by Aspnes to be equivalent to a third derivative function differentiated with respect to energy,

\[ \Delta \varepsilon = \frac{(\hbar \theta)^3}{12 E^2} \frac{\partial}{\partial B^3} (E^2 \varepsilon) \]

From this, it can be shown that the change in dielectric function can be expressed as a third
derivative Lorentzian-like function,

$$\Delta e = (\hbar \theta)^3 \frac{A}{(E_\theta - E + i\Gamma)^n}$$

(1.17)

where $A$ is a real amplitude term, and the value of $n$ depends on the type of critical point under investigation.

When comparing experimental spectra with theory using equation 1.2, it is common to assume that the exciton and non-uniformity terms are unity. In addition to this, the Seraphin coefficients are assumed to be energy independent, and are included as a phase term $\phi$. Thus, in the low field regime, ER spectra are given by,

$$\frac{\Delta R}{R} = (\hbar \theta)^3 \text{Re} \left\{ \frac{A e^{i\phi}}{(E-E_\theta + i\Gamma)^n} \right\}$$

(1.18)

This is an important equation in modulation spectroscopy, and is known as Aspnes' third derivative functional form (TDFF). The TDFF is an approximation to the Airy function expressions introduced in section 1.4.4, but only valid for small electric fields.

An important parameter in equation 1.18 is $n$, the exponent of the Lorentzian-like function. This value depends on the joint density of states of the critical point, which depends on the dimensionality of the critical point. For a detailed explanation of this, see Aspnes (1972b). For three dimensional critical points, such as $E_q$ (F point), $n=5/2$ is used. For two dimensional critical points, such as $E^L$ (I point), $n=3$ is used. For excitons, $n=2$ is used.

1.5 Photoreflectance of Quantum Wells

Photoreflectance (PR) is a useful probe of quantum well structures because higher order confined state transitions, as well as the ground state transitions are usually observed. Over the last decade, PR has been used extensively to investigate the confined states for the $E_q$ critical point transition at the $\Gamma$ point.

PR has several advantages over photoluminescence (PL), which is usually used to measure quantum well transition energies. PL is usually performed at low temperatures because the room temperature spectra are too broad. The features in PR spectra, however, are sufficiently sharp at room temperature. The most important advantage of PR over PL is the ability to measure higher quantum well transitions, as well as ground state transitions. Thus, more information about the confined states in the well can be found.

The mechanism by which PR probes quantum wells is different from that of bulk materials. The effect on a bound state of changing the electric field, is to tilt the confining potential such that electrons and holes become spatially polarised but remain confined. This in turn changes the band structure, and the amount of overlap of the wavefunctions of the confined states. A good review of the differences between the PR of bound and free particles is given by Gleinbocki et al. (1992), and the most important point to note from this summary is that the PR from confined states is first derivative (FDFF), and not third
The first fits of quantum well transitions in PR spectra were performed by Shen et. al. (1986) for GaAs/AlGaAs structures. They obtained reasonable fits to room temperature PR spectra by assuming that the lineshape of the well transitions were TDFFs with $n=3$ in equation 1.18 (i.e., that of a two-dimensional critical point). This was a surprising result at that time, as it is predicted that confined states yield first derivative spectra. In order to clarify this observation, Shanabrook et. al. (1987) compared PR with photoluminescence excitation spectroscopy at temperatures down to 6K. They found that the model that fitted best at low temperatures was an FDFF, but when they increased the temperature to room temperature, the TDFF fitted best. So it appeared that the well transitions were first derivative at low temperatures, and third derivative at room temperatures. Glembocki and Shanabrook (1987) explained this as being temperature dependent inhomogeneous broadening, which changes the absorption profile from Lorentzian-like at low temperatures to Gaussian-like at higher temperatures. This change is not abrupt, and the lineshape takes an intermediate form over a certain temperature range. The reason that Shen et. al. (1986) could fit room temperature PR spectra of quantum well transitions with Lorentzian-like TDFFs, is that they mimic Gaussian-like FDFFs.

1.6 Least Squares Fitting

The key to any PR analysis is the fitting of experimental spectra. The spectra in this work were fitted using a Marquardt least squares fitting routine written by Dr. T. J. C. Hosea. The program was written in BASIC, and allows the user to fit several oscillators simultaneously.

An important aspect of any fit are the values of the initial guesses for all parameters. This can be straightforward for oscillators that are well separated in energy, but becomes difficult for spectra containing overlapping oscillators. A useful method has been developed (Hosea (1995b)) to help the user of the fitting program to choose values for the initial guesses. A PR spectrum can be thought of as the real part of a complex phasor (see equation 1.18). Using a Kramers-Kronig transformation, the imaginary part of the phasor can be found. From the real and imaginary parts of the spectrum, a modulus spectrum can be deduced. Hosea (1994) showed an example of a PR spectrum with three TDFFs, and its corresponding modulus spectrum. This is shown in figure 1.9. Each oscillator is shown as a peak in the modulus spectrum. The position of this peak is an estimate of the oscillator energy, the height of the peak is an estimate of the amplitude of the oscillator, and the half width at half maximum of the peak is an estimate of the broadness of the oscillator. This means that the only parameter for which no information is known is the phase. A discussion of the accuracy of this technique is reported by Hosea (1995b). Where possible, this method was used to fit the TDFF oscillators in this work.

A useful feature of the fitting program is the calculation of a symmetric covariance matrix of the parameters found from the fits. The diagonal elements of this matrix correspond to the uncertainties in the fitted parameters. Therefore, this matrix can be used to determine an error for each parameter in a fit. For a comprehensive description of the

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covariance matrix see Press et al. (1992).

Figure 1.9 A simulated PR spectrum consisting of three TDFF oscillators (dashed curve), and the corresponding modulus spectrum (solid curve) (Hosca (1994)).
Appendix 1

(I) The SiGe Band Structure

The band structures of Si and Ge are shown in figure 1.10. An important feature of the band structures is the bandgap, i.e., the difference in energy between the lowest point in the conduction band and the highest point in the valence band. For both Si and Ge, the valence band maximum is at the Γ-point. The lowest conduction band minimum in Si is located in the (100) direction (about 3/4 of the way between the Γ-point and X-point), and the lowest minimum in Ge is located in the (111) direction (at the L-point). Therefore, the bandgaps of Si and Ge are indirect.

![Figure 1.10 The band structures of Si and Ge (S. M. Sze, Physics of Semiconductor Devices, Wiley, 1981).](image)

It follows from the positions of the valence band maximum in Si and Ge that the valence band maximum for a SiGe alloy is at the Γ-point. The position of the conduction band minimum in such an alloy, however, is not straightforward. Consider a SiGe alloy with a small percentage of Ge. As the Ge composition is increased, one would expect a transition from a Si-like bandgap (with conduction band minimum along the (100) direction) to a Ge-like bandgap (with conduction band minimum along the (111) direction). This transition is shown in figure 1.11, where the bandgap versus percentage of Ge is shown. As Ge is added, the conduction band minima in the (000), (111) and (100) directions move down in energy relative to the valence band maximum, but at different rates. Beyond about 80% Ge, the minimum in the (111) direction dips below the...
minimum in the (100) direction, and then remains the lowest all of the way to Ge. In this region, the bandgap changes more rapidly with Ge composition because the minimum along the (100) direction shifts more slowly with composition than the minimum in the (111) direction.

Figure 1.11 Composition dependence of the bandgap for a Si$_{1-x}$Ge$_x$ alloy (T. P. Pearsall, J. Luminescence, 44, 367 (1989)).

(II) Electro-optic effects

(a) Bulk Semiconductors

When an electric field is applied to bulk materials, the conduction and valence bands are spatially tilted. The wavefunctions representing states in the bands consist of an oscillatory structure, and these are shown in figure 1.12. Transitions can occur below the band edge because wavefunctions have tails in the forbidden gap with some overlap. An oscillatory structure in the absorption is observed for energies greater than the bandgap due to interference effects between the conduction and valence band wavefunctions.

The presence of an electric field has an effect on the joint density of states function. With zero field, the joint density of states of an $M_0$ critical point is zero below the bandgap and non-zero above the bandgap; solid line in figure 1.13. With a finite field, the joint density of states is modified. It has a finite value for energies below the bandgap, and there is oscillatory structure above the bandgap.
Figure 1.12 A schematic diagram of the effect of an electric field on a bulk semiconductor (C. Weisbuch and B. Vinter, *Quantum Semiconductor Structures*, Academic press, 1991).

![Schematic diagram](image)

Figure 1.13 Joint density of states for an $M_0$ critical point with zero electric field (solid curve) and with a finite field (dotted curve) (F. Bassani and G. P. Parravicinici, *Electronic States and Optical Transitions in Solids*, Pergamon press, 1975).

![Graph](image)

(b) Quantum wells

Applying an electric field to quantum wells has a quite different effect. This is shown in figure 1.14. The conduction and valence band wavefunctions occur at discrete energy levels. The probability of a transition between a valence and a conduction band confined
state is given by the overlap integral between the states. For a perfectly abrupt rectangular quantum well without an electric field, only transitions between valence and conduction band states with the same parity can occur i.e. the 'selection rule' is \((m-n)\text{=odd}\) (index \(m\) is electron subband and \(n\) the hole subband).

When a field is applied, the shape of the well changes (figure 1.14). The field shifts the electron and hole confined states closer together, and so changes the transition energies between states; the Quantum Confined Stark Effect (QCSE). In this case, the wavefunctions change dramatically and there is a finite probability for parity forbidden transitions to occur.

![Diagram of an infinite quantum well with and without an electric field](image)

Figure 1.14 A schematic diagram of the effect of an electric field on an infinite quantum well (C. Weisbuch and B. Vinter, Quantum Semiconductor Structures, Academic press, 1991).

The difference between quantum wells with and without an electric field can be shown by considering Schrodinger's equation. For a quantum well with no electric field, the energy eigenvalues \(E\) are given by,

\[
\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right)\psi(x) = E \psi(x) \tag{1.19}
\]

where \(\hbar\) is the Planck constant, \(m\) is the mass, \(x\) is the distance across the well and \(V\) is the potential; zero in the well and a finite value in the barrier. When an electric field \(E\) is applied, the Schrodinger equation becomes,
Introduction

\[
\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) + e\mathcal{E}x\right)\psi(x) = E\psi(x)
\]

(1.20)

where \(e\) is the electronic charge. In this case, the field term is a function of \(x\), and so the wavefunctions given by the solutions of equation 1.20 are different from those given by equation 1.19.

(III) Modulation Doping

The idea behind modulation doping is shown in figure 1.15: Two materials with different bandgaps are grown on top of each other to form a heterojunction. In figure 1.15 these materials are AlGaAs and GaAs. If the material with the larger bandgap (AlGaAs) is doped with shallow donors, the Fermi level is shifted from the middle of the bandgap of AlGaAs to the donor level. In order to maintain a constant Fermi level throughout the two materials, electrons will flow from the AlGaAs to the GaAs. This causes the band edges to bend at the interface. From this band bending, the electrons are confined by an approximately triangular potential and form a two-dimensional electron gas in the GaAs layer. Using this technique, the electrons are physically separated from the charged impurities in AlGaAs.

Figure 1.15 The structure and band diagram of a modulation-doped heterojunction between GaAs and n-type AlGaAs (M. Cardona and P. Y. Yu, Fundamentals of semiconductors, Springer, 1996).
Chapter 2

Experimental Arrangement

The equipment and techniques used to measure photoreflectance (PR) and photoluminescence (PL) spectra are described in this chapter. Infrared PR and PL measurements were performed using a setup developed at the University of Surrey as part of this work. Visible and ultraviolet PR were measured using an existing setup located at the DRA. The refinements made to this system by the author are presented in detail in this chapter.

2.1 Introduction

When measuring PR, a monochromatic beam of light, wavelength \( \lambda \), is focused onto the sample. The light reflected is measured as a dc detector signal \( I(\lambda)R(\lambda) \); where \( I(\lambda) \) is a term that depends on the optical characteristics of the light source, optics and detector, and \( R(\lambda) \) is the reflectance. When a laser beam hits the sample at the same spot as the monochromatic beam, \( R(\lambda) \) changes by an amount \( \Delta R(\lambda) \). If the laser light is chopped periodically, the change in \( R(\lambda) \) can be detected as an ac signal \( I(\lambda)\Delta R(\lambda) \). The PR spectra are given by \( \Delta R/R \), and so \( I(\lambda) \) is eliminated.

To measure PL from a sample, laser light of energy greater than the bandgap must be used. A monochromator is then used to determine the energy of the luminescent light.

2.2 Infrared Photoreflectance

2.2.1 Equipment Setup

Infrared PR was used to investigate the \( E_0 \) and \( E_0 + A_0 \) critical point transitions in III-V materials. A schematic diagram of the apparatus is shown in figure 2.1. The white light source was a 100W Philips tungsten-halogen lamp, powered with a stabilised mains supply. This provided light in the range 0.65eV to 3.00eV, with a maximum output at 1.5eV. The light from the bulb was focused onto the input slit of a monochromator using a concave mirror. The monochromator was a 0.5m Spex 1870, with a 600 lines/mm grating blazed at 1\( \mu \)m, giving a worst-case resolution of 2.1meV at 2.5eV, with a 600\( \mu \)m slit width in first order. This resolution is acceptable, because the features in room temperature PR spectra have widths of the order of 10meV (Pollak (1993)). The widths of the monochromator slits were set between 300\( \mu \)m and 600\( \mu \)m. The probe beam was focused onto the sample with

\(^1\)Defence Research Agency, Malvern, Wors
a 5cm diameter biconvex glass lens, with a 10cm focal length. The light spot on the sample was typically 1mm wide and 2mm high for an incident angle of $50^\circ$ with respect to the normal. The light spot was overlaid with a 2mW or a 5mW HeNe laser (632.8nm) with a 2mm diameter spot, mechanically chopped at frequencies typically between 175Hz and 330Hz.

![Diagram of apparatus used to measure infrared photoreflectance.](image)

**Figure 2.1** Schematic diagram of apparatus used to measure infrared photoreflectance.

The light reflected from the sample was focused onto a detector using a 5cm diameter biconvex glass lens, with a 5cm focal length. To cover the energy range required for experiments, two detectors were used; Si and InGaAs. The Si detector (RS 308-067) was mounted in a diecast steel box and powered using two 9V batteries. The InGaAs detector (A+G FD1000WX) was used for lower energy measurements, and was mounted in a diecast steel box and powered with a mains supply. The system response $I(\lambda)$ for both detectors is shown in figure 2.2. It is clear from this figure that experiments can be performed within the range 0.75eV to 2.50eV. The dc detector output, $R$, was measured using a Keithley 196 digital multimeter, and the ac output, $\Delta R$, was measured using either an EG+G 9503-SC or an EG+G 5110 lock-in amplifier.

Samples were mounted on a microscope slide using melted wax. The slide was clipped to a stage mounted on the rotating table of an adapted prism spectrometer, which allowed the angle of incidence of the monochromator beam on the sample to be accurately set ($\pm 0.5^\circ$). The prism spectrometer is shown in figure 2.3. This consisted of two arms, one fixed and one that could be moved. The lens that focused the probe beam onto the sample...
was mounted on the fixed arm, and the collection lens and detector were positioned on the moveable arm.

**Figure 2.2** Spectral response for the Si and InGaAs detectors, normalised with respect to the peak signals. The peak signal of the Si detector was about 10 times greater than that of the InGaAs detector. The feature at about 0.95eV in the InGaAs spectrum is due to water vapour absorption. The optical characteristics of the apparatus are included.

**Figure 2.3** A photograph of a section of the infrared spectroscopy apparatus. The photograph shows two focusing lenses in place of the one used in this work.
2.2.2 Measuring Infrared Photoreflectance

A BASIC computer program was developed to control the equipment and record spectra using a PC. It was extensively adapted as part of this work from a program previously used to measure PL. A schematic diagram of the program is shown in figure 2.4. The program was based around three menus; information, manipulation and scan menus.

The information menu allowed the user to store sample information, as well as information about the experimental settings. These included temperature, chopper frequency, laser power, lock-in phase, monochromator slit width and incident angle of the probe beam. Measured spectra, and the associated settings from the information menu, were saved in binary format from the manipulation menu. Related spectra were saved in a single file, thus reducing the size of files and disk space used. Ten spectra could be loaded into the program at one time. These spectra could be scaled, offset by a constant value, or divided by another spectrum. In addition, an option allowed all spectra stored in the program to be plotted simultaneously. To ensure compatibility with graphing and fitting programs, spectra could also be saved in ASCII format.

![Figure 2.4](image)

**Figure 2.4** A schematic diagram showing the structure of the BASIC program written to control the equipment and record spectra when measuring infrared photoreflectance.
The scan parameters which could be set include the wavelength limits, number of points, lock-in sensitivity, and the number of scans over which to average. During a scan, the monochromator stepper motor was moved using an RS 440-098 control board, programmed using a language similar to C. The board was connected to the PC via an RS232 interface. The output from the lock-in amplifier was measured using a Keithley 197A digital multimeter. IEEE488 interfaces were used to input R and ΔR from the two multimeters. The simultaneous input of R and ΔR eliminated problems that can occur with systematic drifts in the measurement.

The procedure for measuring a PR spectrum is as follows. The angle of incidence of the probe beam, and the angle of the detector arm were set. The sample was moved using the xyz adjustments until the probe beam spot was at its centre. The detector was moved vertically and horizontally until a maximum in the reflectance amplitude at a certain wavelength was found. This allowed the optimum detector position to be accurately set. The laser beam was directed onto a mirror, which was adjusted until the laser light was superimposed on the probe beam spot. To reduce the amount of reflected laser light measured by the detector, the laser was positioned below the level of the sample. This ensured that the plane of the incident and reflected laser light was different to that of the probe beam ie the laser light was reflected away from the detector.

Once structure in the ΔR spectrum had been observed, the monochromator was moved to a dominant peak in the ΔR spectrum. The lock-in phase was then adjusted to maximise this signal. Caution was observed when adjusting the lock-in phase because a constant offset was usually present in ΔR spectra. This was due to sample luminescence or scattered laser light, both of which are modulated at the same frequency as ΔR. Luminescence often occurs during measurements near the fundamental gap, particularly when a high laser power is used or the temperature is decreased. The amount of scattered laser light incident on the detector was reduced by using a coloured glass light filter which absorbed light above 1.77eV. Where this was inadequate, the laser power was reduced using neutral density filters. A constant background was subtracted from ΔR before dividing by R. This was found by measuring regions of the spectrum where ΔR was expected to be zero.

A problem which occurs when using single pass monochromators is second order grating reflections. For measurements above about 0.88eV (below about 1400nm), the light filter mentioned above reduced the effect of these reflections. Care was taken when interpreting spectra which included energies below this.

2.2.3 Infrared Photoluminescence

To complement the PR measurements, room temperature PL was performed using a setup similar to that shown in figure 2.1. The light source was removed, and the detector positioned in its place. The chopped laser beam was shone onto the same part of the sample as it had been during PR measurements, and light from the luminescence passed backwards through the monochromator. The light emerging from the input slit was focused onto the detector, and the PL signal measured using the lock-in amplifier. Thus, PL could be performed at the same position on the sample as PR simply by moving the detector.
2.3 Ultra Violet Photoreflectance

2.3.1 Equipment Setup

Ultra violet PR was used to investigate the $E_1$, $E_1^+\Delta_1$ and $E_6^*$ critical point transitions in Si, SiGe and III-V materials. A schematic diagram of the apparatus is shown in figure 2.5. The light source was a Cathodeon 150W Xe lamp. A 5cm diameter fused silica plano-convex lens, with an 8cm focal length, focused the light onto the input slit of a 0.22m Spex 1680 double grating spectrometer with two 1200 lines/mm gratings blazed at 0.33μm. The width of the monochromator slits was set at 700μm. The monochromatic probe beam was focused onto the sample using two 5cm diameter fused silica plano-convex lenses with focal lengths of 8cm. The incident angle of the probe beam was set close to the Brewster angle (about 70°), giving a typical probe beam size at the sample of 2x2mm. Fischer and Séraphin (1967) proposed that the PR signal increases at the Brewster angle due to an increase in the Séraphin coefficients.

A 15mW HeNe laser beam was mechanically chopped at frequencies typically between 175Hz and 330Hz, and passed through a beam expander. To minimise the scattered laser light entering the detector, the laser was positioned parallel to the detection optics. If a large background signal, $B$, was observed in the $\Delta R$ signal, the laser power was reduced using...
neutral density filters similar to that done for the infrared measurements.

The reflected probe beam was focused onto a detector using two 5cm diameter fused silica plano-convex lenses with focal lengths of 8cm. A UV enhanced Si detector was used. It was mounted in a diecast steel box and powered with a mains supply. The system response $I(\lambda)$ for the detector is shown in figure 2.6. This figure shows that measurements can be performed within the range 1.5eV to 3.5eV. The ac AR signal was measured using either an EG+G 9503-SC or an EG+G 5210 lock-in amplifier.

Samples were mounted on a microscope slide using either melted wax or adhesive paper. The slide was placed in a mount with xz adjustments, so that the sample could be positioned accurately at the focal point of the beam.

![Figure 2.6 Spectral response for the UV enhanced Si detector, normalised with respect to the peak signal. The optical characteristics of the apparatus are included.](image)

### 2.3.2 Measuring Ultra Violet Photoreflectance

The detector and lock-in signals were input to a PCL 816 data acquisition card installed in a PC; PC1 in figure 2.5. A BASIC program was written on PC1 to process $\Delta R$ and $R$ data. Before a spectrum was measured, the probe beam was covered, and the background signal, $B$, was averaged for 10-20 minutes, depending on the noise. The real time $(\Delta R-B)/R$ was input to PC2, and recorded using Jobin-Yvon commercial spectroscopy software. The background, $B$, was again measured at the end of a scan to ensure that it had not changed significantly.

The procedure for measuring spectra was similar to that described earlier for infrared PR. It should be noted that the signal to noise ratio was smaller for the ultra violet PR, than for the infrared PR. Therefore, the ultra violet PR required more averaging, and more care in determining the background $B$.

### 2.3.3 Low Temperature Ultra Violet Photorelectance

In general, as the temperature is decreased, the broadening of features in PR spectra is decreased. This was used to resolve features close in energy. Low temperature ultra violet PR was performed using a setup based on that described above, and shown in figure 2.5.
Samples were cooled using an MMR Technologies Microminiature Refrigeration System (K2105). The cryostat is shown schematically in figure 2.7. The refrigerator was situated at the end of a raised 'finger'. This ensured that the refrigerator was not in contact with the system base plate. The top half of the cryostat, not shown in figure 2.7, contained a single sapphire window through which the incident and reflected probe beams and laser beam were passed. The transmission of light through the window for the energy range used in this work was constant: 85±5% transmission. To maintain a 70° incident angle, the sample was raised closer to the window using a 9mm high copper block. Silver conductive paint was used to attach the sample to the block, and ZnO paste was smeared on the underside of the block before it was clipped to the refrigerator. This ensured good thermal contacts.

The temperature was measured using an Oxford Instruments (PHZ 0012) rhodium-iron resistance thermometer, covered with ZnO paste and placed in a hole through the copper block. The four wire thermometer was used as a two wire device, as there were only two electrical connections on the cryostat case. This was valid because the resistance of the resistor was much larger than the resistance of the connecting wires inside the cryostat. This was the case for all temperatures.

Cooling was achieved by the Joule-Thompson effect using N\textsubscript{2} gas, filtered to remove water vapour. Once a pressure of 10\textsuperscript{-2} mbar had been achieved using a rotary vacuum pump, the sample was cooled by N\textsubscript{2} gas at pressures between 1500psi and 1800psi. The refrigerator system included a thermometer and a 6W heater, which were connected to a temperature controller. A BASIC program written on a Hewlett Packard computer was connected to the temperature controller via an IEEE488 interface. The program recorded the temperature and heater power, and allowed the required temperature to be set.

![Figure 2.7 Schematic diagram of the base section of the refrigerator system used to cool samples for low temperature ultra violet photoreflectance.](image-url)
Chapter 3

The Effect of Interference on the Photoreflectance of Layered Structures

The aim of the work presented in this chapter is to calculate Séraphin coefficients for semiconductor structures consisting of many layers. Optical interference is included in the analysis by calculating the reflectance using the Jones matrix technique, from which the Séraphin coefficients are found. The calculations are then compared with experimental photoreflectance (PR) spectra of Si/SiGe/Si layers measured by Dr. R. T. Carline at the DRA, and anomalies in these spectra explained in terms of the effect of interference on the Séraphin coefficients. From these calculations, a new method of determining layer thickness from PR spectra is developed, and used to deduce the thickness of the Si cap layer.

3.1 Introduction

Over the past few years, PR has increasingly been used as a research tool to probe semiconductor structures. As this continues, a deeper understanding of the origins of PR spectra is required. The PR of bulk materials is well established, but there are still many uncertainties related to the PR of layered structures. The main aim of the work presented in this chapter is to develop a greater understanding of the underlying mechanisms contributing to the PR of layered structures. The chapter commences by discussing the Séraphin coefficients.

It was shown in chapter 1, that if electron-hole interaction and electric field non-uniformities are negligible, PR can be described in terms of changes in the real and imaginary parts of the dielectric function and the Séraphin coefficients (equation 1.1). The change in reflectance, $R$, resulting from modulation of the dielectric function ($\varepsilon=\varepsilon_1+i\varepsilon_2$) can be expressed as a partial differential equation,

$$\Delta R = -\frac{\partial R}{\partial \varepsilon_2} \Delta \varepsilon_2 + \frac{\partial R}{\partial \varepsilon_1} \Delta \varepsilon_1$$

(3.1)

From this, PR can be expressed by the equation,
The Effect of Interference on the Photoreflectance of Layered Structures

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\[ \frac{\Delta R}{R} = \frac{1}{R} \frac{\partial R}{\partial e_1} \Delta e_1 + \frac{1}{R} \frac{\partial R}{\partial e_2} \Delta e_2 \]  

(3.2)

where the Seraphin coefficients are defined as,

\[ \alpha = \frac{1}{R} \frac{\partial R}{\partial e_1} \]  

(3.3)

\[ \beta = \frac{1}{R} \frac{\partial R}{\partial e_2} \]  

(3.4)

Both \( R \) and \( e \) are functions of energy, so \( \alpha \) and \( \beta \) are also functions of energy.

3.2 Seraphin Coefficients of Bulk Materials

In this section, expressions for the Seraphin coefficients of bulk materials are presented. The reflectance of light at normal incidence to the surface of a bulk material is given by Fresnel's equations, and is dependent on the dielectric function,

\[ R = \frac{\left( e_1^2 + e_2^2 \right)^{\frac{1}{2}} - \left[ 2e_1 + 2 \left( e_1^2 + e_2^2 \right)^{\frac{1}{2}} \right] \frac{1}{2} + 1}{\left( e_1^2 + e_2^2 \right)^{\frac{1}{2}} + \left[ 2e_1 + 2 \left( e_1^2 + e_2^2 \right)^{\frac{1}{2}} \right] \frac{1}{2} + 1} \]  

(3.5)

If equation 3.5 is analytically differentiated according to equations 3.3 and 3.4, then the Seraphin coefficients are given by,

\[ \alpha = \sqrt{2} \left( e_1 - 1 \right) \frac{\left( e_1^2 + e_2^2 \right)^{\frac{1}{2}} + e_1}{\left( e_1^2 + e_2^2 \right)^{\frac{1}{2}} - e_1} \]  

(3.6)

\[ \beta = \frac{-2e_2}{\left( e_1 - 1 \right)^2 + e_2^2} \left[ \frac{\left( e_1 - 1 \right) \left( e_1^2 + e_2^2 \right)^{\frac{1}{2}}}{\sqrt{2} \left( e_1^2 + e_2^2 \right)^{\frac{1}{2}} + e_1} + \frac{e_2 \left( e_1^2 + e_2^2 \right)^{\frac{1}{2}}}{\sqrt{2} \left( e_1^2 + e_2^2 \right)^{\frac{1}{2}} - e_1} \right] \]  

(3.7)

It can be seen from these equations that \( \alpha \) and \( \beta \) are simply functions of the unperturbed dielectric functions. If light is shone onto a surface at non-normal incidence, Fresnel's equations become more complex, and an incident angle \( \phi \) must be considered. The coefficients for this case are polarisation dependent, and are given by (Fischer and Seraphin (1967)),

\[ \alpha_s = \frac{2us}{(u^2+v^2)} \frac{(u^2-3v^2-s^2)}{[(u-s)^2+v^2] [(u+s)^2+v^2]} \]  

(3.8)
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\[ \beta_s = -\frac{2\nu s}{(u^2+v^2)} \frac{(3u^2-v^2-s^2)}{[(u-s)^2+v^2] \cdot [(u+s)^2+v^2]} \]  
(3.9)

\[ \alpha_p = \alpha_p^+ - \frac{2ut}{(u^2+v^2)} \frac{(u^2-3v^2-t)}{[(u-t)^2+v^2] \cdot [(u+t)^2+v^2]} \]  
(3.10)

\[ \beta_p = \beta_p^- - \frac{2vt}{(u^2+v^2)} \frac{(3u^2-v^2-t^2)}{[(u-t)^2+v^2] \cdot [(u+t)^2+v^2]} \]  
(3.11)

where,

\[ s = n_0 \cos \phi \]  
\[ t = n_0 \sin \phi \tan \phi \]  
\[ uv = \frac{\varepsilon_2}{2} \]  
\[ u^2-v^2 = \varepsilon_1 - n_0^2 \sin \phi \]

and \( n_0 \) is the refractive index of the non-absorbing incident medium. So for non-normal incidence there are two sets of coefficients; for \( s \) and \( p \) polarisations. Figure 3.1 shows Seraphin coefficients calculated using equations 3.8 to 3.11 for bulk Ge using experimentally-measured dielectric functions of Ge. From this figure, it can be seen that the \( s \) and \( p \) polarisation coefficients can differ greatly.

![Figure 3.1](image)

Figure 3.1 \( s \) (\( n \)) and \( p \) components of the Seraphin coefficients as a function of the angle of incidence for bulk Ge. The coefficients were calculated at several energies, and for angles near the Brewster angle. (Fischer and Seraphin (1967)).
3.3 Optical Interference in Layered Structures

It is well known that optical interference affects the PR spectra of layered semiconductors. In this section, previous observations of interference effects in the PR of semiconductors are reviewed. The Jones matrix method used in this work to calculate the reflectance is also described in this section, and the technique used to calculate the Séraphin coefficients of each layer in a multilayer stack is shown.

3.3.1 Literature Review

Following the work on the effect of the Séraphin coefficients on the PR of bulk materials shown above, McIntyre and Aspnes (1971) were the first to introduce the problem of optical interference due to overlayers. They derived expressions of $\Delta R/R$ for s and p polarisations using approximations based on the assumption that the thickness of the surface films were very much less than the wavelength of the monochromatic light. Following this, Aspnes (1973a) applied the Jones matrix technique (Klein and Furtak (1986)) to derive an expression for $\Delta R/R$ including thick Ni/Al$_2$O$_3$ layers deposited on Ge. This method described all multiple reflections at the layer interfaces in the form of simple matrices. The derivation assumed that modulation occurred only in the bulk Ge, and considered the normal incidence of light only.

It was not until the 1980s that the problem of interference in the PR of layered semiconductors was addressed again. The development of heterostructures, and in particular quantum wells, has been the driving force behind work on the effects of interference in layered semiconductors.

Klipstein and Apsley (1986) considered electroreflectance (ER) of a single GaAs/AlGaAs quantum well, and used the Jones matrix method to calculate the reflectance from the structure. They considered modulation only in the well, and calculated the ER for various incident light angles. This was done by calculating the reflectance, and then shifting the energy in their dielectric function equation by a small amount. The reflectance was then recalculated and subtracted from the unshifted value. The agreement with experiment was good. Thorn et. al. (1987) used this approach to study the dependence of ER on the incident angle of light and temperature for a single quantum well. They found that an approximation which considered only light reflected from the semiconductor/air and the quantum well interfaces agreed well with the exact matrix calculation. Lineshape broadening was included in this approximation by Shields et. al. (1989). In 1990, the approximate model was extended to describe multiple wells (Shields and Klipstein (1990)). The experimental ER of GaAs/AlGaAs multiple quantum wells, however, did not agree well with the theoretical calculations using this technique (Shields and Klipstein (1991)).

A different approach was considered by Zheng et. al. (1988a). They performed reflectance experiments on GaAs/AlGaAs single quantum wells. To explain their experimental results, the reflectance of these structures was calculated for normal incident light, assuming there were no multiple reflections and that absorption only occurred in the well. An explicit expression for the dielectric function was used, and they found that the reflectance was dominated by two terms. The first was from the air/AlGaAs interface, and the second from the AlGaAs/GaAs interfaces. The Séraphin coefficients for a single quantum well were later calculated by algebraically differentiating the approximate
expression for the reflectance (Zheng et. al. (1988b)), in a similar way to that done in section 3.2. This was considered only to be valid for wells with small discontinuities in the dielectric function. Liu et. al. (1990) used this approximate model and included terms for the angle of the incident light. They found good agreement between experimental and calculated PR spectra for a single quantum well as a function of incident angle of light.

Nakayama et. al. (1990) calculated PR for many repeating GaAs/AlAs layers grown on a GaAs substrate. They considered the GaAs/AlAs layers as being a single layer, and calculated the reflectance for a two layer system. They used the effect of interference to explain the changes in experimental spectra they had observed.

Haraguchi et. al. (1991) calculated the PR for the GaAs buffer of a GaAs/AlAs structure, assuming that the reflection from the top surface of the wells was the dominant term in the reflectance, and that modulation occurred only in the well.

Humlíček et. al. (1991) compared experimental PR of GaAs/AlAs superlattices with numerically differentiated reflectance spectra. In this case, the agreement was poor.

Huang et. al. (1989) observed oscillations below the ground state transition energy in PR spectra of GaAs/AlGaAs quantum wells. They attributed them to interference within the layers, and showed that the thickness of epilayers could be determined using a simple model. Oscillations below the band gap of GaAs in layered structures were observed by Kallergi et. al. (1990). They used the same approach to determine the GaAs layer thickness. Interference effects below the bandgap were also observed in GaAs and InP layered structures by Tober and Bruno (1990) and Lipsanen and Airaksinen (1993).

As can be seen from the above references, many attempts have been made to model the effects of optical interference in PR spectra, but the methods used to date have achieved only limited success in matching the models with experiment.

### 3.3.2 Calculating Reflectance using Jones Matrices

Before the Seraphin coefficients are calculated for a particular layer in a stack, the reflectance of the whole structure must be calculated. This is done using the Jones matrix method and experimentally-determined dielectric functions. The Jones matrix technique (Klein and Furtack (1986)) has been shown to be the most comprehensive way of calculating the reflectance from multilayer systems. This is because all multiple reflections are included, as well as main interface reflections.

Consider the layered structure shown in figure 3.2. This consists of an infinite substrate and k finite layers in air. All reflections at a single interface can be described by the complex refractive indices of the two adjacent layers in the form of a reflection matrix $\mathcal{R}_{ij}$, where $i$ corresponds to the layer above the interface, and $j$ to the layer below the interface. All components of this matrix are derived from Fresnel's equations for the electric field components of the incident and reflected beams. The matrix for s polarised light is given by,

$$
\mathcal{R}_{ij} = \begin{bmatrix}
\frac{1 + n_i \cos \theta_i}{2} & \frac{1 - n_i \cos \theta_i}{2} \\
\frac{1 - n_j \cos \theta_j}{2} & \frac{1 + n_j \cos \theta_j}{2}
\end{bmatrix}
$$

(3.12)
where \( n \) is the complex refractive index and \( \theta \) is the angle of incident light at an interface with respect to the normal. A similar matrix can be derived for \( p \) polarised light, but is not shown here. The propagation of the light through a layer \( j \) is described by a propagation matrix,

\[
\varphi_j = \begin{bmatrix} e^{i \frac{2\pi d_j}{\lambda} n_j \cos \theta_j} & 0 \\ 0 & e^{-i \frac{2\pi d_j}{\lambda} n_j \cos \theta_j} \end{bmatrix}
\] (3.13)

where \( d_j \) is the thickness of layer \( j \), and \( \lambda \) is the wavelength of the light in vacuum. In the Jones matrix formalism, the electric field component of the light incident at the air/first layer interface \( \mathbf{E}_0 \), and the net reflected light \( \mathbf{E} \), can be expressed in terms of the light incident on the last interface \( \mathbf{E}_{k+1} \)

\[
\begin{bmatrix} \mathbf{E}_0 \\ \mathbf{E}_{k+1} \end{bmatrix} = \mathbf{R}_{k+1} \mathbf{\varphi}_1 \mathbf{\varphi}_2 \cdots \mathbf{\varphi}_k \begin{bmatrix} \mathbf{E}_0 \\ 0 \end{bmatrix}
\] (3.14)

Finally, the reflectance \( R \) of the whole structure is given by the ratio of the incident and reflected intensities,

\[
R = \frac{|\mathbf{E}_r|^2}{|\mathbf{E}_0|^2}
\] (3.15)

**Figure 3.2** Schematic diagram of light passing through a stack of \( k \) semiconductor layers on an infinite substrate. The electric field values and angles are those used in equations 3.12 to 3.14.
3.3.3 Calculating Seraphin Coefficients for Many Layers

It was shown in section 3.1 that the Seraphin coefficients for a particular layer in a structure are given by differentiating the reflectance with respect to the dielectric function of that layer (see equations 3.3 and 3.4). This means that each layer has a set of four coefficients; \( \alpha \) and \( \beta \) for each polarisation. As more layers are added to the structure, the algebraic differentiation becomes more complex, and the practical limit is two or three interfaces. A new, but simple method has been employed in this work to overcome these algebraic difficulties.

The Seraphin coefficients for each layer in a multilayer stack are calculated using a method similar to that proposed by Baumeister (1962), and used by Klipstein and Apsley (1986). Baumeister suggested a way of calculating the partial differential \( \frac{\partial R}{\partial t} \) for a particular layer in a stack, where \( R \) was the reflectance and \( t \) the thickness of the layer. To do this, \( R_1 \) was calculated for the structure. The thickness of the layer was then increased or decreased by a small amount \( \delta t \), and \( R_2 \) calculated for the new structure. The differential was then given by,

\[
\frac{\partial R}{\partial t} = \frac{R_2 - R_1}{\delta t}
\]  
(3.16)

In this work, the partial differentials for the Seraphin coefficients (equations 3.3 and 3.4) are evaluated as follows. To calculate \( \alpha^i_s \) for a particular layer \( i \), the s polarised reflectance from the whole structure \( R_s \) is calculated using the Jones matrix method with dielectric functions determined from SE experiments (equation 3.15). The real part of the dielectric function of that layer \( \varepsilon^i_s \) is then changed by a small amount \( \delta \varepsilon^i_s \). The reflectance is again calculated, but this time using the adjusted value of \( \varepsilon^i_s + \delta \varepsilon^i_s \). The difference between the two values of reflectance, \( \delta R^i_s \), can then be found. From equation 3.3, \( \alpha^i_s \) is given by,

\[
\alpha^i_s = \frac{1}{R_s} \frac{\delta R^1_s}{\delta \varepsilon^i_s}
\]  
(3.17)

Similarly, from equation 3.4, \( \beta^i_s \) for the same layer can be expressed as,

\[
\beta^i_s = \frac{1}{R_s} \frac{\delta R^2_s}{\delta \varepsilon^i_s}
\]  
(3.18)

The Seraphin coefficients can be calculated for a single layer in a multilayer stack using this technique, provided that the bulk dielectric functions of the layers are known.

In order to test the validity of this method, the Seraphin coefficients calculated using this technique at an air/layer interface were compared with those obtained using the analytical equations 3.8 to 3.11. This comparison for bulk Si is shown in figure 3.3, where the agreement is excellent. To further check the approximate model, an algebraic differentiation
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of the reflectance was performed for a two layer structure in air, but this derivation is too long to include in this thesis. The Seraphin coefficients calculated from the resulting expressions are compared with the numerical differentiation in figure 3.4, and the agreement is again excellent. The comparisons with the exact solutions showed that the approximate method is accurate to within $\pm 0.5\%$. It was found that the accuracy is not greatly dependent on the magnitude of the small change in dielectric function needed for the calculation. The value used is typically $|\varepsilon|/1000$.

Figure 3.3 A comparison between p polarisation Seraphin coefficients calculated for bulk Si using equations 3.10 and 3.11 (circles), and using the approximate method described in the text (lines). Both calculations were performed for a $70^\circ$ incident angle. The coefficient $\alpha$ is shown in red, and $\beta$ is shown in blue.

Figure 3.4 A comparison between p polarisation Seraphin coefficients calculated explicitly for a 63.5nm $Si_{0.875}Ge_{0.125}$ layer grown on a Si substrate (circles), and using the approximate method described in the text (lines). Both calculations were performed for $70^\circ$ incident angle. The coefficient $\alpha$ is shown in red, and $\beta$ is shown in blue.

3.4 The Effect of Interference in $Si/Si_{1-x}Ge_x$ Layers

Samples with strained epilayers of $Si_{1-x}Ge_x$ ($0.07<x<0.26$) grown on Si (001) were studied using PR by Carlino et. al. (1994b). They showed that the PR consisted of $E_1$ and $E_1+\Delta_1$ transitions from the SiGe layer, and found that the Seraphin coefficients had an important effect on the PR. A device incorporating a SiGe layer would, in practice, be part of a multilayer system. Therefore, studies previously performed on SiGe grown on Si substrates are developed in this work to include more layers. The sample studied in this section is described in Appendix A, labelled o2c29. It was grown at the DRA by low pressure vapour phase epitaxy (LPVPE) for spectroscopic ellipsometry (SE) measurements of layer thicknesses and Ge compositions. Sample o2c29 consists of $Si/Si_{0.825}Ge_{0.175}/Si$ layers, and has been studied using ultra violet PR and SE by Dr. R. T. Carlino. It is important to note that the PR and SE measurements shown in this section were not performed by the author. The nominal thicknesses of the SiGe layer and Si cap are 60nm and 58nm.
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respectively.

PR was measured at three different positions along the radius of the wafer: 15mm, 25mm and 35mm from the edge. The PR spectra are shown in figure 3.5. For Si capped samples, the dominant oscillator in the PR is associated with the Si \( E_0 \) transition (about 3.4eV), and the SiGe \( E_1 \) and \( E_1+\Delta_1 \) oscillators are obscured. In figure 3.5, the lineshapes of the three spectra at energies near the Si \( E_0 \) transition are similar, whereas for energies corresponding to the SiGe \( E_1 \) and \( E_1+\Delta_1 \) transitions, the spectra differ greatly.

SE was performed at the same positions on the wafer as the PR was measured. A detailed description of SE is not warranted here; it is enough to say that SE directly measures the pseudo-dielectric function of a sample. That is, a composite dielectric function made up of all penetrable layers. The imaginary parts of this pseudo-dielectric function measured at the three positions is shown in figure 3.6. It is clear from this figure that the SE spectra are also different for each position on the sample. Similar structure is observed in the pseudo-dielectric functions near the Si \( E_0 \) energy, but they vary greatly for energies below this.

It is possible to determine the compositions and thicknesses of layers within a sample from SE spectra. Analysis of the SE showed that the only difference between the measurements is the thickness of the Si cap, and the Si cap thicknesses deduced from the analysis are 55nm, 45nm and 33nm for positions 15mm, 25mm and 35mm respectively from the edge of the wafer. It is believed that a radial temperature gradient during growth resulted in a radial variation of the Si cap thickness.

The differences observed in the PR spectra originate from the different interference effects given by different cap thicknesses. The terms in the expression for the PR (equation 1.1) that are influenced by the interference are the Séraphin coefficients. Therefore, the Séraphin coefficients for the SiGe layer in the above structure are calculated using the method outlined in section 3.3. The reference dielectric functions used are those previously obtained for bulk Si and Si\(_{0.32}\)Ge\(_{0.17}\) using SE (Carlone (1993a)). The coefficients for the SiGe layer calculated for p polarised light, which is believed to be dominant in the experiment, are shown in figure 3.7. Above about 3.35eV, the Séraphin coefficients are almost zero for all three cap thicknesses. This is consistent with the PR shown in figure 3.5, where the SiGe features occur at lower energies. Below this energy, however, the coefficients vary significantly for different cap thicknesses. This suggests that the differences in PR lineshape observed in figure 3.5 can be explained in terms of changes in Séraphin coefficients resulting from changes in optical interference due to different Si cap thicknesses.

In summary, differences in PR spectra measured along the radius of a Si/Si\(_{0.32}\)Ge\(_{0.17}\)/Si layered structure have been observed for energies in the region of the SiGe \( E_1 \) and \( E_1+\Delta_1 \) transitions. In addition, differences in SE spectra were also observed for the different positions. The Séraphin coefficients for the SiGe layer vary greatly over the energy range that the PR varies. Thus, it is likely that the differences in the PR spectra may be explained in terms of changes in the Séraphin coefficients due to changes in optical interference from the variations in the thickness of the Si cap layer.
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**Figure 3.5** Photoreflectance spectra measured at three positions along the radius of wafer o2c29. The positions are 15mm (blue), 25mm (red) and 35mm (green) from the edge of the wafer. The expected SiGe transition energies are shown as arrows.

**Figure 3.6** The imaginary part of the pseudo-dielectric function for sample o2c29, measured at the same positions on the wafer as the PR in figure 3.5. Measurements were performed using spectroscopic ellipsometry. The positions were 15mm (blue), 25mm (red) and 35mm (green) from the edge of the wafer.

**Figure 3.7** p polarised Séraphin coefficients calculated for the Si$_{0.827}$Ge$_{0.173}$ layer of sample o2c29, measured 15mm (blue), 25mm (red) and 35mm (green) from the edge of the wafer.
3.5 Calculation of Layer Thickness using Photoreflectance Phase Shifts

As observed in the previous section, the Seraphin coefficients can greatly influence the lineshape of oscillators in PR spectra. Hosea et al. (1995a) used Seraphin coefficients calculated using the same method as that reported in this chapter, to describe phase shifts of oscillators in PR spectra. Not only were they able to explain the phase shifts in terms of Seraphin coefficients, but they used the phases to predict the layer thickness of a GaAs cap in a GaAs/AlGaAs quantum well structure as it was progressively etched. In this section, PR of Si/SiGe/Si structures is used to predict the Si cap layer thicknesses, and this is then compared with results from SE. Both the PR and SE measurements were performed by Dr. R. T. Carline.

3.5.1 Photoreflectance Spectra and Fitting

Two samples were investigated, and in both cases it is known from SE measurements that the Si cap layer varies in thickness across the wafer. The nominal structures of the samples are shown in Appendix A, labelled o2c29 and o2c31. The first is that studied in the previous section; a Si (001) substrate with a layer of about 58nm of Si0.82Ge0.173 and a 60nm Si cap. The second consists of a Si (001) substrate with a layer of about 48nm of Si0.764Ge0.236 and a 60nm Si cap.

It was known that the thickness of the Si cap layer varies across the wafer for both samples, so a systematic study across the wafer was performed. PR and SE spectra were measured at six positions 4mm apart along the radius of both 100mm diameter wafers, starting 20mm from the centre. The PR probe beam was 4mm long and about 5mm wide. A schematic diagram of the positions on the wafer is shown in figure 3.8, where '1' refers to the position closest to the centre of the wafer. The PR spectra for samples o2c29 and o2c31 are shown in figures 3.9 and 3.10 respectively. As observed in the previous section, the lineshapes of all spectra measured for a particular sample are similar near the Si E\text{\textsubscript{0}}' transition (about 3.4eV), but change dramatically with wafer position for lower energies.

![Figure 3.8](image_url)

Figure 3.8 A schematic diagram of the six positions at which PR and SE were measured for samples o2c29 and o2c31.

The spectra were fitted with three TDFFs, associated with the Si E\text{\textsubscript{0}}' transition, and the SiGe E\text{\textsubscript{i}} and E\text{\textsubscript{i}}+Δ\text{\textsubscript{i}} transitions. Least squares fits were performed using n=3 for the SiGe oscillators, and n=5/2 for the Si oscillator (see equation 1.18). The transition energies E\text{\textsubscript{g}} and
broadening parameters $I_j$ vary little across the wafer, and the largest variations in the Si$_x$Ge$_{1-x}$ critical point energy correspond to a variation in $x$ of less than 0.01. Thus, the only differences between the fitted parameters for each spectrum is the phase term $\phi$. This phase parameter is related to the Seraphin coefficients. It is likely that the position dependent spectral change of the PR for each wafer is due to changes in the Seraphin coefficients resulting from changes in interference between the layers. It should be noted at this point, that if spectra are fitted using $n=3$ for the Si transition, the fit is improved, but the transition energies do not change significantly.

![Figure 3.9](image)

**Figure 3.9** Photoreflectance spectra measured at different positions along the radius of sample o2c29. Position 1 refers to the position closest to the centre of the wafer. Spectra are offset for clarity. The expected SiGe transition energies are shown as arrows.

![Figure 3.10](image)

**Figure 3.10** Photoreflectance spectra measured at different positions along the radius of sample o2c31. Position 1 refers to the position closest to the centre of the wafer. Spectra are offset for clarity. The expected SiGe transition energies are shown as arrows.

### 3.5.2 The Experimental Phase

It was established in the previous section that the only difference between the PR spectra measured at different positions along the radius of the samples is the phase $\phi$. The phase parameter used in TDFF fitting is not always a good indication of the phase of an oscillator in experimental PR spectra. Not only are the phases of each oscillator assumed to be independent of energy in the model, but many experimental spectra consist of several
oscillators which overlap and distort the phase information. Consequently, the phase of the whole spectrum is more useful. Hosea et al. (1995a) demonstrated that the phase of a whole experimental spectrum could be deduced by a Kramers-Kronig transformation. The experimental PR was considered as being the real part of a phasor, with a Kramers-Kronig transformation yielding the imaginary part of this phasor. The energy dependent modulus and phase angle were found from the measured real part, and the transformed imaginary part, of the phasor. Indeed, the modulus spectrum has been shown to contain information about the strength, broadening and energy of critical point transitions (see Hosea (1995b) and chapter 1). Phase information similar to that determined for the GaAs/AlGaAs structure by Hosea is found for the first time for Si/SiGe structures in this thesis.

![Figure 3.11](image1.png)  
**Figure 3.11** The phase angles for sample o2c29, given by the spectra shown in figure 3.9 (solid lines). The circles show the phases given by TDFF fitting, and are plotted at the fitted critical point energies.

![Figure 3.12](image2.png)  
**Figure 3.12** The phase angles for sample o2c31, given by the spectra shown in figure 3.10 (solid lines). The circles show the phases given by TDFF fitting, and are plotted at the fitted critical point energies.

The phase angles for samples o2c29 and o2c31, determined from the spectra in figures 3.9 and 3.10 are shown as lines in figures 3.11 and 3.12. The phases are indeterminate by integral multiples of $\pi$, so the relative position of each curve is arbitrarily chosen within an integral multiple of $\pi$. It can be seen from the figures that at high energies, where the Si transition dominates, the phase shift between spectra is zero (or multiples of $2\pi$ which is equivalent to zero). This can be compared to the PR spectra in the high energy range (figures 3.9 and 3.10), where the lineshape of the Si oscillator does not change significantly.
between spectra measured at different positions. Over the energy range corresponding to the SiGe transitions, however, a systematic phase shift between positions is observed, indicative of a systematic change in structure across the wafer. The values of phase \( \phi \) found from the TDFF fits are shown as circles in figures 3.11 and 3.12, and they are plotted at the transition energies given by the fits. For the two oscillators at the extremes of the spectra, the fitted phase values agree well with the experimental phases. The phase of the higher energy SiGe oscillator, however, does not correspond well with the experimental phase for any position on the wafer. Thus, we can conclude that the phase information for the SiGe \( E_1 + \Delta_1 \) oscillator given by the fits must be distorted by its overlap with the Si oscillator. This correlation between the fitted and experimental phases gives confidence in the TDFF interpretation of isolated oscillators, but shows that caution must be observed when considering the phase of closely spaced oscillators.

3.5.3 The Theoretical Phase

In the previous section, the experimental PR was transformed into the experimental phase by assuming that the PR is the real part of a phasor. If that phasor has a magnitude \( M \) and a phase angle \( \gamma \), then the experimental PR for a particular layer is given by,

\[
\frac{\Delta R}{R} = \text{Re}[M e^{i\gamma}] \tag{3.19}
\]

So comparing this with equation 1.1,

\[
M e^{i\gamma} = (\alpha - i\beta) (\Delta e_1 + i\Delta e_2) \tag{3.20}
\]

From this equation, it can be shown that,

\[
M = [(\alpha^2 + \beta^2) (\Delta e_1^2 + \Delta e_2^2)]^{\frac{1}{2}} \tag{3.21}
\]

and

\[
\gamma = \arctan\left(-\frac{\beta}{\alpha}\right) + \arctan\left(\frac{\alpha \Delta e_2 \Delta e_1}{\alpha^2 + \beta^2}\right) \tag{3.22}
\]

So each layer has an associated PR magnitude and phase which dominates the overall magnitude and phase over an energy range corresponding to the critical point transitions of that layer. If the spectral changes across the wafer observed in this chapter are due to changing Seraphin coefficients of a single layer, and not changing electric fields (which would change \( \Delta \alpha \)), then the phase difference between two positions on a wafer would be given by (equation 3.22),

\[
\Delta \gamma = \arctan\left(-\frac{\beta_1}{\alpha_1}\right) - \arctan\left(-\frac{\beta_2}{\alpha_2}\right) \tag{3.23}
\]
where $\alpha_1$ and $\beta_1$ are the coefficients for a single layer at position 1, and $\alpha_2$ and $\beta_2$ are the coefficients for the same layer at position 2.

### 3.5.4 Phase Shift Analysis

It has been shown in previous sections that an experimental phase can be extracted from a PR spectrum, and that the phase change between two similar structures can be determined by the Seraphin coefficients of those structures (equation 3.23). Thus, it is useful to compare experimental phase shifts between two spectra measured at different positions on the wafer with theoretical phase shifts calculated from the Seraphin coefficients. These relative phase shifts can be realised in two ways. The first is used for sample o2c29, where the phase shift with respect to the position closest to the wafer edge is found for each of the remaining positions. For sample o2c31, the phase shift between adjacent positions is found starting at the position closest to the centre of the wafer. Using these methods, the experimental phase shifts are given by subtracting the phases shown in figures 3.11 and 3.12, and are shown as symbols in figures 3.13 and 3.14.

![Figure 3.13](image1.png)  
**Figure 3.13** The phase differences between the spectra at positions 1 to 5 with respect to position 6, for sample o2c29. The phase differences are plotted over the energy range of the SiGe transitions.

![Figure 3.14](image2.png)  
**Figure 3.14** The phase differences between the spectra at positions 2 to 6 with respect to adjacent positions, for sample o2c31. The phase differences are plotted over the energy range of the SiGe transitions.
If the angle of incident light and the dielectric functions of the layers in the structures are known, the only parameters that are unknown in the Seraphin coefficient calculation are the layer thicknesses. If the only difference between the PR measured at two different positions on the wafer is the thickness of one of the layers, the difference in thickness between the two positions can be found by comparing the experimental phase difference with the theoretical phase difference.

As mentioned earlier, SE was performed at the same positions on the wafers as the PR. The SE light spot was 1mm long, compared with the 4mm PR spot. The SE analysis showed that the SiGe layers on both samples varied little across the wafer, and were shown to be 57.7±0.2nm and 48.4±0.4nm for samples o2c29 and o2c31 respectively. The analysis also showed that the Si cap layer varies greatly across the wafer. The cap thicknesses measured by SE for both samples along the radius of the wafers are shown in figures 3.15 and 3.16.

If the thickness of the Si cap is known for the reference position from which the experimental phase difference is calculated, the thickness of subsequent positions can be determined by comparing the experimental phase with the theoretical phase. The reference thicknesses used are those given by the SE. The phase differences are matched over the energy range of the SiGe critical point transitions, so the Seraphin coefficients of the SiGe layer are used to calculate the theoretical phase difference. The p polarised coefficients are used in the calculation, but it is only weakly dependent on the polarisation. The thickness of the Si cap was adjusted until the calculated phase change matched the experimental phase change as well as possible. The calculated phase differences are shown as solid lines in figures 3.13 and 3.14. The agreement is clearly satisfactory. The Si cap thicknesses deduced from the PR are shown as blue circles in figures 3.15 and 3.16. The horizontal PR error bars represent the length of the probe beam image at the sample, and the vertical bars represent the uncertainties in matching the experimental and theoretical Ay. The agreement between PR and SE is very good, and within the errors of both techniques.

The PR was performed with the probe beam incident at 70 degrees to the normal, but it was found that the angle could be varied by ±5 degrees in the calculation with little change in the theoretical phase shift. The calculation was also shown to be insensitive to the thickness of the SiGe layers. These could be varied by ±30nm with little change in phase shift. It was also found that the choice of the reference thicknesses was not crucial. These could vary by ±5nm and ±10nm for samples o2c29 and o2c31 respectively, without a significant difference in the thickness changes deduced.

In summary, PR spectra have been measured across the radius of two Si/SiGe/Si wafers. The features in the energy range of the SiGe E_u and E_i±Δ_i transitions change with position on the wafer for both samples. The experimental phases of the spectra have been shown to agree well with the phases found from the TDFP fits for the SiGe E_u and Si E_i transitions, but not for the SiGe E_i±Δ_i transition. The theoretical Seraphin coefficients have been calculated for the SiGe layer, and the results of this calculation used to find a theoretical phase. From comparisons between the theoretical and experimental phases, the thickness variation of the Si layer across the wafers has been deduced. These thicknesses agree well with those found from SE measurements.
3.6 Conclusions and Future Work

The work presented in this chapter has demonstrated the importance of the effect of optical interference in photoreflectance spectra. This has been shown by the effect of interference on the Seraphin coefficients, which have been calculated for a semiconductor stack using a numerical differentiation of the reflectance. This method has been shown to agree well with analytical solutions for one and two layer systems in air, and has been used to calculate the coefficients for a three layer system.

The unique Seraphin coefficient calculation has been used to find energy-dependent theoretical phases. Experimental and theoretical phases for a Si/SiGe/Si structure have been used to find the thicknesses of the Si cap layer, which varied across two wafers with similar structures. The thicknesses found from the PR of such structures agreed well with the thicknesses found using SE. This is a new method of using PR to calculate the thickness changes of layers in a multilayer structure.

A useful progression of this work would be the construction of PR spectra from the Seraphin coefficients of individual layers and the numerically differentiated dielectric functions, similar to that done previously for a SiGe layer grown on Si (Carline (1994b)).

The dielectric functions used to calculate Seraphin coefficients in this work were determined using spectroscopic ellipsometry. If the dielectric functions of quantum wells...
could be found, or accurately predicted, then this work could be extended to describe transitions of confined states in quantum wells.

The success of this technique implies that PR could be used to monitor thickness variations during growth, or to detect undesirable thickness variations across wafers.
Chapter 4

Photoreflectance of Thin Strained Si$_{1-x}$Ge$_x$ Layers ($0.17 \leq x \leq 0.23$)

In this chapter, ultra violet photoreflectance (PR) measurements of thin SiGe layers are presented. The experiments were performed by the author at the DRA.\(^\text{1}\) The spectra are fitted with third derivative functions (TDFFs). The critical point energies found from the fits are compared with the results of calculations using a simple square quantum well model, and with calculations based on the effects of composition grading at the SiGe interfaces.

4.1 Introduction

The importance of Si based structures as electronic devices, in particular strained SiGe structures, has been outlined in chapter 1. As devices become smaller, and their structures become more complex, conventional growth and processing techniques are stretched to the limit. Optical monitoring techniques, in particular spectroscopic ellipsometry (SE), are being developed to provide the real-time control of epilayer composition and thickness necessary for optimum performance in such devices. At the DRA, real-time in-situ SE is being applied to low pressure vapour phase epitaxial growth (LPVPE) of strained Si/SiGe structures (Pickering et al. (1995)). SE measured in the energy range of the E$_l$/E$_{l+\Delta}^0$ critical point transitions at the L point of Si$_{1-x}$Ge$_x$ has been used to determine alloy composition and layer thicknesses. The composition dependence of the E$_l$ and E$_{l+\Delta}^0$ transitions for SiGe layers grown on Si (001) is given by the equations (Carline et al. (1994a)),

\[
E_{g}^{E_l} = 3.395 - 1.421x - 0.005x^2 \quad (4.1)
\]

\[
E_{g}^{E_{l+\Delta}^0} = 3.424 - 0.848x + 0.214x^2 \quad (4.2)
\]

Ex-situ SE performed on Si/SiGe structures with thin SiGe layers (<50Å) were found to underestimate the Ge fraction when compared with double crystal X-ray diffraction (DCXRD) measurements (Carline et al. (1993b)). Two possible causes of this underestimation were suggested: confinement effects at the L point and grading at the SiGe interfaces. Recently, Pickering et al. (1995) showed that the Si/SiGe interface in such structures is not abrupt. The grading, however, did not explain the observed discrepancy in composition found from Carline's SE analysis.

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The main aim of this work is to use PR to investigate SiGe layers as thin as 30Å. To this end, the two explanations proposed for the anomalies in the SE described above are modelled, and compared with the PR results. These are quantum confinement and composition grading. In particular, PR should shed light on the possible presence of quantum confinement in such thin SiGe layers. Although little information is available in the literature discussing confinement at the L point in Si/SiGe structures, PR and ER have been used to observe confinement at the L point in III-V materials. Pearsall et al. (1986) are the only authors to have investigated confinement at the L point in Si/SiGe quantum wells. They studied structures with compositions $x=0.45$ and $x=0.65$, and observed energy variations for the $E_1$ and $E_1+\Delta_1$ transitions compared with unstrained SiGe. These energy differences were attributed to the effect of strain only. Indeed, the confinement of the electrons and holes for these transitions is expected to be small because of the heavy electron and hole masses that occur at the L point.

4.2 Photoreflectance Measurements and Fitting

PR spectra of thin strained Si$_{1-x}$Ge$_x$ layers ($x=0.2$) grown on Si (001) consist of features from three critical point transitions. The $E_1$ and $E_1+\Delta_1$ transitions from the SiGe are observed on the low energy side of the most dominant Si $E_0'$ transition, as was shown in chapter 3. The seven samples studied in this chapter are described in Appendix A. They consist of single and multiple Si/SiGe layered structures grown on Si (001) substrates using LPVPE at the DRA. The number of Si/SiGe periods varies between 1 and 20, with widths of the SiGe layer varying between 30Å and 105Å and compositions, $x$, between $x=0.17$ and $x=0.23$. Some of the samples studied have previously been investigated by SE (Carline et al. (1993b)). As part of that work, the composition and thickness of the Si$_{1-x}$Ge$_x$ layers were deduced from DCXRD and cross-sectional transmission electron microscopy (XTEM). It was found that the variations in composition, $x$, and well width from the nominal growth parameters were ±0.01 and ±5Å respectively.

Room temperature PR measurements were performed on the seven samples, and these are shown as blue circles in figure 4.1. The oscillators of the three critical point transitions overlap considerably, and it is not possible to identify the individual lineshapes. This means that fitting the spectra is difficult, because even the modulus spectrum does not distinguish between the individual oscillators. Despite this, it was possible to perform least squares fits for each spectrum. With the exception of the spectrum from the sample with the thinnest SiGe layer (33c4), the spectra could not be fitted with less than three TDFF oscillators. This gives confidence as to the presence of the three expected critical point transitions. Despite obtaining an adequate fit to the spectrum of sample 33c4 with two TDFFs, three TDFFs were used to fit this spectrum. The $E_1$ and $E_1+\Delta_1$ transitions are two dimensional critical points, and so were fitted using $n=3$ in equation 1.18. The Si $E_0'$ transition is a three dimensional critical point, and should be fitted using $n=5/2$. It was found in chapter 3, however, that using $n=3$ for the Si oscillator in structures similar to those studied here did not affect the oscillator energy, but improved the quality of the fit. In this case, the overlap of oscillators is such that the quality of the fit is important, so $n=3$ was used for all of the Si $E_0'$ critical points.
Figure 4.1 Room temperature PR measurements (blue circles) and TDFF fits (red lines) for the seven samples with different SiGe layer widths (shown in brackets). The critical point energies of the individual TDFF oscillators are also shown. Spectra are offset for clarity.
Figure 4.2 A breakdown of the TDFF oscillators fitted to the experimental PR spectra in figure 4.1, for the seven samples with different SiGe layer widths (shown in brackets). Spectra are offset for clarity.
Figure 4.3 PR (blue circles) and fitted (red lines) spectra for the two samples with the thinnest SiGe layers measured at 150K. A breakdown of the TDFF oscillators fitted to the spectra is shown in green. Spectra are offset for clarity.

The fitted PR spectra are shown as solid lines in figure 4.1. The fits are good for all spectra, except for the high energy region of the 22c3 and c20f25 spectra. As an aid to the reader, the critical point energies deduced from the fits are also plotted in figure 4.1. On closer inspection of these energies, it appears that the energy of the Si $E_0'$ transition remains constant between samples within some random error. The SiGe $E_1$ and $E_1+\Delta_1$ transition energies, however, appear to increase as the SiGe layer width is decreased.

The individual TDFF oscillators for each sample are plotted in figure 4.2. It is interesting to note from this figure that the lowest energy oscillator from the SiGe $E_1$ transition is the broadest and weakest in most of the spectra. This is not what is expected, as in general the $E_1$ transition is more dominant than the $E_1+\Delta_1$ transition. In addition, the oscillator from the SiGe $E_1+\Delta_1$ transition appears to be similar in magnitude and broadness to the Si $E_0'$ oscillator for some of the spectra. This differs from the observations of the PR from thicker SiGe layers shown in chapter 3, where the Si $E_0'$ oscillator was found to be dominant. The reasons for this are not clear.

It can be seen from figure 4.1, that for the samples with the thinnest SiGe layers, the
features are not as well resolved as those in the other spectra. Indeed, the spectrum from sample 33c4 appears to resemble a single TDFF oscillator. In an attempt to better resolve the features for the two samples with the thinnest SiGe layers, low temperature PR was performed. These measurements were performed at 150K using the cold finger cryostat described in chapter 2. The low temperature PR spectra of these two samples are shown in figure 4.3. In low temperature PR, the broadness of each oscillator is expected to decrease. For sample 33c4, the apparent single oscillator in the room temperature spectrum is shown to consist of features from more than one oscillator. Similarly, the features from the lower energy oscillators for sample 22c84 are clearer at 150K than at room temperature.

![Figure 4.4](image.png)

Figure 4.4 The variation of the energy with SiGe layer width for the two lowest energy TDFF oscillators in the fits to the PR spectra, corresponding to the $E_1$ (blue) and $E_1 + \Delta_1$ (red) critical point transitions. The results for the samples with $x=0.17$, $x=0.20$ and $x=0.23$ are shown as squares, circles and triangles respectively. The errors in energy are given by the covariance matrix from the least squares fitting (see chapter 1).

As was done for the room temperature PR, the low temperature spectra were fitted with three TDFFs. These fits are shown as red lines in figure 4.3, and the breakdown of the individual TDFF oscillators is also shown in figure 4.3. In this case, the three TDFF oscillators are similar in magnitude and broadness. It can be seen from these fits that the
Si $E_2'$ transition energies are greater than those given by the room temperature fits. This is consistent with previous observations of the Si $E_2'$ transition (Lautenschlager et al. (1987)). Although the low temperature study is not comprehensive, it shows the oscillators more clearly than the room temperature PR, and gives more confidence in the interpretation of the room temperature spectra. The reader may be interested to note the change with temperature of the broadness parameters. For example, for sample 33c4 these are 0.08, 0.07 and 0.06 for the $E_2'$, $E_1$ and $E_1' + \Delta_1$ transitions respectively at 150K, and 0.10, 0.18 and 0.13 for the $E_2'$, $E_1$ and $E_1' + \Delta_1$ respectively at room temperature.

The energies of the $E_1$ and $E_1' + \Delta_1$ Si$_{1-x}$Ge$_x$ transitions from the fits to the room temperature PR are shown as a function of layer width in figure 4.4, where the compositions $x=0.17$, $x=0.20$ and $x=0.23$ are shown as triangles, circles and squares respectively. It is evident from this figure, that for layer widths greater than about 50Å, the energies do not vary significantly with the layer width. For layer widths less than about 50Å, however, there is a definite increase in the critical point energies.

In summary, the increase in SiGe transition energies with decreasing layer width observed in PR is consistent with previous measurements of thin SiGe layers using SE (Carlile et al. (1993b)), where SE underestimated the composition.

### 4.3 A Quantum Well Model

A possible explanation for the increase in energy of the SiGe $E_1$ and $E_1' + \Delta_1$ transitions observed in the fits to the PR spectra is quantum confinement in the SiGe layer. The effect of confinement would be to increase the SiGe transition energies, but the Si energies would not be affected. To investigate this, quantum well transitions between electron and hole ground state confined energy levels are calculated using a simple square quantum well model. This is based on that given by Greenhow (1990). For a square well, width $2a$, such as that shown schematically in figure 4.5a, the Schrödinger equation in the well is given by,

$$-rac{\hbar^2}{2m_w} \nabla^2 \psi_w(x) = E \psi_w(x)$$  \hspace{1cm} (4.3)

and in the barrier the Schrödinger equation is given by,

$$-rac{\hbar^2}{2m_b} \nabla^2 \psi_b(x) = (E-V) \psi_b(x)$$  \hspace{1cm} (4.4)

where $V$ is the depth of the well, $E$ is the energy of the confined state, $\hbar$ is the Planck constant and $m_w$ and $m_b$ are the particle masses in the well and barrier respectively. The solutions of the above equations for the ground state energy are of the form,

$$\psi_w(x) = A \cos(kx)$$  \hspace{1cm} (4.5)

$$\psi_b(x) = B e^{-k'x}$$  \hspace{1cm} (4.6)

From these solutions, it can be shown that,

$$k = \frac{[2m_wE]}{\hbar} \frac{1}{2}$$  \hspace{1cm} (4.7)

$$k' = \frac{[2m_b(V-E)]}{\hbar} \frac{1}{2}$$  \hspace{1cm} (4.8)
From the boundary conditions and the substitution \( \theta = k a \),

\[
z = \tan \theta = \left( \frac{\gamma^2 - \frac{m_b}{m_w}}{\theta^2} \right)^{\frac{1}{2}}
\]

where,

\[
\gamma = \frac{a [2m_b V]}{E} \quad \text{(4.10)}
\]

\[
\theta = \frac{\alpha [2m_w E]}{h} \quad \text{(4.11)}
\]

If the two expressions for \( z \) in equation 4.9 are plotted as a function of \( z \), then the value of \( z \) at the point of intersection of the curves corresponds to a value for the confined energy \( E \). Such a plot is shown in figure 4.5b.

![Figure 4.5](image)

**Figure 4.5** (a) The lowest confined state in a finite quantum well (b) The graphical method used to calculate the confinement energy \( E \).

The conduction and valence band masses are important parameters in the confinement model. Each of the seven samples investigated here was grown on a Si (001) substrate, and therefore any confinement that is observed in the PR occurs along the (001) direction. The effective mass in the (111) direction (at the L point) in the (001) growth direction is given by,

\[
\frac{1}{m} = \frac{1}{3} \left( \frac{1}{m_i} + \frac{1}{m_e} \right)
\]

where \( m_i \) and \( m_e \) are the transverse and longitudinal masses at the L point. The electron masses used in this work are those calculated by Rieger and Vogl (1993); for Si \( m_i^e = 1.693m_o \), \( m_e^e = 0.130m_o \) and for Si\(_{0.3}\)Ge\(_{0.7} \), \( m_i^e = 1.680m_o \), \( m_e^e = 0.124m_o \), where \( m_o \) is the free electron mass. The hole masses used are based on the masses of Si and Ge calculated by Dresselhaus and Dresselhaus (1967). For Si \( E_i \), \( m_i^h = 1.530m_o \), \( m_e^h = 0.230m_o \) and Si \( E_i + \Delta_i \), \( m_i^h = 1.530m_o \), \( m_e^h = 0.210m_o \). To establish values of masses for Si\(_{0.3}\)Ge\(_{0.7} \), it is assumed that the masses vary linearly with Ge composition for the valence bands of both \( E_i \) and \( E_i + \Delta_i \) critical points. This assumption yields: for Si\(_{0.3}\)Ge\(_{0.7} \), \( E_i \), \( m_i^h = 1.486m_o \), \( m_e^h = 0.208m_o \) and
\( \text{Si}_{0.8}\text{Ge}_{0.2} \ E_1^+ \Delta_1 \ m_e^h = 1.486m_0, \ m_h^h = 0.194m_0. \)

The confined energies of electrons and holes were calculated using a MATHCAD\(^2\) routine. The bulk critical point energies for the strained Si\(_{1-x}\)Ge\(_x\) layers used in the calculation are those given by equations 4.1 and 4.2. Calculations were performed for the structure in figure 4.6.

**Figure 4.6** A schematic diagram of the possible electron and hole confinement in the SiGe quantum wells with Si barriers.

**Figure 4.7** Quantum well transition energies as a function of the well width calculated using the square well model for a 20% (blue), 50% (black) and 80% (green) valence band offset. These are calculated for composition \( x = 0.20. \)

\(^2\text{MATHCAD 5.0+ (1994) © Mathsoft Inc.} \)
It is well known that confinement at the $\Gamma$ point in SiGe heterostructures occurs mainly in the valence band (Van de Walle and Martin (1986)), but there has been no evidence to suggest that this is the case at the L point. Consequently, the band offset was treated as a variable in the analysis. Confinement energies calculated for valence band offsets between 20% and 80% are shown in figure 4.7. As can be seen from this figure, the value of the band offset has little influence on the calculated confined energies. Therefore, the transition energy does not depend greatly on the distribution of confinement between conduction and valence bands. This was also found to be the case for the compositions $x=0.17$ and $x=0.23$.

![Figure 4.8](image)

**Figure 4.8** The critical point energies found from the PR fits (symbols) compared with the calculated quantum well transition energies (solid lines). The confinement calculation for $x=0.17$, $x=0.20$ and $x=0.23$ are given by the dashed, solid and dotted lines respectively.

In figure 4.8, the calculated confinement energies are compared with the energies found from the PR fits. Despite the simplicity of the square well model, the predicted transitions agree well with the energies from the PR fits.

In summary, confinement energies calculated using a finite square quantum well model predict a similar shift in SiGe $E_1$ and $E_1+\Delta_1$ transition energies to that observed from the PR. The confinement energies are most significant for SiGe widths less than about 50 Å. This means that quantum confinement is a possible explanation for the energy shifts.
4.4 The Effect of Composition Grading

Given that in-situ SE measurements of the growth of thin SiGe layers performed by Pickering et al. (1995) at the DRA showed that the Si/SiGe interface is graded in composition, this effect must be considered as an alternative explanation for the energy shifts. The importance of the composition grading was realised after the PR energies had been compared with the confinement model. The aim of this section is to examine the possibility of explaining the energy shifts observed in the PR spectra in terms of composition grading at the SiGe interfaces. This is done below in two ways, and in both the possibility of quantum confinement in the SiGe layer is ignored.

To establish the extent of grading in SiGe structures grown at the DRA, Electron Energy Loss Spectroscopy (EELS) was performed by Mr. T. Whalter3 on a nominally 100Å Si0.80Ge0.20 layer. This EELS composition profile is shown in figure 4.9 as blue circles, where OA corresponds to the centre of the SiGe layer. It can be seen from this figure that the profile consists of a flat central region where the Ge composition is lower than the nominal (x=0.20). In addition to this, the composition tails off towards the Si/SiGe and SiGe/Si interfaces. It is clear from figure 4.9 that the composition profile is similar in appearance to a truncated Gaussian function (shown in figure 4.9 as a solid red line). The Gaussian agrees well with the EELS data, and so is subsequently used as an approximation to the composition profile.

The PR signal for bulk samples is believed to originate from the largest value of the electric field within the layer (Pollak and Shen (1993)). The position of the maximum electric field can be found from the Ge composition profile if it is assumed that the band energy E0 is proportional to the composition x. From this, the electric field E is given by,

$$E = \frac{\partial E_0}{\partial y} = \frac{\partial x}{\partial y}$$

(4.13)

where y is the distance across the layer. Therefore, numerically differentiating the composition profile shown in figure 4.9 yields relative electric field values along the width of the layer. Although this analysis does not yield absolute values for the field, it does indicate the position in the SiGe layer of the largest electric field. The electric field profile, given by the differentiation of the flattened Gaussian function in figure 4.9, is shown in figure 4.10. From this figure, the maximum in the field occurs at a distance of 38Å from the centre of the layer for the 100Å wide alloy layer. To give an indication of the values of the SiGe transitions across the layer, the Gaussian composition profile in figure 4.9 is converted into energy profiles of the E1 and E1+Δ1, critical point transitions, and shown in figure 4.11. It is important to realise that this profile is not the energy profile of the conduction or valence band, but that of the energy gap. Also shown in figure 4.11, is the position of the maximum electric field, as found from figure 4.10.

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From similar EELS measurements to that shown above, it was found that during the growth of layers thinner than 100Å, the tails of the interfaces do not change significantly. Therefore the composition profiles of 50Å and 30Å layers are estimated from the data for the 100Å layer shown in figure 4.9. This is done by shifting the composition profiles of both Si/SiGe and SiGe/Si interfaces towards the centre of the layer. These profiles are shown in figure 4.12. At about 50Å, the flat region has almost disappeared, and at 30Å, a triangular profile with a maximum Ge composition much lower than that from the 100Å profile is...
shown. Thus, the EELS data has allowed the position of the maximum electric field to be estimated along with the composition profiles of the SiGe layers studied here.

Assuming that the PR signal from the 100Å alloy layer originates from the position of the maximum electric field, then the composition corresponding to that position can be found from figures 4.9 and 4.10. An analysis of the profiles in figure 4.12, revealed that the composition at the maximum field is independent of the layer width. Therefore, if the PR measurements are sensitive to the composition grading, the energies of the $E_1$ and $E_1+\Delta_1$ transitions should be higher than the energies expected from the nominal Ge compositions, but independent of the width of the SiGe layer. The maximum field for the 100Å alloy layer occurs 38Å from the centre of the layer (figure 4.10). This position corresponds to a Ge composition $x=0.127$, or $E_1$ and $E_1+\Delta_1$ energies of 3.215eV and 3.320eV respectively. These energies are plotted as solid lines in figure 4.13, and compared with the energies from the PR fits. The energies corresponding to the compositions at the maximum field were also estimated for the two samples with nominal compositions $x=0.17$ and $x=0.23$, and these are also shown in figure 4.13. It is clear from the figure that this explanation of the energy shifts is not satisfactory.

![Figure 4.13](image_url)  

**Figure 4.13** $E_1$ and $E_1+\Delta_1$ TDFF oscillator energies as a function of layer width (symbols), compared with the energies corresponding to the composition at the maximum value of the electric field (lines). The compositions $x=0.17$, $x=0.20$ and $x=0.23$ are given by dashed, solid and dotted lines respectively.
An alternative explanation for the shift in PR energies can be considered by assuming that the PR originates from an "average" SiGe layer composition. To investigate this, the composition profiles expected for each layer width were estimated, as in figure 4.12. The composition profiles were averaged over the expected layer width, and the $E_1$ and $E_1 + \Delta_1$ transition energies corresponding to these compositions calculated. A comparison between the critical point energies found from the PR, and those determined from the average Ge compositions is shown in figure 4.14. The energies given by the average compositions agree reasonably well with the PR energies for layer widths greater than about 50Å. The averaging appears to underestimate the PR energies for widths smaller than this.

![Figure 4.14](image-url)

**Figure 4.14** Energies of the $E_1$ and $E_1 + \Delta_1$ TDDF oscillators from the PR fits as a function of layer width (filled symbols), compared with the energies found when averaging the compositions of the layers (open symbols). The compositions $x=0.17$, $x=0.20$ and $x=0.23$ are shown as squares, circles and triangles respectively.

An important observation from the energy values found from the PR fits should be considered at this point. If the Ge composition measured by the PR is less than the nominal value, then the different gradients of equations 4.1 and 4.2 mean that the separation of the $E_1$ and $E_1 + \Delta_1$ energies is expected to decrease (for a graphical confirmation of this, see Carline et al. (1994b)). Consequently, as the SiGe layer width is decreased, the separation
of transition energies would also be expected to decrease. It is clear from figure 4.14, however, that this is not the case, and that the separation of SiGe transitions does not change systematically with layer width. Thus, it is likely that the shifts in energy observed in the PR are due only partially to composition grading at the interfaces.

In summary, composition profiles for the SiGe layers are estimated from an EELS composition profile of a 100 Å Si_{0.80}Ge_{0.20} layer. Using these profiles, the position within the layer of the maximum electric field has been found. When the SiGe $E_1$ and $E_1+\Delta_1$ transition energies corresponding to this position are compared with the energies found from fitting the PR spectra, the agreement is poor. If, however, the PR is assumed to originate from an average Ge composition across the layer width, the energies match reasonably well with experiment for layers greater than about 50 Å, but not for thinner layers.

4.5 Conclusions and Future Work

In an attempt to investigate anomalous compositions determined from SE of thin strained SiGe layers, PR spectra were fitted with three TDFF oscillators, representing the Si $E_1$ transition, and the SiGe $E_1$ and $E_1+\Delta_1$ transitions. From these fits, it appears that the SiGe transition energies increase as the SiGe layer width is decreased. This is consistent with the underestimation of composition observed in the SE. From EELS measurements, it is known that the SiGe interfaces are graded in composition, but the aim of this work has been to determine whether this can satisfactorily explain the energy shifts, or if there is confinement at the L point in the SiGe layer.

The SiGe $E_1$ and $E_1+\Delta_1$ transition energies from a square quantum well model show the correct trend and reasonable agreement with the fitted PR energies, but predict energies slightly lower than those found from experiment. No account of the grading was included in this model. If an "average" composition across the SiGe layer width is considered, based on measured composition profiles, then the unconfined bulk $E_1$ and $E_1+\Delta_1$ energies found from this composition agree well with the calculated transition energies for layers greater than about 50 Å, but not for thinner layers. The most likely explanation appears to be a combination of both composition grading (dominant for layers >50 Å) and quantum confinement. More definitive conclusions about the origins of the energy shifts could be found by modelling the SiGe layers as quantum wells with graded interfaces.
Chapter 5

Analysis of Franz-Keldysh Oscillations in III-V Materials

In this chapter, room temperature photoreflectance (PR) spectra with Franz-Keldysh oscillations (FKO) are compared with the Franz-Keldysh theory. Firstly, an asymptotic approximation of the period of FKO is described. Then, work on the analysis of FKO using Airy function expressions is presented. These two methods of analysis are compared with FKO observed in PR spectra from InGaAsP and InP.

5.1 Introduction

The driving force behind research into III-V materials has been their use as optoelectronic devices. As the number of applications increase, so characterisation of the materials becomes increasingly important. PR has been shown to be a useful characterisation tool in the low field regime, but for the intermediate field regime researchers have encountered difficulties in matching electromodulation theory with the FKO that are observed in spectra.

In recent years, FKO have been used to study electric fields and their related effects. For example, Gaskill et. al. (1988) studied the surface space-charge layer in GaAs films, Bhattacharya et. al. (1988) investigated doping levels and Fermi pinning in (In-Sn-O)/InP and crystal quality of GaAs/AlGaAs structures has been studied by Yin et.al. (1990). Many of these studies have relied on approximations to the FKO to determine electric fields, and few workers have used the complete electromodulation theory. The main reason for this has been the complexity of the Airy function expressions present in this theory.

The aim of this work is to model FKO in PR spectra with the simplest, physically significant, Airy function model. The FKO measured for InGaAsP layers are analysed using Aspnes' asymptotic approximation. These FKO are then fitted with Airy function expressions. The conclusions from the fits to the InGaAsP FKO are applied to FKO in spectra from InP layers.

5.2 Asymptotic FKO Analysis

The theoretical interpretation of FKO has proved difficult to compare directly with experiment, mostly because of the difficulty of calculating the complicated theoretical functions which are based on Airy functions and their derivatives. In 1973, Aspnes and Studna (1973b) avoided this problem by reporting a simple method of interpreting FKO. They showed that the subsidiary oscillations in FKO spectra, at energies larger than the energy gap, could be expressed in terms of a cosine function multiplied by a decaying
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Chapter 5

exponential function,

\[ \frac{\Delta R}{R} = \frac{A\Phi}{(E-E_g)^{1/3}} \cos \left[ \Phi + \frac{4}{3} \left( \frac{E-E_g}{\hbar\theta} \right)^{1/3} \right] \]  \hspace{1cm} (5.1)

where \( \Phi \) is a phase factor depending on the electron-hole interaction strength, dimensionality, short range scattering processes and optical interference, \( A \) is the magnitude, \( \Gamma \) is the Lorentzian broadening, \( E \) is the energy, \( E_g \) is the critical point energy gap, and \( \hbar\theta \) is the electro-optic energy. Since successive extrema in equation 5.1 represent a change of \( \pi \) in the argument of the cosine term, Aspnes deduced that,

\[ n\pi = \Phi + \frac{4}{3} \left[ \frac{E_n-E_g}{\hbar\theta} \right]^{1/3} \]  \hspace{1cm} (5.2)

where \( E_n \) is the energy of the extremum labelled \( n \) (\( n=1,2,3,... \)). Using this equation, the value of \( \hbar\theta \), and so the magnitude of the electric field (see equation (1.8)), can be found from the slope of a plot of \( (E_n-E_g)^{1/3} \) vs \( n \). So, the field can be found simply from the positions of the FKO extrema.

This method of analysis is useful when the energy gap \( E_g \) is known, but not if \( E_g \) is unknown. In this case, an alternative analysis can be performed by rearranging the terms in equation 5.2, such that,

\[ E_n = \hbar\theta F_n + E_g \]  \hspace{1cm} (5.3)

where

\[ F_n = \left[ \frac{3}{4} \left( n\pi - \Phi \right) \right]^{1/3} \]  \hspace{1cm} (5.4)

The energy gap \( E_g \) is given by the intercept of a plot of \( E_n \) vs \( F_n \), and \( \hbar\theta \) is given by the gradient. Although this alternative plot is desirable when the energy gap is not known, it is necessary to assume a value for the phase \( \Phi \). Aspnes and Studna (1973b) reported that the phase depends on the critical point dimensionality,

\[ \Phi = - \frac{\pi (d-1)}{4} \]  \hspace{1cm} (5.5)

where \( d \) is the dimension of the critical point, and \( \Phi \) has units of radians. There is much scepticism as to the validity of equation 5.5, as the phase is dependent on several processes not included in the equation such as electron-hole interaction strength, short range scattering.
and optical interference. A further limitation in using this alternative analysis is that it relies on the correct assignment of the extremum number n. If the extrema were wrongly labelled, then the analysis would be in error.

Both forms of this asymptotic analysis have formed the basis of much of the FKO analysis performed to date.

5.3 Airy Function FKO Analysis

Despite the problems when using the electromodulation theory to describe experimental spectra, several authors have recently attempted to do so. The Airy function analysis published in the literature is reviewed in this section, followed by a detailed description of the Airy function expressions used to fit PR spectra in this work.

5.3.1 Literature Review

Following the work of Aspnes and co-workers, it was not until the 1980s, when computational methods became more sophisticated, that the rigorous Airy function analysis of FKO was applied directly to experimental spectra. Since then, FKO from ER and PR have been used to study electric field effects in different material systems, and in a variety of different structures.

Bhattacharya et al. (1988) studied the space-charge region of an (In-Sn-O)/InP structure using ER and PR. Previous theories describing the electric field induced changes in the dielectric function due to modulation, considered modulation from the flatband condition. That is, the difference in the value of the dielectric function between a finite and zero field. Bhattacharya proposed a generalised Franz-Keldysh theory, based on Aspnes' Airy function analysis (Aspnes et al. (1968)) that considered the presence of a constant dc field superimposed on the modulated ac field. This dc field component was shown to influence the functions F(x) and G(x) (see equations 1.11 and 1.12), but they did not calculate theoretical ER or PR spectra from these functions. They did, however, use the asymptotic expression described in the previous section to show that the period of the experimental FKO was dependent on the constant dc field, and not dependent on the ac modulating field. They also showed that the envelope function of the spectra depends on the ac modulating field.

Van Hoof et al. (1989) investigated electric fields in a GaAs depletion region using PR. They observed FKO, and attributed them to light and heavy hole transitions at the GaAs E_g critical point. They assumed that the modulation of the imaginary part of the dielectric function, \( \Delta \varepsilon_2 \), was negligible, and described the PR using two expressions for the light and heavy hole \( \Delta \varepsilon_{lh} \) and \( \Delta \varepsilon_{hh} \). Experimental spectra were fitted with this model. The agreement was good, despite not including the effects of broadening.

Batchelor et al. (1990) studied GaAs using electrolyte ER. They calculated theoretical spectra, and found that the theory mimicked the experiment if an empirical exponential expression for the broadness, \( \Gamma = \Gamma_0 \exp[\delta(E-E_g)] \), was used. Their explanation for this was simply that the broadness increased with energy, due to the more rapid relaxation of higher energy electrons. The theoretical FKO were not compared with the ER spectra.

Shen and Pollak (1990) presented a generalisation of the Franz-Keldysh theory, similar to that given by Bhattacharya et al. (1988), and described above. They considered ac and
dc electric field components, and included the effects of broadening. They showed that the period of the FKO was influenced only by the dc component of the field. The theory was not compared with experimental results.

Estrera et al. (1994) used simple Airy function expressions with the energy dependent exponential broadness used by Batchelor et al. (1990). The exponential broadness was reported to account for the effects of non-uniform electric fields, non-flatband modulation and collision broadening. Experimental PR spectra of bulk GaAs, InP and InGaAs were fitted with Airy function expressions, and the fits agreed well with experiment when a contribution from light and heavy holes was considered.

Hsu et al. (1994) considered a uniform electric field in δ-doped GaAs. They observed FKO in experimental PR and ER spectra, and used the model given by Bhattacharya et al. (1988) to describe the FKO observed i.e. they included the effect of a dc electric field. Two Airy function expressions were used to describe light and heavy holes, and although theoretical spectra were calculated, they were not compared with experiment.

A recent paper by Shen and Dutta (1995) reviews previous studies of FKO and the effects contributing to spectra during electromodulation.

In summary, although much work has been reported on the effects and origins of FKO in ER and PR spectra, only two authors (Van Hoof and Estrera) have successfully fitted experimental spectra with the Airy function expressions derived in chapter 1.

5.3.2 Fitting using Airy Function Expressions

It was shown in chapter 1 that changes in the real and imaginary parts of the dielectric function due to modulation at an Mq critical point can be expressed in terms of Airy functions and their derivatives (Aspnes (1967)). More recently, Batchelor et al. (1990) showed that,

\[ \Delta \varepsilon_1 = B \theta \frac{1}{2} \text{Im} \left[ \frac{H(z)}{(E-i\Gamma)^2} \right] \] (5.6)

\[ \Delta \varepsilon_2 = B \theta \frac{1}{2} \text{Re} \left[ \frac{H(z)}{(E-i\Gamma)^2} \right] \] (5.7)

where,

\[ z = \frac{(E - E_g)}{h\theta} + i\Gamma \] (5.8)

\( B \) is the amplitude, \( E \) is the energy, \( E_g \) is the energy gap, \( \Gamma \) is the collision broadness, \( h\theta \) is the electro-optic energy and \( H(z) \) is given by,

\[ H(z) = 2\pi \left[ e^{-i\frac{\pi}{3}} A'_1(z) A_1(z) e^{-i\frac{2\pi}{3}} + ze^{-i\frac{2\pi}{3}} A_1(z) A'_1(z) \right] + i\sqrt{E} \] (5.9)

where \( A_1 \) and \( A'_1 \) are the Airy function and its derivative respectively. Thus, the PR given by equation 1.1 can be expressed as,

\[ \frac{\Delta R}{R} = \text{Re} \left[ \frac{A e^{i\Phi}}{(E-i\Gamma)^2} H(z) \right] \] (5.10)
where \( A \) is the amplitude and \( \phi \) is a phase term representing the effect of the Seraphin coefficients.

It can be seen from equation 5.9 that the function \( H(z) \) is comprised of the Airy function \( A_i \) and its derivative \( A'_i \). In this work, these are calculated using the summations given by Abramowitz and Stegun (1965),

\[
A_i(z) = c_1 f(z) - c_2 g(z) \quad (5.11) \quad A'_i(z) = c_1 f'(z) - c_2 g'(z) \quad (5.12)
\]

where

\[
f(z) = \sum_{k=0}^{\infty} 3^k \left( \frac{1}{3} \right)_k \frac{z^{3k}}{(3k)!} \quad (5.13) \\
g(z) = \sum_{k=0}^{\infty} 3^k \left( \frac{2}{3} \right)_k \frac{z^{3k+1}}{(3k+1)!} \quad (5.14)
\]

\[
f'(z) = \sum_{k=0}^{\infty} 3^k \left( \frac{1}{3} \right)_k \frac{3k z^{2k+1}}{(3k)} \quad (5.15) \\
g'(z) = \sum_{k=0}^{\infty} 3^k \left( \frac{2}{3} \right)_k \frac{(3k+1) z^{3k+1}}{(3k+1)!} \quad (5.16)
\]

\( c_1 = 0.35502 \) and \( c_2 = 0.25881 \). A detailed description of calculating complex Airy functions is given by Schulten et al. (1979).

Although successful, calculating the Airy functions using equations 5.11 and 5.12 proved to be time consuming. It was found that for high energies, a large number of terms were required in the series approximations given by equations 5.13 to 5.16. An approximation to the Airy functions, valid at high energies was used to reduce the time taken when calculating them. This approximation was originally reported by Aspnes (1974), and consisted of an expression with TDFF and oscillatory terms. Aspnes concluded that this function provided a good representation of the exact Airy function lineshape when \((E-E_g)>2\hbar\). It is important to note that the approximation in the paper by Aspnes contained errors, and so the correct expression is given by,

\[
H(z) \approx \frac{1}{4z} - \frac{1}{32z^\frac{5}{2}} \quad (5.17)
\]

The first term in equation 5.17 is an oscillatory term, and the second is a TDFF. Dr. T. J. C. Hosea\(^1\) found that the Airy function calculation is only necessary within a certain range of \( \Gamma \) and \( h\). He compared the approximation with the Airy function calculation and established an empirical boundary in \( z \). Outside this boundary the error in the approximation when compared with the Airy function calculation is 1\% or better when the error is defined as,

\[
\frac{|H(z)_{\text{Airy}} - H(z)_{\text{APPR}}|}{H(z)_{\text{MAX AIRY}}} \quad (5.18)
\]

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In addition, Dr. T. J. C. Hosea found that only a TDFF, or only a oscillatory function are needed to approximate the Airy function calculation for certain ranges of $z$. The boundary of the region where only the TDFF term in equation 5.17 is required, is when the magnitude of the maximum value of the TDFF is 100 times that of the oscillatory term. Similarly, the boundary for the region where only the oscillatory term in equation 5.17 is required, is when the magnitude of the maximum value of the oscillatory term is 100 times that of the TDFF. These ranges are shown schematically in figure 5.1. Inside the central region in this figure, Airy functions are required to describe the lineshape, but outside this region the spectra can be described by the approximation. The time taken to calculate the Airy functions was significantly reduced by using this approximate expression for the high energy points in the spectra.

The main aim of this work is to fit PR spectra with Airy function expressions. The program used to fit TDFF functions was written in BASIC (see chapter 1), and so it was convenient to calculate $H(z)$ using a BASIC routine. This was written by Dr. T. J. C. Hosea and later incorporated into the least squares fitting program. Before using the Airy functions to fit experimental spectra, it is useful to compare the functions calculated in BASIC with those calculated using another method. The values of $H$ calculated from the BASIC routine were compared with those calculated from a FORTRAN program incorporating a NAG routine (S17DGF) which calculated $A_1$ and $A_1'$. This comparison is shown in figure 5.2, where the real and imaginary parts of $H$ ($H=F+iG$) were calculated using the two programs for typical values of broadness, $\Gamma$, and electro-optic energy, $\hbar\Theta$. It can be seen from this figure that there is good agreement between the data from the two sources.

As an additional check, and to show the transition between the Airy function and approximate expressions, $F$ and $G$ were calculated using the BASIC program for various values of $\Gamma/\hbar\Theta$, encompassing three of the regions shown in figure 5.1. This is shown in figure 5.3. For comparison, $F$ and $G$ calculated using the FORTRAN program described above are also shown in figure 5.3. There are no visible discontinuities at the junction between the Airy function calculation and the approximation.

In order to show the importance of the two parameters $\Gamma$ and $\hbar\Theta$, they are varied independently in figures 5.4 and 5.5. In figure 5.4, $\hbar\Theta$ is varied between $0.15\text{eV}$ and $0.50\text{eV}$ with $\Gamma=0\text{eV}$. The effect of increasing $\hbar\Theta$ is to increase the period of the oscillations. In figure 5.5, $\Gamma$ is varied between $0.05\text{eV}$ and $0.25\text{eV}$. The effect of increasing $\Gamma$ is to dampen the oscillations, so much so that they are no longer visible in $F$ and $G$ for $\Gamma=0.25\text{eV}$. In addition, increasing $\Gamma$ has the effect of decreasing the amplitude of $F$ and $G$.

In summary, the method used to calculate Airy functions in this work has been described in detail, including an approximation employed for high energies.
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Figure 5.1 Methods of calculating the functions \( F(z) \) and \( G(z) \) used in the fitting program for certain ranges of the real and imaginary parts of \( z \).

Figure 5.2 A comparison of the functions \( F \) (red) and \( G \) (blue) calculated using equations 5.11 to 5.16 in the BASIC routine (circles), and calculated using the FORTRAN NAG routine (lines). For these calculations, \( \Gamma = 0.01 \text{eV} \) and \( \hbar = 0.05 \text{eV} \). G is offset for clarity.

Figure 5.3 \( F \) (red) and \( G \) (blue) calculated using the BASIC routine (circles), and the FORTRAN routine (lines). The values of \( (E-E_g)/\hbar \) where the Airy function calculation ends and the various approximations begin are shown as vertical lines.
Figure 5.4 The influence of $\hbar \Theta$ on the functions $F$ (red) and $G$ (blue). These are calculated with $\Gamma = 0\text{eV}$. Spectra are offset for clarity.

Figure 5.5 The influence of $\Gamma$ on the functions $F$ (red) and $G$ (blue). These are calculated with $\hbar \Theta = 0.1$. Spectra are offset for clarity.

5.4 Analysis of FKO from $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$

The samples studied in this section are described in Appendix A, labelled MR358 to MR361. They were grown by metal-organic vapour phase epitaxy (MOVPE) by C. C. Button. The nominal structures consist of a single strained $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}$ quantum well with $\text{In}_{0.74}\text{Ga}_{0.26}\text{As}_{0.35}\text{P}_{0.44}$ barriers lattice matched to InP substrates. The $\text{InGaAsP}$ barriers are made up of an undoped spacer layer grown next to the well, and a Zn-doped p-type layer. The samples were originally grown to investigate hole masses in transport measurements, but the heavy doping provides large electric fields at the interfaces, ideal for measuring FKO in PR spectra. The only difference between the samples is the width of the doped and undoped $\text{InGaAsP}$ barrier layers, which vary between 125Å and 200Å and 150Å and 200Å respectively. The PR from the structures is not expected to vary significantly because the four samples are similar. PR was measured at room temperature over the energy range of the $\text{InGaAsP} E_0$ critical point transition for the four samples, and the spectra are shown in figure 5.6. It is clear from this figure that similar lineshapes are observed in the spectra from three of the samples; MR358, MR359 and MR361. The spectrum from sample MR360, however, is significantly different. Not only is the amplitude smaller than the other three spectra, but features are present below the expected barrier energy (0.98eV).

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Figure 5.6 Room temperature PR spectra (blue circles) and modulus spectra (green lines) in the energy range of the InGaAsP $E_0$ critical point transition for samples MR358 to MR361. The numbered extrema correspond to the values of $n$ in equation 5.3. Spectra are offset for clarity.
The modulus spectra calculated using a Kramers-Kronig transformation (see chapter 1) are also shown for each sample in figure 5.6. The modulus spectrum can provide critical point transition information (see chapter 1). The modulus spectra calculated from PR with FKO are difficult to interpret because each FKO extremum shows either a peak or a dip in the modulus spectrum. In addition, the modulus spectra near the transition energy in figure 5.6 show a single broad peak, adding to the difficulty in determining the \( E_g \) bandgap energy. Despite these difficulties, the main peak in the modulus spectra does give an indication of the \( E_g \) bandgap energy, and these modulus peaks are at 0.981eV, 0.987eV, 0.944eV and 0.981eV for samples MR358, MR359, MR360, MR361 respectively.

From the PR and modulus spectra for sample MR360, it is obvious that the \( E_g \) bandgap is lower in energy than for the other samples. In addition, two features are observed below the \( E_g \) bandgap in both PR and modulus spectra. These are most likely to be quantum well transitions. These two peaks occur in the modulus spectrum at about 0.90eV and 0.92eV.

It is important to note that no quantum well transitions were observed for samples MR358, MR359 and MR361. This is a surprising result, but a possible explanation is the migration of Zn dopant into the InGaAs well. The effect of this would be to quench any quantum well transitions. When these results were presented to the sample suppliers, they commented that at the time at which the samples were grown there were problems with the control of gas flow in the MOVPE chamber. The PR measurements performed during this work highlighted problems experienced during growth, and as a result of this a new series of similar samples were grown. The PR of these samples is presented in chapter 6. So, although Zn migration is a possible explanation, it is not fully understood why no quantum well transitions were observed for three of the samples.

### 5.4.1 Asymptotic Analysis of the InGaAsP FKO

The commonly used asymptotic analysis was performed to establish an initial impression of the parameters associated with the FKO in the spectra. Due to the uncertainties in composition of the In\(_{1-x}\)Ga\(_x\)As\(_y\)P\(_{1-y}\) layers that occur during growth, the value of the \( E_g \) energy gap is not well known. This means that the alternative asymptotic expression must be used in this case (equation 5.3). This expression assumes that the phase term is known and that the energy gap is not known. As explained in section 5.2, two problems exist when using this expression. Firstly, the identification of the first extremum is crucial, and this is particularly difficult for the spectrum of sample MR360, where the structure from the critical point transition is obscured by quantum well transitions. For the spectra in figure 5.6, the main peaks in the modulus spectra were used as references when assigning values of \( n \). The integers \( n \) assigned to the FKO extrema are shown in figure 5.6. Secondly, there is the problem of the phase. The \( E_g \) critical point is three dimensional, and so the phase given by equation 5.5 is \( \Phi = -\pi/2 \) radians (270°). The asymptotic analysis was performed using this phase value, and the plots of \( E_n \) vs \( F_n \) for each sample are shown as circles in figure 5.7. The lines in the figure are a linear regression of the circles, and the values of the intercept \( (E_0) \) and gradient \( (\delta \theta) \) found from the regression are shown in table 5.1.

The alloy compositions corresponding to the energy gaps given by the analysis are found using the equation given by Nahory et al. (1978) for In\(_{1-x}\)Ga\(_x\)As\(_y\)P\(_{1-y}\) lattice matched to InP.
The values of $y$ are shown in table 5.1. For all four samples, the As composition appears to be greater than nominal, and for sample MR360, $y$ is much greater than nominal (0.56).

A value for the reduced mass is required to calculate the magnitude of the electric field from the value of $\omega_0$ given by the gradient (see equation 1.8). It is not clear from the analysis if the FKO originate from a heavy or light hole transition, or a combination of both, because the $E_0$ critical point transition energy of unstrained InGaAsP is the same for light and heavy holes. The field is therefore calculated using the reduced mass of light holes and also calculated using the reduced mass of heavy holes. The reduced mass is given by equation 1.4, and the value of the heavy hole mass for all compositions is given by Adachi (1992); $m_{hh}=0.46m_0$, where $m_0$ is the free electron mass. The values of the light hole and electron masses are calculated for the compositions determined above using the equations given by Adachi (1992) for In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ lattice matched to InP,

$$m_e = 0.079 - 0.038y$$  \hspace{1cm} (5.20)

$$m_{lh} = 0.120 - 0.099y + 0.030y^2$$  \hspace{1cm} (5.21)

and these masses are used to calculate the electric fields, which are shown in table 5.1.

It is clear from the values of $E_0$ and $\omega_0$ in table 5.1, that samples MR358, MR359 and MR361 are indeed similar. The field values found from the analysis show that similar fields are present in the three structures. An interesting observation to emerge from the analysis is that for all four samples, the energy gaps given by the asymptotic analysis are about 10meV lower than the peaks in the modulus spectra.

One of the problems with the $E_n$ vs $F_n$ asymptotic plot mentioned in section 5.2, is the uncertainty in the value of the phase term $\Phi$. This not only depends on the dimensionality of the critical point, but also on processes which are difficult to quantify i.e electron-hole interaction strength, short range scattering and optical interference. Consequently, it should be remembered that the phase used in this analysis is unlikely to be the true phase. Hughes et. al. (1995) have compared the two methods of asymptotic analysis described in section 5.2. They found that the uncertainties in the energy gap of the GaAs $E_0$ critical point when using the alternative analysis could be as much as 10meV. An important effect of an error in the phase when using such a plot is to change the value of $\omega_0$. This then changes the value of the electric field found from the analysis.

In summary, the alternative asymptotic analysis of the FKO in the PR spectra has shown that the composition and electric fields of the InGaAsP layers are similar for three of the four samples. The analysis shows a significant difference between these three samples and MR360.
Figure 5.7 Asymptotic FKO plots from the spectra of samples MR358 to MR361 shown in figure 5.6, as described by the alternative asymptotic analysis (circles). The value of the phase is \(-\pi/2\) radians. The solid lines are the results of a linear regression through the circles, and the parameters from the regression are shown in table 5.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intercept (E_o) (eV)</th>
<th>Gradient (\hbar\theta) (eV)</th>
<th>(y)</th>
<th>(\text{Field}_{\text{el}}) (kV/cm)</th>
<th>(\text{Field}_{\text{hh}}) (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR358</td>
<td>0.974±0.0002</td>
<td>0.0139±0.00004</td>
<td>0.58</td>
<td>19.0</td>
<td>14.5</td>
</tr>
<tr>
<td>MR359</td>
<td>0.978±0.0003</td>
<td>0.0141±0.00006</td>
<td>0.57</td>
<td>19.4</td>
<td>14.9</td>
</tr>
<tr>
<td>MR360</td>
<td>0.936±0.0021</td>
<td>0.0160±0.00039</td>
<td>0.64</td>
<td>22.7</td>
<td>16.4</td>
</tr>
<tr>
<td>MR361</td>
<td>0.970±0.0003</td>
<td>0.0140±0.00005</td>
<td>0.59</td>
<td>19.2</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Table 5.1 Results of the asymptotic analysis of the FKO from the In_{1-x}Ga_xAs_yP_{1-y} spectra shown in figure 5.6. The plots of \(E_n\) vs \(F_n\) are shown in figure 5.7. The gradients and intercepts are given by a linear regression, and the errors are standard errors. The electron and hole masses used to calculate the electric field values are given in the text. The compositions are calculated using equation 5.19 (the nominal composition is \(y=0.56\)).
5.4.2 Fitting the InGaAsP FKO with one Airy Function Expression

The next stage in the analysis of the InGaAsP spectra is to fit them with one Airy function expression, as given by equation 5.10. This is the simplest model and should be tried first. The values of $E_0$ and $\delta\theta$ given by the asymptotic analysis were used as initial guesses in the fits. To account for the two quantum well features observed for sample MR360 (figure 5.6), this spectrum was fitted with one Airy function expression and two TDFFs. The experimental and fitted spectra are shown in figure 5.8, and the fitted parameters are shown in table 5.2. The parameters of the two TDFFs fitted to the spectrum of MR360 are shown in table 5.3. As was done for the asymptotic analysis, the electric fields are calculated for both heavy and light holes using the masses given in section 5.4.1. These electric field values are shown in table 5.2.

The $E_0$ critical point energies from the fits for samples MR358, MR359 and MR361 are similar to those found from the asymptotic analysis. In addition, the values of $\delta\theta$ for MR358 and MR359 are similar to those found from the asymptotic analysis, but $\delta\theta$ differs for MR361.

The energies of the two TDFFs in the fit for sample MR360 are 0.891eV and 0.925eV. The lower energy TDFF is consistent with the peak in the modulus spectrum (0.90eV), but the TDFF at 0.925eV is higher in energy than the barrier (0.920eV). Although confined states above the barrier have been observed in the PR of double quantum wells (Nakayama et al. (1995)), none have been reported in single quantum well structures such as those investigated here. So, although the fit with a single Airy function for sample MR360 is good, the respective energies of the barrier and TDFFs are not physically meaningful.

If the fits in figure 5.8 are examined closely, it is clear that the period of the fitted spectra match the experiment well, but the oscillations appear to decay more rapidly in the experimental spectra. It was shown in figure 5.5 that the effect of increasing the broadness, $\Gamma$ is to dampen the oscillations, and this seems to be what is required in this case. Therefore, the spectra were also fitted using an Airy function expression with an energy dependent broadness term. The empirical expression used for the broadness is that proposed by Batchelor et al. (1990), and used by Estrera et al. (1994) to include the effects of non-uniform electric fields and non-flatband modulation; $\Gamma = \Gamma_0 \exp[\delta(E-E_g)]$. Surprisingly, the exponentially increasing broadness had little effect on the fits, and the values of $\delta$ are smaller than most of those reported by Estrera et al. (1994). The parameters from these fits are shown in table 5.4. The spectra fitted using the energy dependent broadness were similar to those shown in figure 5.8, and so are not shown here. It should be noted that the energies of the two TDFFs for sample MR360 did not change significantly with the introduction of the energy dependent broadness. Therefore, the respective energies of the barrier and TDFFs are still not physically meaningful.

In summary, FKO from InGaAsP have been fitted using one Airy function expression. The period of the fitted spectra match the experiment well, but the oscillations appear to decay more rapidly in the experimental spectra. The inclusion of an exponential broadness term has little effect on the fits.
Figure 5.8 Experimental (blue circles) and fitted (red lines) PR in the energy range of the InGaAsP $E_c$ critical point transition for samples MR358 to MR361. The fits were performed using one Airy function expression. For MR360, two TDFFs were included in the fit. Spectra are offset for clarity.
Table 5.2 Parameters from the least squares fits of the FKO from InGaAsP using one Airy function expression. The electric fields are calculated using the masses given by equations 5.20 and 5.21. The parameters for the two TDFFs used to fit the spectrum of sample MR360 are shown in table 5.3.

Table 5.3 Parameters of the two TDFFs included in the spectra of sample MR360 when fitting the FKO from the InGaAsP barrier with one Airy function expression.

Table 5.4 Parameters from the least squares fits of the FKO from InGaAsP using one Airy function expression and an empirical exponentially decaying broadness. The parameters for the two TDFFs used to fit the spectrum of sample MR360 are similar to those found for the fit with an energy independent broadness shown in table 5.3, and so are not presented.
5.4.3 Fitting the InGaAsP FKO with two Airy Function Expressions

Only limited success was achieved using one Airy function expression, so the model is now developed to include a second Airy function expression. Van Hoof et. al. (1989) were the first to fit FKO using two Airy function expressions i.e an expression for both light and heavy holes. This model is initially applied to the InGaAsP FKO in this work using an energy independent broadness, $\Gamma$. The InGaAsP barrier is unstrained, and so the $E_{g}$ energy gap is the same for the light and heavy holes. The energy gaps for both Airy function expressions were therefore forced to be equal in the fits, and all other parameters were varied independently. The experimental and fitted spectra are shown in figure 5.9, and the parameters from the fits are shown in table 5.5. The parameters of two TDFFs used to fit the spectrum of sample MR360 are shown in table 5.6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{g}$ (eV)</th>
<th>$\phi$ (degrees)</th>
<th>$\theta$ (eV)</th>
<th>$F_{hh}$ (kV/cm)</th>
<th>$\phi$ (degrees)</th>
<th>$\theta$ (eV)</th>
<th>$F_{lh}$ (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR358</td>
<td>0.966</td>
<td>0.1495</td>
<td>19.3</td>
<td>0.0131</td>
<td>17.3</td>
<td>0.0957</td>
<td>0.0190</td>
</tr>
<tr>
<td>MR359</td>
<td>0.972</td>
<td>0.0987</td>
<td>37.6</td>
<td>0.0430</td>
<td>17.1</td>
<td>0.0638</td>
<td>0.0178</td>
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<tr>
<td>MR360</td>
<td>0.935</td>
<td>0.0253</td>
<td>161.7</td>
<td>0.0160</td>
<td>22.7</td>
<td>0.0258</td>
<td>0.0235</td>
</tr>
<tr>
<td>MR361</td>
<td>0.969</td>
<td>0.1676</td>
<td>84.1</td>
<td>0.0122</td>
<td>15.6</td>
<td>0.0980</td>
<td>0.0190</td>
</tr>
</tbody>
</table>

Table 5.5 Parameters from the least squares fits of the FKO from InGaAsP using two Airy function expressions. The parameters for the two TDFFs used to fit the spectrum of sample MR360 are shown in table 5.6.

<table>
<thead>
<tr>
<th>$A$</th>
<th>$E_{g}$ (eV)</th>
<th>$\Gamma$ (eV)</th>
<th>$\phi$ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.61</td>
<td>0.922</td>
<td>0.0129</td>
<td>62.9</td>
</tr>
<tr>
<td>96.52</td>
<td>0.892</td>
<td>0.0084</td>
<td>119.0</td>
</tr>
</tbody>
</table>

Table 5.6 Parameters of the two TDFFs used when fitting the FKO from the InGaAsP barrier in the spectrum of sample MR360 with two Airy function expressions.
Figure 5.9 Experimental (blue circles) and fitted (red lines) PR in the energy range of the InGaAsP $E_c$ critical point transition for samples MR358 to MR361. The fits were performed using two Airy function expressions, and two TDFFs were included below $E_c$ for sample MR360. Spectra are offset for clarity.
It can be seen from figure 5.9 that this model matches the experiment much better than the previous one. Indeed, the fitted spectra match the experiment exceptionally well. If this light/heavy hole model is valid, however, the parameters found from the fits must be physically meaningful. The electric field values calculated for light and heavy holes must be similar if the PR is sensitive to light and heavy holes, because they must originate from the same field within the structure. This is certainly the case for all four samples, giving confidence in the model.

For sample MR360, the TDFF energies are similar to those found from the modulus spectrum i.e. the TDFF are lower in energy than the $E_0$ energy gap, and so are physically reasonable. This also gives confidence in the model.

It can be seen from table 5.5, that the amplitudes of the Airy function expressions obtained for the heavy holes are greater than those for the light holes for the three samples MR358, MR359 and MR361. This is consistent with the observations of Estrera et al. (1994). When an exponential broadness is included in the two Airy function fits described here, the fitted spectra do not change significantly. Consequently the results for the exponential broadness are not presented here.

When fitting spectra consisting of several overlapping oscillators, it is important to examine the contribution of the individual oscillators to the spectrum. This is done in figure 5.10, where the two oscillators from the fit to the spectrum of sample MR358 are shown. Only the breakdown for this sample is shown because the other three samples are similar. It is interesting to observe that few FKO are present in either oscillator, and that there is a destructive interference effect for energies close to $E_0$.

![Figure 5.10](image)

**Figure 5.10** The light (red) and heavy (blue) hole Airy function oscillators contributing to the spectrum of sample MR358 from fig 5.9, and their sum (green).
In summary, adding a second Airy function expression has significantly improved the fit to the experimental PR. The values of $\alpha$ and $\Gamma$ given for all spectra are consistent with the PR originating from light and heavy hole band edges. In addition, the energies of the TDFFs for sample MR360 are physically meaningful, i.e., they are both below the $E_g$ energy gap.

5.5 Analysis of FKO from InP

The samples studied in this section are described in Appendix A, labelled MOQT1442 to MOQT1445. They were grown by MOVPE by P. Thijs. The structures consist of either a single or a pair of strained InGaAs quantum wells, with InP barriers grown on InP substrates. The composition of the InGaAs wells varies between samples, yielding different strains in the quantum well layer. The nominal structures of the four samples are as follows:

(a) MOQT1442 is a pair of $\text{In}_{0.70}\text{Ga}_{0.30}\text{As}$ (compressive strain) wells
(b) MOQT1444 is a pair of $\text{In}_{0.60}\text{Ga}_{0.40}\text{As}$ (compressive strain) wells
(c) MOQT1443 is a pair of $\text{In}_{0.50}\text{Ga}_{0.50}\text{As}$ (unstrained) wells
(d) MOQT1445 is a single $\text{In}_{0.20}\text{Ga}_{0.80}\text{As}$ (tensile strain) well.

The InP barriers consist of an undoped spacer layer next to the well, and a p-type layer, similar to the series studied in the previous section. The samples were originally grown to investigate hole masses in transport measurements. PR was measured in the energy range of the InP $E_g$ and spin split-off $E_g+\Delta_0$ critical point transitions, and the spectra are shown in figure 5.11.

The spectra appear to consist of a dominant feature from the $E_g$ transition, and a smaller feature from the $E_g+\Delta_0$ transition. From the literature, the energy gaps of these transitions are expected to be 1.349 eV and 1.472 eV respectively (Lahtinen and Tuomi (1985)), and these energies are shown as arrows in figure 5.11. Weak features at about 1.25 eV are observed in the PR of samples MOQT1443 to MOQT1445. These are most likely to be quantum well transitions. Indeed, quantum well transitions are observed for energies below those shown in figure 5.11, and these are studied in chapter 6.

The modulus spectra for all four samples, calculated with a Kramers-Kronig transformation (see chapter 1), are also shown in figure 5.11. A peak below the $E_g$ bandgap is observed for some of the spectra. This is consistent with below bandgap features observed in PR and ER of GaAs, InP, and InGaAs (Sydor et al. (1989) and Estrera et al. (1994)), where they were attributed to excitonic effects. The features in the modulus spectra were examined closely, and where possible peaks near the expected bandgap energies are assigned to the critical points. The energies of these peaks are shown in table 5.7. It should be emphasised that these energies deduced from the modulus spectra are only crude guesses of the actual transition energies.

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Figure 5.11 PR spectra (blue circles) and modulus spectra (green lines) in the energy range of the InP $E_0$ and $E_0 + \Delta_0$ critical point transitions for samples MOQT1442 to MOQT1445. The numbered extrema correspond to the values of $n$ in the asymptotic expression. The accepted energy gaps of the InP $E_0$ and $E_0 + \Delta_0$ critical point transitions are shown as arrows. Spectra are offset for clarity.
Table 5.7 Possible transition energies extracted from the modulus spectra for the energy range of the $E_q$ and $E_q + \Delta_q$ critical point transitions in InP for samples MOQT1442 to MOQT1445.

### 5.5.1 Asymptotic Analysis of the FKO

As was done for the InGaAsP FKO, the alternative asymptotic expression is applied to the four spectra in figure 5.11. When using this expression, it is assumed that the phase is known, but the energy gap is not known. The choice of extrema in this analysis is crucial, but assigning numbers to the extrema of the InP FKO is more difficult than in the study of InGaAsP FKO, because the FKO of the $E_q$ and $E_q + \Delta_q$ transitions overlay and interfere with each other. This is particularly severe for MOQT1445, where no distinct FKO can be identified. Consequently, no asymptotic analysis was performed for this sample. The integers $n_i$ chosen for the remaining three samples, correspond to the numbered extrema in figure 5.11. The $E_q$ critical point is three dimensional, so the phase used in the asymptotic expression is $\Phi = -\pi/2$ radians ($270^\circ$) (equation 5.5). Plots of $E_n$ vs $F_n$ for samples MOQT1442 to MOQT1444 are shown as circles in figure 5.12. The lines in the figure are linear regressions to the circles, and the values of the intercept ($E_0^0$) and gradient ($\eta_0$) found from the regression are shown in table 5.8. The $E_q$ energy gaps found from the analysis agree well with the accepted value (1.349 eV). Some of the FKO extrema in the spectrum of sample MOQT1444 are greater in energy than the expected $E_q + \Delta_q$ transition energy. Thus, it is possible that these FKO originate from the split-off band transition. This possibility warrants a more detailed investigation. The asymptotic analysis described above was also performed for sample MOQT1444 using only the extrema labelled 7 to 14 in figure 5.11, but renumbered 1 to 8. This plot of $E_n$ vs $F_n$ is shown in figure 5.12 as squares, and the results of the linear regression to the plot are shown in table 5.8. The $E_q + \Delta_q$ transition energy from this analysis agrees well with the accepted value (1.472 eV).

The InP hole masses used to calculate the values for the electric fields in table 5.8 are those calculated by Lawaetz (1971); $m_{h_\text{cr}} = 0.85 m_n$, $m_{h_\text{cr}} = 0.089 m_n$, $m_{h_\text{cr}} = 0.17 m_0$. The InP electron mass used is that calculated by Bowers (1969) and also by Palik and Wallis (1961); $m_e = 0.077 m_0$. 

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_q &lt; E_0$ (eV)</th>
<th>$E_0$ (eV)</th>
<th>$E_0 + \Delta_0$ (eV)</th>
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<tbody>
<tr>
<td>MOQT1442</td>
<td>1.340</td>
<td>1.350</td>
<td>1.453</td>
</tr>
<tr>
<td>MOQT1444</td>
<td>1.354</td>
<td>1.354</td>
<td>1.446</td>
</tr>
<tr>
<td>MOQT1443</td>
<td>1.339</td>
<td>1.360</td>
<td>1.436</td>
</tr>
<tr>
<td>MOQT1445</td>
<td>1.364</td>
<td>1.364</td>
<td>1.446</td>
</tr>
</tbody>
</table>
Figure 5.12 The alternative asymptotic FKO plots from the spectra of samples MOQT1442 to MOQT1444 shown in figure 5.11, as described by equation 5.3 (circles). The solid lines are linear regressions through the symbols, and the parameters from the regression are shown in table 5.8. The alternative asymptotic FKO plot for sample MOQT1444, found by assuming that the eight higher energy extrema originate from the split-off band transition, is shown as squares.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intercept E₀ (eV)</th>
<th>Gradient ℏθ (eV)</th>
<th>Field₉₉ (kV/cm)</th>
<th>Field₉₈ (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOQT1442</td>
<td>1.348±0.0027</td>
<td>0.0140±0.0007</td>
<td>22.4</td>
<td>17.2</td>
</tr>
<tr>
<td>MOQT1444</td>
<td>1.359±0.0027</td>
<td>0.0232±0.0001</td>
<td>47.8</td>
<td>36.7</td>
</tr>
<tr>
<td>MOQT1443</td>
<td>1.355±0.0027</td>
<td>0.0163±0.0006</td>
<td>28.1</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Table 5.8 Results of the alternative asymptotic analysis of the FKO from the InP spectra shown in figure 5.11. The plots of E₉ vs Fₖ are shown in figure 5.12. The gradients and intercepts are given by linear regressions, and the errors are standard errors. The electron and hole masses used to calculate the electric field values are given in the text. The alternative analysis for the E₀+Δ₀ transition for sample MOQT1444 was performed using the extrema labelled 7 to 14 in figure 5.11, but renumbered 1 to 8.
The energy of the $E_g$ critical point transition in InP is well known, so it makes more sense to use the first asymptotic expression described by equation 5.2. This assumes that the energy gap is known, but the phase is not. The InP $E_g$ critical point energy (1.349eV) was used in equation 5.2, and the corresponding plots of $(E-E_g)^2$ vs $n$ are shown as circles in figure 5.13. The linear regressions to the circles are shown as lines in the figure, and the results from the regressions are shown in table 5.9. The extrema labelled 7 to 14 for MOQT1444 in figure 5.11 are again used in the analysis for the $E_g+\Delta_0$ transition. This plot is shown as squares in figure 5.13, and the results from the linear regression are shown in table 5.9.

Surprisingly, the phases found from this analysis (table 5.9), which assumes that the phase is unknown, are close to those expected for a three dimensional critical point ($270^\circ$ (-71/2 radians)). Also, the energies found from the alternative analysis (table 5.10), where the energy is unknown, are close to the expected $E_g$ critical point transition energy (1.349eV). When the FKO in the spectrum from sample MOQT1444 are assumed to originate from the $E_g$ transition, the value of $h0$, and consequently the field, is much larger than that found for samples MOQT1442 and MOQT1443. If the transition is assumed to originate from the $E_g+\Delta_0$ transition, then the resulting field value is consistent with the fields found for samples MOQT1442 and MOQT1443. Therefore, it is most likely that the FKO at energies higher than the $E_g+\Delta_0$ critical point transition originate from this transition for MOQT1444, and not from $E_g$.

![Figure 5.13 Asymptotic FKO plots from the spectra of samples MOQT1442 to MOQT1444 shown in figure 5.11, as described by equation 5.2 (circles). The solid lines are results of linear regressions through the symbols, and the parameters from the regressions are shown in table 5.9. The asymptotic FKO plot for sample MOQT1444, assuming that the extrema originate from the split-off band transition, is shown as squares.](image)
Table 5.9 Results of the asymptotic analysis of the FKO from the InP spectra shown in figure 5.11. The plots of \((E_n - E_0) vs n\) are shown in figure 5.13. The gradients and intercepts are given by a linear regression, and the errors are standard errors. The electron and hole masses used to calculate the electric field values are given in the text. The analysis for the \(E_0 + \Delta_0\) transition for sample MOQT1444 was performed using the extrema labelled 7 to 14 in figure 5.11, but renumbered 1 to 8.

In summary, two methods of asymptotic analysis have been applied to the InP FKO originating from the \(E_0\) and \(E_0 + \Delta_0\) critical point transitions. There is good agreement between the two methods, despite the difficulties that arise due to the overlap of the features from the two transitions. There is some uncertainty as to whether the higher energy FKO originate from the \(E_0\) or \(E_0 + \Delta_0\) transitions for sample MOQT1444, but from the deduced field values it is most likely that the oscillations originate from the \(E_0 + \Delta_0\) transition.

### 5.5.2 Airy Function Analysis of the FKO

The Airy function analysis of the FKO from InGaAsP presented in section 5.4, was initiated by fitting the FKO with the simplest model i.e. a single Airy function expression. It was found, however, that the best fit for InGaAsP was achieved using two Airy function expressions. Not only was this fit visually better, but the parameters found from the fits agreed well with the assumption that the spectra originate from light and heavy hole bands. The InP FKO observed in the PR spectra shown in this chapter were also fitted with two Airy function expressions. In the energy range of the InP spectra, two energy transitions are expected; \(E_0\) and \(E_0 + \Delta_0\). So in this case, three Airy function expressions are required to fit the spectra, corresponding to the light, heavy and spin split-off holes. A feature below the \(E_0\) transition energy was observed in the modulus spectra of samples MOQT1442 and MOQT1443 (figure 5.11). The presence of a below bandgap feature in all spectra became apparent when fitting, in that the spectra could only be fitted with three Airy function expressions if a TDFF describing this feature was included. Consequently, all four spectra were fitted using one TDFF and three Airy function expressions with energy independent
broadness. The spectra were fitted for energies greater than 1.3 eV in order to exclude any possible quantum well transitions. The experimental and fitted spectra are shown in figure 5.14, and the values of the parameters from the fits are shown in tables 5.10 and 5.11.

It can be seen from figure 5.14 that the fitted spectra agree very well with the experimental PR in the region of the transition energies. For energies greater than this, the fit agrees well with experiment for sample MOQT1442, but not for the other three samples. In particular, the high energy oscillations in the experimental spectrum of sample MOQT1444 are not present in the fitted spectrum.

The $E_g$ energy gaps for samples MOQT1442 to MOQT1444 are similar to those deduced from the asymptotic analysis. The variation in the fitted $E_g$ energy gap between samples MOQT1442 and MOQT1444 is 7 meV, and the variation in the $E_g + \Delta_0$ energy gap is 9 meV. The correlation between the electric field values found from each fit is considered to be important in the interpretation of the fits. With the exception of the spectrum from sample MOQT1445, the light and heavy hole electric fields agree well for each sample. In the case of the split-off holes, however, the electric field values are not consistent with the light and heavy hole values. This is significant, because the fits deteriorate for energies greater than the $E_g + \Delta_0$ transition. The value of the amplitude for the heavy holes is larger than that for the light holes, which is similar to the InGaAsP fits.

The InP spectra were also fitted using an exponential broadness term in the Airy function expressions. Adding this term had little effect on the fit or fitted parameters, as was the case for the InGaAsP FKO in section 5.4. Therefore the results are not presented here.

From the parameters in tables 5.10 and 5.11, and the spectra in figure 5.14, it appears that the Airy function fits match the experiment well near the $E_g$ energy gap, but at higher energies the fits are not as good. Also, the value for the $E_g + \Delta_0$ energy gap is lower than expected in each case. Problems while fitting the energy region between the $E_g$ and $E_g + \Delta_0$ in InP FKO were overcome by Estrera et al. (1994). They included a second TDFF below the $E_g + \Delta_0$ bandgap, and found that the fit was improved. When a second TDFF was added to the fit of the InP spectra in this work, it was found that the fit improved visually, but the parameters were similar to those found from the fit without the extra TDFF. It should also be mentioned that Estrera gave no clear physical explanation for including a TDFF below the $E_g + \Delta_0$ energy.

To show the contribution of the TDFF and three Airy function expressions to the fits, a breakdown of them for sample MOQT1443 is shown in figure 5.15. As found when fitting the InGaAsP FKO in the section 5.4 (figure 5.10), few FKO are present in the individual oscillators.

In summary, the FKO in PR spectra from InP have been successfully fitted near the $E_g$ and $E_g + \Delta_0$ critical point transition energies, using a TDFF to describe a feature below the $E_g$ bandgap, and three Airy function expressions to describe the light, heavy and split-off holes. There appear to be problems in fitting energies near the $E_g + \Delta_0$ transition energy in all spectra. Using an exponentially decaying broadness term, or an additional TDFF below the $E_g + \Delta_0$ bandgap energy does not significantly improve the fits.
Figure 5.14 Experimental (blue circles) and fitted (red lines) PR in the energy range of the InP $E_0$ and $E_0 + \Delta_0$ critical point transitions for samples MOQT1442 to MOQT1445. The fits were performed using three Airy function expressions and one TDFF below the $E_0$ transition. Spectra are offset for clarity.
### Table 5.10 Light and heavy hole parameters from the least squares fits of the InP FKO using one TDFF and three Airy function expressions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_0$</th>
<th>$\Delta_0$</th>
<th>$\Gamma$</th>
<th>$\phi$ (degrees)</th>
<th>$\eta_0$ (eV)</th>
<th>$F_{bh}$ (kV/cm)</th>
<th>$A$</th>
<th>$\Gamma$ (eV)</th>
<th>$\phi$ (degrees)</th>
<th>$\eta_0$ (eV)</th>
<th>$F_{bh}$ (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOQT 1442</td>
<td>1.355</td>
<td>0.0030</td>
<td>0.0168</td>
<td>38.1</td>
<td>0.0124</td>
<td>18.0</td>
<td>0.0013</td>
<td>0.0111</td>
<td>279.0</td>
<td>0.0175</td>
<td>24.0</td>
</tr>
<tr>
<td>MOQT 1444</td>
<td>1.362</td>
<td>0.0037</td>
<td>0.0227</td>
<td>173.6</td>
<td>0.0164</td>
<td>28.7</td>
<td>0.0036</td>
<td>0.0229</td>
<td>12.4</td>
<td>0.0200</td>
<td>29.3</td>
</tr>
<tr>
<td>MOQT 1443</td>
<td>1.356</td>
<td>0.0424</td>
<td>0.0199</td>
<td>351.6</td>
<td>0.0157</td>
<td>26.9</td>
<td>0.0174</td>
<td>0.0196</td>
<td>158.7</td>
<td>0.0187</td>
<td>26.5</td>
</tr>
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<td>36.9</td>
<td>0.0053</td>
<td>0.0144</td>
<td>336.1</td>
<td>0.0275</td>
<td>47.3</td>
</tr>
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</table>

### Table 5.11 Split off hole and TDFF parameters from the least squares fits of the InP FKO using one TDFF and three Airy function expressions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_0^d + \Delta_0^d$ (eV)</th>
<th>$A$</th>
<th>$\Gamma$ (eV)</th>
<th>$\phi$ (degrees)</th>
<th>$\eta_0$ (eV)</th>
<th>$F_{bh}$ (kV/cm)</th>
<th>$A$</th>
<th>$E_g$ (eV)</th>
<th>$\Gamma$ (eV)</th>
<th>$\phi$ (degrees)</th>
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<tr>
<td>MOQT 1442</td>
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<td>0.0482</td>
<td>0.0009</td>
<td>213.0</td>
<td>0.0250</td>
<td>46.6</td>
<td>18.73</td>
<td>1.337</td>
<td>0.0146</td>
<td>73.2</td>
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<tr>
<td>MOQT 1444</td>
<td>1.440</td>
<td>4.9809</td>
<td>0.0059</td>
<td>178.5</td>
<td>0.0164</td>
<td>24.8</td>
<td>14.86</td>
<td>1.340</td>
<td>0.0217</td>
<td>130.0</td>
</tr>
<tr>
<td>MOQT 1443</td>
<td>1.431</td>
<td>0.4660</td>
<td>0.0055</td>
<td>183.6</td>
<td>0.0203</td>
<td>34.1</td>
<td>6.88</td>
<td>1.331</td>
<td>0.0230</td>
<td>61.0</td>
</tr>
<tr>
<td>MOQT 1445</td>
<td>1.436</td>
<td>4.7436</td>
<td>0.0028</td>
<td>220.3</td>
<td>0.0257</td>
<td>48.6</td>
<td>5.00</td>
<td>1.337</td>
<td>0.0380</td>
<td>6.9</td>
</tr>
</tbody>
</table>
5.6 Conclusions and Future Work

Franz-Keldysh oscillations (FKO) have been observed in PR spectra of InGaAsP barriers from InGaAs/InGaAsP quantum wells with tensile strain. It is clear from the PR and modulus spectra that the composition of one of the samples differs significantly from the nominal value. Another anomaly in the spectra is that no quantum well transitions are observed for the three remaining samples. From these PR measurements, problems in the growth process have been revealed.

From asymptotic analysis of the FKO, it has been found that the magnitude of the electric field in the barrier is about 20kV/cm. When the FKO in the spectra from the InGaAsP barrier are fitted with a single Airy function expression, the period of the oscillations match the PR, but the experimental oscillations decay more rapidly than the fitted spectra. Introducing an energy dependent exponential broadness term for the single Airy function expression model has little effect on the fits. When two Airy function expressions with energy independent broadnesses were used in the fitting, the fitted spectra matched the experiment well. The values of the electro-optic energy $\delta \theta$ and broadness $\Gamma$ were consistent with the presence of light and heavy hole band edges. An exponential broadness was not required to attain a good fit. This is contrary to the observations of Estrera et. al. (1994), where the energy dependent broadness term was important.

FKO are also observed in the PR of InP barriers from InGaAs/InP quantum wells with compressive or tensile strain. The spectra consist of overlapping features from the $E_0$ and $E_0+\Delta_0$ critical point transitions. The FKO were analysed using two asymptotic expressions, where one assumes that the phase is known, and the other assumes that the energy gap is known. These two methods were consistent, and the electric field values found from them
were about 20kV/cm, similar to those observed for the InGaAsP layers.

The FKO from the InP layers were fitted with three Airy function expressions representing the light, heavy and spin split-off holes. In addition, a TDFF was required to describe a feature below the bandgap of the $E_0$ critical point transition. Using an energy dependent exponentially increasing broadness term did not significantly improve the fits. When an extra TDFF with energy below the bandgap of the $E_0 + \Delta_0$ critical point transition was added to the fits the fit was still not significantly improved.

It would be interesting to investigate from which interface, or interfaces, the FKO originate from. It is possible that the spectra consist of features from more than one interface. The origins of the FKO could be investigated by progressively etching away the layers, and measuring the PR between each etch, as done by Hughes et. al. (1995).

The most rigorous improvement to the Airy function expressions would be to include the theory reported by Bhattacharyya et. al. (1988). They proposed that electric fields are not modulated from the flatband condition, but that the field includes a dc component. To do this, the expression for $\Delta \varepsilon$ would have to include two terms; one for the electric field before modulation and one for the electric field after modulation. If this effect were included, it may be possible to fit the FKO with a single Airy function expression.
Chapter 6

Confined States in Strained III-V Quantum Wells.

In this chapter, the optical transitions between confined states in strained III-V quantum well structures are investigated using room temperature photoreflectance (PR). Transition energies deduced from fitting PR spectra of InGaAs/InGaAsP quantum wells, and InGaAs/InP quantum wells are presented. These energies are then compared with theoretical calculations of the confined states.

6.1 Introduction

As outlined in chapter 1, the number of applications of III-V materials are increasing, and the recent introduction of strain into layered structures has increased the scope of these materials even further. As new applications are realised, knowledge of the fundamental properties becomes of utmost importance. The main aim of this chapter is to investigate the properties of strained quantum well structures.

The quantum well structures investigated in this work consist of strained InGaAs layers. These are studied using two series of samples; the first with InGaAsP barriers, and the second with InP barriers. The first series of quantum wells have tensile strain, with strain varying from 0.6% to 1.5%, and the InGaAsP barriers are lattice matched to InP. The strain in the second series of samples varies between 1.2% compressive and 1.6% tensile. To investigate the properties of these quantum wells, the energies of transitions between quantum confined states in the wells are found using PR. These energies are then compared with a quantum well model in an attempt to match theory with experiment.

An important parameter in the match between the experimental and theoretical quantum well transitions is the offset of the bands between the barrier and the quantum well. Using PR to do this is not new; several authors (e.g. Hosea et. al. (1996)) have previously used modulation spectroscopy to determine the band offset between two materials. Little experimental work has been published in the literature concerning experimentally determined band offsets of strained materials, and one of the aims of this work is to determine the band offsets of strained InGaAs/InGaAsP and InGaAs/InP.

6.2 Theoretical Modelling of Quantum Well Transitions

Before presenting the photoreflectance of quantum wells, it is useful to begin this chapter with a description of the quantum well model. The model itself was not developed by the author, so only the essential information is collated here. The section continues with a brief review of band offsets. It is then concluded with a description of the method used to compare the confined transition energies found from PR with those given by the model.
6.2.1 Quantum Well Model

The model used in this chapter to analyse the optical transitions between confined states in quantum wells has been developed by Dr. M. Silver. The calculations are performed using a FORTRAN program QUAT95, which has been refined over several years by comparing the model with experimental results. The confined states are calculated using the effective mass formalism (Andreani et al. (1987)), with the bulk valence band described by a 3-band k.p Hamiltonian (O'Reilly (1989)). The conduction band confined states are assumed to be decoupled from the valence band states. This assumption is valid because of the large bandgap of the materials. Coupling between the light hole and spin orbit split-off band is included, but non-parabolicity effects are not. The excitonic binding energy is not considered in the model, but is believed to be included implicitly because the material parameters have been derived from a comparison with experimental results.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>InAs</th>
<th>GaAs</th>
<th>InP</th>
<th>GaP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant a (Å)</td>
<td>6.058</td>
<td>5.653</td>
<td>5.869</td>
<td>5.451</td>
</tr>
<tr>
<td>Bandgap $E_0$ (eV)</td>
<td>0.36</td>
<td>1.42</td>
<td>1.35</td>
<td>2.74</td>
</tr>
<tr>
<td>Spin-orbit splitting $\Delta_0$ (eV)</td>
<td>0.380</td>
<td>0.340</td>
<td>0.114</td>
<td>0.080</td>
</tr>
<tr>
<td>Electron mass $m_e/m_0$</td>
<td>0.0223</td>
<td>0.0665</td>
<td>0.079</td>
<td>0.17</td>
</tr>
<tr>
<td>Heavy hole mass $m_h/m_0$</td>
<td>0.342</td>
<td>0.382</td>
<td>0.56</td>
<td>0.79</td>
</tr>
<tr>
<td>Light hole mass $m_l/m_0$</td>
<td>0.0225</td>
<td>0.08</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>Valence band average $E_{va,av}$ (eV)</td>
<td>-6.68</td>
<td>-6.84</td>
<td>-7.04</td>
<td>-7.06</td>
</tr>
<tr>
<td>Valence band hydrostatic deformation  $a_v$ (eV)</td>
<td>1.00</td>
<td>1.16</td>
<td>1.27</td>
<td>1.7</td>
</tr>
<tr>
<td>Conduction band hydrostatic deformation $a_c$ (eV)</td>
<td>-5.88</td>
<td>-8.06</td>
<td>-6.18</td>
<td>-9.45</td>
</tr>
<tr>
<td>Elastic constant $C_{11}$ (10^{12} dyn cm^{-2})</td>
<td>0.83</td>
<td>1.18</td>
<td>1.62</td>
<td>1.41</td>
</tr>
<tr>
<td>Elastic constant $C_{12}$ (10^{12} dyn cm^{-2})</td>
<td>0.45</td>
<td>0.54</td>
<td>0.58</td>
<td>0.62</td>
</tr>
<tr>
<td>Shear deformation potential $b$ (eV)</td>
<td>-1.62</td>
<td>-1.53</td>
<td>-1.35</td>
<td>-1.35</td>
</tr>
<tr>
<td>Bandgap bowing (eV)</td>
<td>0.41 (InGaAs)</td>
<td>0.79 (GaInP)</td>
<td>0.28 (InPAs)</td>
<td>0.21 (GaPAs)</td>
</tr>
</tbody>
</table>

Table 6.1 Material parameters used to interpolate the InGaAs and InGaAsP parameters.

---

1Department of Physics, University of Surrey, Guildford, Surrey
The interpolation formulae used to map the binary compounds onto the ternary compounds, and the ternary compounds onto the quaternary compounds are given by Krijn (1991). The material parameters used in the program are shown in table 6.1. They are based on those given by Krijn (1991) and O'Reilly (1989), but the values of the bowing parameters and shear deformation potentials have recently been adjusted to match PR measurements (Rowland (1996)).

For quantum wells with finite well depths, allowed transitions between electron subbands (index m) and hole subbands (index n) obey the selection rule (m-n)=even. In certain circumstances, such as wavefunction mixing or the presence of electric fields (Shen et al. (1992)), this rule may be violated and 'forbidden' transitions with (m-n)=odd occur. Quantum well transitions between an electron state m, and a light hole or heavy hole state n will be subsequently denoted $h_m$ and $l_n$, respectively.

6.2.2 Band Offset

One of the most important parameters in the design and analysis of quantum well devices is the heterojunction band offset, which describes the lineup of the bands of two adjacent materials. Low dimensional structures are routinely used as devices, but there is still controversy over the values of the band offsets. It is possible to determine the band offsets indirectly by experiment. One of the aims of this work is to use PR to determine the band offset of the structures studied. This is achieved by considering the band offset as a variable when matching the experimental and theoretical quantum well transitions. The details of this method are described later. These experimentally determined band offsets are compared with those expected from the solid model theory (Van de Walle and Martin (1986)), using the interpolation parameters given in table 6.1.

There have been several definitions for the band offset published in the literature, so it is important to define the offset used in this work. The conduction band offset is defined as,

$$Q_c = \frac{\Delta E_c}{\Delta E_c + \Delta E_c^{hh}}$$  \hspace{1cm} (6.1)

where $\Delta E_c$ is the discontinuity in the conduction band between the two materials, and $\Delta E_c^{hh}$ is the discontinuity in the heavy hole valence band. The offset between two materials is shown schematically in figure 1.4.

Although band offsets cannot be measured directly, a number of experimental techniques have been used to deduce them. The values of band offsets reported in the literature for the materials studied in this work are reviewed here.

For the InGaAs/InP interface, much work on In$_{0.53}$Ga$_{0.47}$As layers which are lattice matched to InP has been published, but little on strained InGaAs layers. For lattice matched InGaAs, transport and optical techniques have been used to determine $Q_c$. The $Q_c$ values found using these techniques for unstrained In$_{0.53}$Ga$_{0.47}$As are summarised in table 6.2. There is much evidence that the value of the conduction band offset for the unstrained In$_{0.53}$Ga$_{0.47}$As/InP interface is about 0.40. To the author's knowledge, no values of $Q_c$ for strained InGaAs have previously been deduced from experiment.
The only experimental determination of the band offset for InGaAs/InGaAsP structures was performed on materials lattice matched to InP by Soucail et al. (1990a/1990b). They measured photoluminescence excitation spectroscopy of In$_{0.53}$Ga$_{0.47}$As/In$_{0.25}$Ga$_{0.75}$As$_{0.4}$P$_{0.6}$, grown by metal-organic chemical vapour deposition (MOCVD), and found the band offset $Q_c=0.43\pm0.02$.

<table>
<thead>
<tr>
<th>$Q_c$</th>
<th>Technique</th>
<th>Growth</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.87</td>
<td>Subnikov de Haas</td>
<td>MOCPE</td>
<td>Guldner et al. (1982)</td>
</tr>
<tr>
<td>0.39±0.01</td>
<td>Capacitance-Voltage</td>
<td>LPE</td>
<td>Forrest et al. (1984)</td>
</tr>
<tr>
<td>0.50</td>
<td>Absorption / PL</td>
<td>MBE</td>
<td>Temkin et al. (1985)</td>
</tr>
<tr>
<td>0.60</td>
<td>PLE</td>
<td>CBE</td>
<td>Sauer et al. (1986)</td>
</tr>
<tr>
<td>0.38</td>
<td>PL/PLE/ER/Photo-current</td>
<td>MOCVD</td>
<td>Skolnick et al. (1986)</td>
</tr>
<tr>
<td>0.42±0.02</td>
<td>Admittance Spectroscopy</td>
<td>MBE</td>
<td>Lang et al. (1987a/1987b)</td>
</tr>
<tr>
<td>0.38±0.03</td>
<td>Absorption</td>
<td>MOCVD</td>
<td>Skolnick et al. (1987)</td>
</tr>
<tr>
<td>0.45</td>
<td>Absorption / PL</td>
<td>MOCVD</td>
<td>Westland et al. (1987)</td>
</tr>
<tr>
<td>0.58</td>
<td>X-ray photoemission spectroscopy</td>
<td>MBE</td>
<td>Waldrop et al. (1989)</td>
</tr>
<tr>
<td>0.36±0.01</td>
<td>Electrochemical Capacitance-Voltage</td>
<td>LPE</td>
<td>Furtado et al. (1989)</td>
</tr>
<tr>
<td>0.36</td>
<td>Capacitance-Voltage</td>
<td>-----</td>
<td>Zachau et al. (1989)</td>
</tr>
<tr>
<td>0.43</td>
<td>X-ray photoemission spectroscopy</td>
<td>MBE</td>
<td>Waldrop et al. (1991)</td>
</tr>
</tbody>
</table>

Table 6.2 Values of the conduction band offset $Q_c$ for unstrained In$_{0.53}$Ga$_{0.47}$As grown on InP, found using various experimental techniques.

6.2.3 Comparison of Experiment with Theory

It seems appropriate at this point to describe the method used to compare experimental and theoretical quantum well transitions. It is well known that the material compositions and layer widths can vary from the nominal growth values. Therefore, these two parameters should be considered as variables in the quantum well model. As mentioned earlier in this chapter, the band offset is also an unknown parameter in the model.

The procedure for matching experiment with theory is as follows. The energies of the quantum well transitions are calculated as a function of the conduction band offset using
the nominal composition and quantum well width. These energies are compared with those found from the PR using a plot similar to that shown in figure 6.1. In this plot, the fitted energies are shown as blue horizontal lines, and the calculated energies are shown as red sloping lines. To obtain a match between the fitted and theoretical energies, the well composition and the well width are varied within reason until the intersection of each experimental and theoretical line occurs close to a single value of the band offset. Using this method, the match between experiment and theory can be judged by eye. The greatest weight can then be given to the match of the more dominant transitions in the PR spectra. Errors in well composition, well width and band offset are then given by the range of values for which the match between experiment and theory is considered reasonable.

![Figure 6.1](image)

**Figure 6.1** A plot showing the method used to match quantum well transition energies found from PR fitting (horizontal blue lines) with those calculated from the model (sloping red lines) for sample MR688 (see section 6.3). The vertical green line shows the choice of band offset.

### 6.3 Photorelectance of Strained InGaAs/In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ Quantum Wells

The quantum wells studied in this section were grown as a result of the PR measurements of samples MR358 to MR361 described in chapter 5. The PR of those samples revealed problems with the growth, and so a new series of four samples were grown. These are described in Appendix A, labelled MR688, MR744, MR742 and MR738, and were grown by metal-organic vapour phase epitaxy (MOVPE) by C. C. Button. The structures consist of a single 90Å wide InGaAs quantum well with tensile strain. The barriers are nominally In$_{0.77}$Ga$_{0.23}$As$_{0.19}$P$_{0.51}$ lattice matched to an InP substrate. The nominal composition and strain are as follows (a) MR688 In$_{0.32}$Ga$_{0.68}$As (1.47% tensile strain) (b)

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(a) EPSRC Facility for III-V Semiconductors, University of Sheffield, Sheffield

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MR744 In$_{0.35}$Ga$_{0.65}$As (1.27% tensile strain) (c) MR742 In$_{0.46}$Ga$_{0.54}$As (0.92% tensile strain) 
(d) MR738 In$_{0.45}$Ga$_{0.55}$As (0.58% tensile strain).

6.3.1 Experimental and Fitted Spectra

PR was measured in the energy range of the InGaAs quantum well transitions and the $E_g$ critical point transition of the InGaAsP barrier. In addition, photoluminescence (PL) was performed on the same spot on the sample and under the same conditions as the PR. The PR and PL measurements for each sample are shown in figures 6.2 to 6.5 as blue circles and green lines respectively. From these figures, the energy of the barrier transition in the PR spectra appears to be about 1.02eV for each sample. Two dominant quantum well transitions are observed in each spectrum, most likely to be the ground state light and heavy hole transitions. Two peaks are also observed in the PL spectra, and these appear to correspond in energy with the ground state light and heavy hole quantum well transitions observed in the PR. For sample MR738, the lower energy peak appears as a shoulder on the side of the main PL peak, and is therefore not clearly resolved in the PL, while the PR shows the two features as clearly separated. It is clear from the energies of the features in the PL and PR spectra that the ground state light and heavy hole transitions increase in energy as the Ga composition, and so the tensile strain, is increased.

It should be noted that the water vapour absorption features observed at about 0.9eV in the reflectance spectra measured using the InGaAs detector (see chapter 2) also appear in the PR spectra. This is a surprising result because such features are expected to be eliminated during the normalisation $AR/R$. This feature resulted in problems when least squares fitting the spectra, especially for the spectrum of sample MR744, where a quantum well transition peak occurs at about 0.9eV.

The PR spectra in figures 6.2 to 6.5 were fitted using the least squares routine described in chapter 1. The spectra were fitted with the minimum number of TDFF oscillators, and the value $n=3$ in equation 1.18 was used for each TDFF. For a more detailed description of fitting quantum well transitions, see chapter 1. The fitted spectra are shown as red lines in figures 6.2 to 6.5. These figures show that the fitted spectra agree well with the experiment. In order to clarify the influence of each TDFF on the overall fitted spectrum, a breakdown of the individual TDFF oscillators is shown for each sample in figures 6.2 to 6.5. The energies found from the fits to the PR for each spectrum are shown in tables 6.3 to 6.6. It can be seen from these tables, that for all four samples, the energies of the ground state quantum well transitions agree well with the energies estimated from the PL peaks.

When fitting the barrier region in the PR spectra of quantum well structures, it is often possible to use a single TDFF oscillator. Surprisingly, this could not be done for the InGaAsP barrier features observed here. This is unusual because transitions which do not exhibit clear FKO can usually be fitted with TDFFs. To fit the barrier feature, the results of fitting InGaAsP FKO spectra in the previous chapter must be considered. No FKO are observed in the barrier region of the PR for this series because the barriers are not doped, and so the electric fields at the barrier interfaces are smaller.
Figure 6.2 Experimental PL (green line) and PR (blue circles) spectra for sample MR688. Also shown is the fitted PR spectrum (red line), and its constituent TDFF oscillators. The strain shown in the label is the nominal value. Spectra are offset for clarity.
Figure 6.3 Experimental PL (green line) and PR (blue circles) spectra for sample MR744. Also shown is the fitted PR spectrum (red line), and its constituent TDFF oscillators. The strain shown in the label is the nominal value. Spectra are offset for clarity.
Figure 6.4 Experimental PL (green line) and PR (blue circles) spectra for sample MR742. Also shown is the fitted PR spectrum (red line), and its constituent TDFF oscillators. The strain shown in the label is the nominal value. Spectra are offset for clarity.
Figure 6.5 Experimental PL (green line) and PR (blue circles) spectra for sample MR738. Also shown is the fitted PR spectrum (red line), and its constituent TDFF oscillators. The strain shown in the label is the nominal value. Spectra are offset for clarity.
### Table 6.3 Quantum well transition energies from the PL, the PR fit, and the theoretical model for sample MR688. The nominal barrier composition is y=0.49. The theory values are those given by the best match with PR. The PR errors are given by the covariance matrix found from the least squares fit.

<table>
<thead>
<tr>
<th>Transition</th>
<th>PL (eV)</th>
<th>PR Fit (eV)</th>
<th>Theory (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_{11}$</td>
<td>0.848</td>
<td>0.845±0.001</td>
<td>0.848</td>
</tr>
<tr>
<td>$h_{11}$</td>
<td>0.922</td>
<td>0.922±0.001</td>
<td>0.919</td>
</tr>
<tr>
<td>$h_{12}$</td>
<td>--------</td>
<td>0.939</td>
<td></td>
</tr>
<tr>
<td>$l_{12}$</td>
<td>--------</td>
<td>0.956±0.007</td>
<td>0.951</td>
</tr>
<tr>
<td>$h_{13}$</td>
<td>--------</td>
<td>0.973±0.018</td>
<td>0.972</td>
</tr>
<tr>
<td>$h_{14}$</td>
<td>--------</td>
<td>1.012±0.012</td>
<td>1.014</td>
</tr>
<tr>
<td>Barrier</td>
<td>--------</td>
<td>1.029±0.002</td>
<td>(y=0.48)</td>
</tr>
</tbody>
</table>

### Table 6.4 Quantum well transition energies from the PL, the PR fit, and the theoretical model for sample MR744. The nominal barrier composition is y=0.49. The theory values are those given by the best match with PR. The PR errors are given by the covariance matrix found from the least squares fit.

<table>
<thead>
<tr>
<th>Transition</th>
<th>PL (eV)</th>
<th>PR Fit (eV)</th>
<th>Theory (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_{11}$</td>
<td>0.841</td>
<td>0.839±0.001</td>
<td>0.840</td>
</tr>
<tr>
<td>$h_{11}$</td>
<td>0.898</td>
<td>0.896±0.001</td>
<td>0.896</td>
</tr>
<tr>
<td>$h_{12}$</td>
<td>--------</td>
<td>0.918</td>
<td></td>
</tr>
<tr>
<td>$l_{12}$</td>
<td>--------</td>
<td>0.942</td>
<td></td>
</tr>
<tr>
<td>$h_{13}$</td>
<td>--------</td>
<td>0.954±0.004</td>
<td>0.952</td>
</tr>
<tr>
<td>$h_{14}$</td>
<td>--------</td>
<td>0.995</td>
<td></td>
</tr>
<tr>
<td>Barrier</td>
<td>--------</td>
<td>1.002±0.001</td>
<td>set at</td>
</tr>
</tbody>
</table>

### Table 6.5 Quantum well transition energies from the PL, the PR fit, and theoretical model for sample MR742. The nominal barrier composition is y=0.49. The theory values are those given by the best match with PR. The PR errors are given by the covariance matrix found from the least squares fit.

<table>
<thead>
<tr>
<th>Transition</th>
<th>PL (eV)</th>
<th>PR Fit (eV)</th>
<th>Theory (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_{11}$</td>
<td>0.836</td>
<td>0.832±0.001</td>
<td>0.834</td>
</tr>
<tr>
<td>$h_{11}$</td>
<td>0.869</td>
<td>0.876±0.004</td>
<td>0.876</td>
</tr>
<tr>
<td>$h_{12}$</td>
<td>--------</td>
<td>0.898</td>
<td></td>
</tr>
<tr>
<td>$h_{13}$</td>
<td>--------</td>
<td>0.935</td>
<td></td>
</tr>
<tr>
<td>$l_{12}$</td>
<td>--------</td>
<td>0.937</td>
<td></td>
</tr>
<tr>
<td>$h_{14}$</td>
<td>--------</td>
<td>0.982±0.008</td>
<td>0.983</td>
</tr>
<tr>
<td>Barrier</td>
<td>--------</td>
<td>1.020±0.003</td>
<td>(y=0.50)</td>
</tr>
</tbody>
</table>

### Table 6.6 Quantum well transition energies from the PL, the PR fit, and the theoretical model for sample MR738. The nominal barrier composition is y=0.49. The theory values are those given by the best match with PR. The PR errors are given by the covariance matrix found from the least squares fit.

<table>
<thead>
<tr>
<th>Transition</th>
<th>PL (eV)</th>
<th>PR Fit (eV)</th>
<th>Theory (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_{11}$</td>
<td>0.827</td>
<td>0.819±0.009</td>
<td>0.821</td>
</tr>
<tr>
<td>$h_{11}$</td>
<td>0.839</td>
<td>0.836±0.001</td>
<td>0.835</td>
</tr>
<tr>
<td>$h_{12}$</td>
<td>--------</td>
<td>0.859</td>
<td></td>
</tr>
<tr>
<td>$h_{13}$</td>
<td>--------</td>
<td>0.898</td>
<td></td>
</tr>
<tr>
<td>$l_{12}$</td>
<td>--------</td>
<td>0.921</td>
<td></td>
</tr>
<tr>
<td>$h_{14}$</td>
<td>--------</td>
<td>0.951</td>
<td></td>
</tr>
<tr>
<td>Barrier</td>
<td>--------</td>
<td>1.022±0.001</td>
<td>set at</td>
</tr>
</tbody>
</table>

(y=0.49)
For the PR spectra of InGaAsP barriers measured in chapter 5, it was found that the best fit was achieved when the effect of light and heavy holes was considered. Therefore, it is logical to assume that the barrier features in the InGaAsP spectra in this chapter also contain contributions from light and heavy holes. From these considerations, the barrier region in all four spectra were fitted with two Airy function expressions. If the electric field is small enough, then these expressions are approximated by TDFF oscillators. The barrier energies, and corresponding compositions y (see equation 5.19) found from the fits are shown in tables 6.3 to 6.6.

In summary, there is good agreement between quantum well transition energies found from PL measurements and those found from least squares fits to PR measurements. The compositions of the InGaAsP barriers deduced from fitting the spectra with two Airy function expressions agree well with the nominal compositions.

### 6.3.2 Comparison of Well Transitions with Theory

Now that the transition energies between confined electron and hole states have been determined from the PR spectra, the next stage is to compare these energies with those given by the quantum well model. The InGaAsP barrier $E_0$ transition energies are known from the fits to the barrier region of the PR. It is assumed that the barrier remains lattice matched to InP, and the composition is then given by equation 5.19. Using these barrier compositions, the energies from the quantum well model were compared with those from the PR, as described in section 6.2.3. The three variables in such an analysis are the quantum well composition, the well width and the band offset. The theoretical energies from the best match are shown in tables 6.3 to 6.6, where they are compared with the PR oscillator energies.

A more informative presentation of the best match between experiment and theory is to plot the theoretical energy vs PR fit energy. In such a plot, the points for a perfect match would lie on a straight line with slope equal to unity. Such plots are shown in figures 6.6 to 6.9, for the PR and model data shown in tables 6.3 to 6.6. It can be seen from the tables and figures that for all four samples, the values of the theoretical energies agree well with the fitted PR energies.

Most important in matching theory with experiment, are the values of well composition, well width and conduction band offset. These are shown along with the nominal values in table 6.7. For all four samples, the Ga compositions are close or identical to the nominal values, and the well widths are consistently greater than nominal. A curious result of this analysis is the band offsets deduced from the match between experiment and theory. The model solid theory predicts an offset of 0.32 for the least strained InGaAs well, decreasing to 0.14 for the well with the most tensile strain. A significant observation from this work, however, is that the offset varies little as the Ga composition, and so the strain, of the InGaAs layer changes.
Figure 6.6 Energies of the quantum well transitions calculated from the theoretical match with experiment, compared with the energies given by the fit to the PR for sample MR688. The strain given in the label is the deduced value.

Figure 6.7 Energies of the quantum well transitions calculated from the theoretical match with experiment, compared with the energies given by the fit to the PR for sample MR744. The strain given in the label is the deduced value.

Figure 6.8 Energies of the quantum well transitions calculated from the theoretical match with experiment, compared with the energies given by the fit to the PR for sample MR742. The strain given in the label is the deduced value.

Figure 6.9 Energies of the quantum well transitions calculated from the theoretical match with experiment, compared with the energies given by the fit to the PR for sample MR738. The strain given in the label is the deduced value.
Table 6.7 The nominal and deduced compositions and widths of the In$_{x}$Ga$_{1-x}$As quantum wells from the match of theoretical transition energies with those from the PR fits. Also shown are the conduction band offsets $Q_{c}$ given by this match, and those given by the solid model theory.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal $x$</th>
<th>Deduced $x$</th>
<th>Nominal width (Å)</th>
<th>Deduced width (Å)</th>
<th>Nominal tensile strain (%)</th>
<th>Deduced tensile strain (%)</th>
<th>Model $Q_{c}$</th>
<th>Deduced $Q_{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR688</td>
<td>0.68</td>
<td>0.68±0.01</td>
<td>90</td>
<td>100±5</td>
<td>1.47</td>
<td>1.47±0.07</td>
<td>0.14</td>
<td>0.07±0.05</td>
</tr>
<tr>
<td>MR744</td>
<td>0.65</td>
<td>0.65±0.01</td>
<td>90</td>
<td>97±5</td>
<td>1.27</td>
<td>1.27±0.07</td>
<td>0.17</td>
<td>0.06±0.05</td>
</tr>
<tr>
<td>MR742</td>
<td>0.60</td>
<td>0.62±0.01</td>
<td>90</td>
<td>98±5</td>
<td>0.92</td>
<td>1.06±0.07</td>
<td>0.25</td>
<td>0.06±0.05</td>
</tr>
<tr>
<td>MR738</td>
<td>0.55</td>
<td>0.56±0.01</td>
<td>90</td>
<td>97±5</td>
<td>0.58</td>
<td>0.64±0.07</td>
<td>0.32</td>
<td>0.06±0.05</td>
</tr>
</tbody>
</table>

An important result from the analysis described above is the variation of the light and heavy hole quantum well ground states, $l_{11}$ and $h_{11}$, with strain. The energies of the states given by the PR are shown as a function of the deduced strain in figure 6.10. On close examination of this figure, it appears that both $l_{11}$ and $h_{11}$ points lie on two straight lines. Therefore, a linear regression to both sets of points is also shown in figure 6.10. If both regression lines are extrapolated, they intersect at 0.42% tensile strain with an energy of 0.812eV.

![Figure 6.10](image)

Figure 6.10 The variation of the ground state $h_{11}$ (red) and $l_{11}$ (blue) quantum well transitions given by the PR. The strain is determined from the match of theory with experiment, and the error in strain is given by the error in the deduced well composition. The solid lines are linear regressions to the circles.

In summary the experimental PR energies have been compared with a theoretical
quantum well model, where the well composition, well width and conduction band offset are variables. From a match between experiment and theory, it has been found that the composition of the InGaAs layer is close to the nominal value for each sample, and that the well widths are between 7Å and 10Å greater than nominal. The most significant result however, is that the value of the conduction band offset given by the match does not change significantly with tensile strain, and has a value of about Qo ~0.06. This observation is contrary to the variation in band offset with tensile strain given by the solid model theory (0.14 to 0.32).

6.4 Photoreflectance of Strained InGaAs/InP Quantum Wells

The samples studied in this section were investigated in chapter 5, where the FKO of the InP Eg critical point transition in each PR spectrum was fitted using Airy function expressions. The four samples are described in Appendix A, labelled MOQT1442 to MOQT1445, and were grown by MOVPE by P. Thijs to investigate hole masses in transport measurements. They consist of either a single or a pair of strained InGaAs quantum wells, with InP barriers grown on InP substrates. The strain of the quantum well varies between samples by varying the composition. The nominal structures and strains of the four samples are as follows (a) MOQT1442 is a pair of InGaAs wells (1.15% compressive strain) (b) MOQT1444 is a pair of InGaAs wells (0.81% compressive strain) (c) MOQT1443 is a pair of InGaAs wells (unstrained) (d) MOQT1445 is a single InGaAs well (1.61% tensile strain). The InP barriers consist of an undoped spacer layer next to the well, and a Zn doped p-type layer.

6.4.1 Experimental and Fitted Spectra

As was done for the InGaAs/InGaAsP samples, PR and PL measurements were performed for all four samples at room temperature in the energy range of the InGaAs quantum well transitions. The PR measurements were performed 6 months prior to the PL, and so there may be some discrepancy between the position at which the PR and PL were measured. Also, at the time the PL was measured, no signal from sample MOQT1444 could be obtained. The PR and PL measurements for these samples are shown in figures 6.11 to 6.14. In contrast to the samples examined earlier, a single broad peak is observed in the PL. It is not possible to resolve the light and heavy hole transitions from the PL, whereas the PR shows these two transitions quite well resolved. The estimated energies of the PL peaks are shown in tables 6.8, 6.10 and 6.11. In all cases, this peak corresponds roughly in energy with the most prominent feature in the PR. If the PR spectra in figures 6.11 to 6.14 are examined, it can be seen that the spectra stop abruptly at the low energy end. The InGaAs detector response decreases rapidly for energies below about 0.8eV (see figure 2.2), and so the signal to noise ratio of R and AR also decreases. Consequently, any features in the spectra that occur below these energies cannot be measured reliably by the InGaAs detector.

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Figure 6.11 Experimental PL (green line) and PR (blue circles) spectra for sample MOQT1442. Also shown is the fitted PR spectrum (red line), and its constituent TDFF oscillators. The strain given in the label is the nominal value. Spectra are offset for clarity.
Figure 6.12 Experimental PR (blue circles) spectrum for sample MOQT1444. Also shown is the fitted PR spectrum (red line), and its constituent TDFF oscillators. The strain given in the label is the nominal value. Spectra are offset for clarity.
Figure 6.13 Experimental PL (green line) and PR (blue circles) spectra for sample MOQT1443. Also shown is the fitted PR spectrum (red line), and its constituent TDFF oscillators. The strain given in the label is the nominal value. Spectra are offset for clarity.
Figure 6.14 Experimental PL (green line) and PR (blue circles) spectra for sample MOQT1445. Also shown is the fitted PR spectrum (red line), and its constituent TDFF oscillators. The strain given in the label is the nominal value. Spectra are offset for clarity.
The PR spectrum from sample MOQT1445, in figure 6.14, is somewhat unusual in appearance, with multiple oscillations of roughly equal amplitude. These features do not resemble any quantum well transitions published in the literature. The well is wide, and so many transitions are expected from this sample, and it is clear that the PR spectrum must be made up of many transitions. What is unusual, however, is that the higher order transitions are not apparently weaker than the ground state ones. The reason for this unusual result is not clear at this time.

The PR spectra in figures 6.11 to 6.14 were fitted using the least squares routine described in chapter 1. The value \( n = 3 \) was used for each TDFF, and the spectra were fitted with the least number of TDFFs possible. Analysis of the barrier was shown in chapter 5, but the accepted value of the InP \( E_g \) transition was used for all four samples (1.349 eV). It is important when considering PR fits to plot the individual oscillators that make up the spectra, so a breakdown of the fitted oscillators for each spectrum is shown in figures 6.11 to 6.14, and the energies of the oscillators are shown in tables 6.8 to 6.11. An unexpected observation from the PL and PR energies should be noted here; the lowest energy found from the PR fit does not correspond with the energy from the PL for sample MOQT1442. This is a peculiar result, and is discussed in more detail later.

<table>
<thead>
<tr>
<th>Transition</th>
<th>PL (eV)</th>
<th>PR Fit (eV)</th>
<th>Theory (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( h_{11} )</td>
<td>0.793</td>
<td>0.793±0.001</td>
<td>0.794</td>
</tr>
<tr>
<td>( l_{11} )</td>
<td>(-)</td>
<td>0.919±0.001</td>
<td>0.927</td>
</tr>
<tr>
<td>( h_{12} )</td>
<td>(-)</td>
<td>0.980±0.004</td>
<td>0.981</td>
</tr>
<tr>
<td>( l_{12} )</td>
<td>(-)</td>
<td>(-)</td>
<td>1.081</td>
</tr>
<tr>
<td>( l_{13} )</td>
<td>(-)</td>
<td>1.082±0.006</td>
<td>1.081</td>
</tr>
<tr>
<td>( l_{14} )</td>
<td>(-)</td>
<td>1.081</td>
<td>1.081</td>
</tr>
</tbody>
</table>

**Table 6.8** Quantum well transition energies from the PL, the PR fit, and the theoretical match for sample MOQT1442. The theory values are those given by the best match with experiment. The PR errors are given by the covariance matrix from the least squares fit.

<table>
<thead>
<tr>
<th>Transition</th>
<th>PR Fit (eV)</th>
<th>Theory (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( h_{11} )</td>
<td>0.773±0.001</td>
<td>(-)</td>
</tr>
<tr>
<td>( h_{12} )</td>
<td>0.889±0.010</td>
<td>0.887</td>
</tr>
<tr>
<td>( l_{11} )</td>
<td>(-)</td>
<td>0.891</td>
</tr>
<tr>
<td>( h_{13} )</td>
<td>1.017±0.001</td>
<td>1.032</td>
</tr>
<tr>
<td>( l_{12} )</td>
<td>1.070±0.004</td>
<td>1.063</td>
</tr>
<tr>
<td>( l_{13}/l_{14} )</td>
<td>1.123±0.034</td>
<td>1.120</td>
</tr>
<tr>
<td>(-)</td>
<td>1.167±0.004</td>
<td>(-)</td>
</tr>
</tbody>
</table>

**Table 6.9** Quantum well transition energies from the PR fit and the theoretical model for sample MOQT1444. The theory values are those given by the best match with experiment. The PR errors are given by the covariance matrix from the least squares fit.
<table>
<thead>
<tr>
<th>Transition</th>
<th>PL (eV)</th>
<th>PR Fit (eV)</th>
<th>Theory (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h₁₁</td>
<td>0.789</td>
<td>0.813±0.001</td>
<td>0.813</td>
</tr>
<tr>
<td>l₁₁</td>
<td>0.829±0.002</td>
<td>0.852</td>
<td></td>
</tr>
<tr>
<td>h₁₂</td>
<td>0.928±0.001</td>
<td>0.921</td>
<td></td>
</tr>
<tr>
<td>h₁₃</td>
<td>0.949±0.001</td>
<td>0.954</td>
<td></td>
</tr>
<tr>
<td>l₁₂</td>
<td>0.982</td>
<td>0.994</td>
<td></td>
</tr>
<tr>
<td>l₁₃</td>
<td>1.029±0.001</td>
<td>1.015</td>
<td></td>
</tr>
<tr>
<td>h₂₃</td>
<td>1.064±0.001</td>
<td>1.063</td>
<td></td>
</tr>
<tr>
<td>l₁₄</td>
<td>1.161±0.001</td>
<td>1.154</td>
<td></td>
</tr>
<tr>
<td>h₂₄</td>
<td>1.156</td>
<td>1.244</td>
<td></td>
</tr>
<tr>
<td>l₂₃</td>
<td>1.295</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.10 Quantum well transition energies from the PL, the PR fit, and the theoretical model for sample MOQT1443. The theory values are those given by the best match with experiment. The PR errors are given by the covariance matrix from the least squares fit.

<table>
<thead>
<tr>
<th>Transition</th>
<th>PL (eV)</th>
<th>PR Fit (eV)</th>
<th>Theory (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>l₁₁</td>
<td>0.803</td>
<td>0.833±0.001</td>
<td>0.835</td>
</tr>
<tr>
<td>l₂₁</td>
<td>1.029±0.001</td>
<td>1.015</td>
<td></td>
</tr>
<tr>
<td>l₁₂</td>
<td>0.924±0.001</td>
<td>0.917</td>
<td></td>
</tr>
<tr>
<td>h₁₁</td>
<td>0.978±0.001</td>
<td>0.978</td>
<td></td>
</tr>
<tr>
<td>l₂₂</td>
<td>0.974</td>
<td>0.964</td>
<td></td>
</tr>
<tr>
<td>h₂₂</td>
<td>1.030±0.003</td>
<td>1.026</td>
<td></td>
</tr>
<tr>
<td>h₂₃</td>
<td>1.042±0.002</td>
<td>1.039</td>
<td></td>
</tr>
<tr>
<td>l₂₄</td>
<td>1.074</td>
<td>1.121</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.11 Quantum well transition energies from the PL, the PR fit, and the theoretical model for sample MOQT1445. The theory values are those given by the best match with experiment. The PR errors are given by the covariance matrix from the least squares fit.
In summary, the energies of transitions between confined electron and hole states in strained InGaAs quantum wells with InP barriers have been found from PR and PL measurements. For sample MOQT1442, the PL peak does not correspond in energy with the lowest energy TDFF from the PR fit. This is a surprising result.

### 6.4.2 Comparison of Well Transitions with Theory

The next stage in the analysis is to compare the transition energies found from the PR with those given by the theoretical model. This was done as described in section 6.2.3. Starting with the nominal parameters, the well compositions, well widths and conduction band offsets were varied until the transition energies from the theoretical model matched as well as possible those from the PR fits. When trying to match these energies, it became apparent that the lowest energy transitions from the PR fits are about 25 meV below those predicted by the model using the nominal well composition and well width. This difference is too great to be explained in terms of likely discrepancies between the nominal and growth well composition and well width.

To ascertain whether the well compositions and well widths vary significantly from the nominal values, double-crystal X-ray diffraction measurements (DCXRD) were performed on sample MOQT1445 by Mr. H. Colson. This sample is the only one in the series in which the quantum well layer is wide enough to be analysed using DCXRD. The measured X-ray plot, and the simulated X-ray data are shown in figure 6.15. The composition and width of the In$_{1-x}$Ga$_x$As quantum well deduced from the match between the simulation and experiment are $x=0.67\pm0.05$ and $160\pm10\text{Å}$. Thus, the X-ray measurement shows that for sample MOQT1445, the well composition and well width are close to the nominal values ($x=0.70$ and width=160Å). This gives confidence in the expectation that the well compositions and well widths for the other three samples are close to the nominal values.

![Experimental and simulated DCXRD spectra for sample MOQT1445.](image)

**Figure 6.15** Experimental (red) and simulated (blue) DCXRD spectra for sample MOQT1445. The results for the In$_{1-x}$Ga$_x$As layer given by the simulation are $x=0.67\pm0.005$ and well width=160±10Å.
Given the results of the X-ray analysis and the theoretical predictions of the quantum well transition energies, it is obvious that the lowest energy TDFF in all four PR spectra is lower in energy than any predicted quantum well transition. There are several possible explanations for this. Two of these are associated with the limitations of the apparatus. The energies of the features are close to the limit of the light filter positioned in front of the detector. This means that second order grating reflections may be detected. In addition to this, the detector response is poor at these energies, decreasing rapidly below 0.8eV. It is therefore possible that the anomalous features observed in the PR spectra are due to a feature in detector response, second order grating reflections, or a combination of both.

For samples MOQT1443 and MOQT1445, the estimated energy of the PL peak is close to the lowest energy TDFF. Thus, it is unlikely that this feature originates from a limitation of the apparatus. A TDFF oscillator lower in energy than the expected ground state transition for an InGaAs quantum well lattice matched to InP was reported by Airaksinen et al. (1990). Their lowest energy TDFF was about 20meV below the expected heavy hole ground state transition, but they offered no explanation as to its origin. This is consistent with those found here, which are about 25meV below the lowest expected quantum well transitions. Features about 10meV below the bandgap of bulk InGaAs have previously been observed by Estrera et al. (1994) when fitting FKO from InGaAs, and by Gaskill et al. (1990) when investigating the strain dependence of the bandgap in InGaAs. Both authors attributed the feature below the bandgap to excitons. Indeed, such features have been observed in the room temperature PR spectra of several materials, including the InP PR in chapter 5, where features were observed between 8meV and 25meV below the E\text{g} critical point transition. It is therefore possible that the features observed in this work are due to excitons. In general, the energy shifts observed in this case are slightly larger than the energy shifts previously attributed to excitons.

A further explanation of the anomalous feature in the PR could lie in the presence of Zn doping in the InP barrier layers. It is possible that Zn has migrated into the InGaAs well layer and formed a shallow impurity state. It is known that Zn forms an acceptor level about 28meV above the valence band maximum (Bhattacharya et al. (1983)), and this seems to be the most likely explanation for the feature observed about 25meV below the predicted ground state quantum well transition energy for each sample.

Assuming that the lowest energy TDFF oscillator is not a quantum well transition, the energies from the PR fits were matched with those from the quantum well model, as described in section 6.2.3. It was found that if this assumption was made, a good agreement between experiment and theory was achieved. The theoretical energies found from the match are shown in tables 6.8 to 6.11, and the energies from the PR fits and the model are compared in figures 6.16 to 6.19.

It is common to observe forbidden transitions in PR measurements, as described earlier in this chapter (section 6.2.1). There is concern, however, that for samples MOQT1443 and MOQT1445, some forbidden transitions appear to be observed, whereas some allowed transitions are not. For example, the $h_{32}$ transition is not observed for MOQT1443, but $h_{33}$ is observed (table 6.10), and $l_{22}/l_{33}$ transitions are not observed for MOQT1445, while $l_{23}$ is observed (table 6.11). This perhaps casts doubt on the validity of the match between experiment and theory for these two samples. It may be significant that there is doubt in the interpretation of the spectra with the most quantum well transitions. There is still considerable doubt as to the reasons why certain transitions are observed in PR spectra of
quantum wells, yet others are not. The results of the present work indicate that considerable effort has still to be made before the PR of quantum wells can be fully understood.

**Figure 6.16** Energies of the quantum well transitions calculated from the theoretical match compared with the energies given by the fit to the PR for sample MOQT1442. The strain given in the label is the deduced value.

**Figure 6.17** Energies of the quantum well transitions calculated from the theoretical match compared with the energies given by the fit to the PR for sample MOQT1444. The strain given in the label is the deduced value.

**Figure 6.18** Energies of the quantum well transitions calculated from the theoretical match compared with the energies given by the fit to the PR for sample MOQT1443. The strain given in the label is the deduced value.

**Figure 6.19** Energies of the quantum well transitions calculated from the theoretical match compared with the energies given by the fit to the PR for sample MOQT1445. The strain given in the label is the deduced value.
Despite the difficulties that have arisen during the investigation of these samples, the values of the In$_{1-x}$Ga$_x$As quantum well compositions and widths deduced from the best match of experiment with theory are shown in table 6.12. It can be seen from the table that the deduced compositions are similar or identical to the nominal values. Also, the deduced well widths are identical to the nominal values for samples MOQT1442 and MOQT1443, but slightly greater than nominal for MOQT1444 and MOQT1445.

The values of the conduction band offsets deduced from the match between experiment and theory, and those given by the solid model theory are also shown in table 6.12. The deduced values agree well with those given by the model, except the offset of sample MOQT1442, which is slightly lower than that given by the model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal $x$</th>
<th>Deduced $x$</th>
<th>Nominal width (Å)</th>
<th>Deduced width (Å)</th>
<th>Nominal strain (%)</th>
<th>Deduced strain (%)</th>
<th>Model $Q_c$ (Å)</th>
<th>Deduced $Q_c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOQT1442</td>
<td>0.30</td>
<td>0.27±0.01</td>
<td>30</td>
<td>30±5</td>
<td>1.15</td>
<td>1.35±0.07</td>
<td>0.40</td>
<td>0.25±0.05</td>
</tr>
<tr>
<td>MOQT1444</td>
<td>0.35</td>
<td>0.35±0.01</td>
<td>45</td>
<td>47±5</td>
<td>0.81</td>
<td>0.81±0.07</td>
<td>0.39</td>
<td>0.39±0.05</td>
</tr>
<tr>
<td>MOQT1443</td>
<td>0.47</td>
<td>0.46±0.01</td>
<td>75</td>
<td>75±5</td>
<td>0.00</td>
<td>0.05±0.07</td>
<td>0.38</td>
<td>0.34±0.05</td>
</tr>
<tr>
<td>MOQT1445</td>
<td>0.70</td>
<td>0.67±0.01</td>
<td>160</td>
<td>167±5</td>
<td>-1.61</td>
<td>-1.40±0.07</td>
<td>0.31</td>
<td>0.28±0.05</td>
</tr>
</tbody>
</table>

Table 6.12 The nominal and deduced compositions and widths of the In$_{1-x}$Ga$_x$As quantum wells from the best match of theoretical transition energies with those from the PR fits. Also shown are the conduction band offsets $Q_c$ given by this match, and those given by the solid model theory. Tensile strain is denoted as a negative value.

In summary, energies from the fits to the PR spectra have been compared with the theoretical model. It is clear from this comparison that the lowest energy TDFF does not correspond to a quantum well transition. The most likely explanation for this feature is concluded to be a Zn impurity state within the well. Despite these difficulties, a good match with the quantum well model has been achieved for each sample. The well compositions and widths found from the match agree well with the nominal values. Also, the conduction band offsets found from this match agree with those found from the solid model theory.

6.5 Conclusions and Future Work

Photoreflectance (PR) and Photoluminescence (PL) measurements have been performed on samples with tensile strained InGaAs quantum wells, and InGaAsP barriers lattice matched to InP. The ground state light and heavy hole transitions were observed as two peaks in the PL spectra, which corresponded in energy with the main features in the PR spectra. The energy range corresponding to the $E_0$ critical point transition of the InGaAsP
barriers were successfully fitted with two Airy function expressions. The critical point
energies found from the barrier fits agree well with the energies expected from the nominal
compositions. The PR spectra were fitted with TDFF oscillators to determine the quantum
well transition energies for each sample. Transition energies calculated using a quantum
well model agree well with the experimental energies for well compositions close to the
nominal, and well widths about 8Å greater than nominal. The band offsets deduced from
the match with theory vary little with tensile strain ($Q_s \sim 0.06$). This is the first experimental
determination of the band offset for strained InGaAs/InGaAsP interfaces. These deduced
band offsets disagree with those calculated from the solid model theory.

If more InGaAs/InGaAsP samples were available, with compressive as well as tensile
strain, a complete picture of the variation of the ground state transitions, and the band offset
with strain could be found. This characterisation would be useful in the design of
semiconductor devices in the future.

PR and PL measurements have been performed on samples with compressive, tensile
and unstrained InGaAs quantum wells with InP barriers. One broad peak is observed in the
PL spectra, and this corresponds roughly in energy with a feature in the PR spectra. During
analysis, a feature was identified in the PR at an energy lower than the expected ground
state transition. The most likely explanation of this feature is the presence of a Zn acceptor
level in the InGaAs quantum well, due to migration of Zn from the p-doped InP barriers.
This effect should be investigated further. The transition energies given by PR fits match
those given by the quantum well model if the lowest energy TDFF is assumed not to be
associated with a quantum well transition. The band offsets found from this match vary
between 0.25 and 0.39. This is the first experimental determination of the band offsets in
strained InGaAs/InP. The values for the band offsets agree well with previous measurements
for unstrained InGaAs/InP interfaces, and also agree with those given by the solid model
theory.
Appendix A

Sample Structures

The nominal structures of the samples studied in this thesis are listed in this appendix.

(1) Si/SiGe Layers

These samples are studied in chapter 3, and were grown at the DRA, Malvern in 1995. They were grown by low pressure vapour phase epitaxy (LPVPE) for spectroscopic ellipsometry measurements, with a view to using SE for growth control in the VPE reactor.

\( \begin{array}{|c|c|}\hline
600\text{Å} & \text{Si cap} \\
580\text{Å} & \text{Si}_{0.827}\text{Ge}_{0.173} \\
500\text{Å} & \text{Si buffer} \\
600\text{Å} & \text{Si substrate} \\
\hline
\end{array} \)

\( \begin{array}{|c|c|}\hline
600\text{Å} & \text{Si cap} \\
480\text{Å} & \text{Si}_{0.76}\text{Ge}_{0.236} \\
500\text{Å} & \text{Si buffer} \\
500\text{Å} & \text{Si substrate} \\
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\end{array} \)

(2) Si/SiGe Quantum Wells

These samples are studied in chapter 4, and were grown by LPVPE at the DRA, Malvern between 1994 and 1996. Some were grown to study the effects of thin SiGe layers on spectroscopic ellipsometry measurements, and others were grown for this work.

\( \begin{array}{|c|c|}\hline
20\text{Å} & \text{Si cap} \\
400\text{Å} & \text{Si x10 barrier} \\
30\text{Å} & \text{Si}_{0.89}\text{Ge}_{0.30} \times 10 \text{ quantum well} \\
400\text{Å} & \text{Si x10 barrier} \\
500\text{Å} & \text{Si buffer} \\
600\text{Å} & \text{Si substrate} \\
\hline
\end{array} \)

\( \begin{array}{|c|c|}\hline
20\text{Å} & \text{Si cap} \\
480\text{Å} & \text{Si x20 barrier} \\
36\text{Å} & \text{Si}_{0.37}\text{Ge}_{0.23} \times 20 \text{ quantum well} \\
480\text{Å} & \text{Si x20 barrier} \\
500\text{Å} & \text{Si buffer} \\
600\text{Å} & \text{Si substrate} \\
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InGaAs/InGaAsP Quantum Wells

These samples are studied in chapter 5, and were grown by metal–organic vapour phase epitaxy (MOVPE) at the EPSRC Facility for III-V Semiconductors, University of Sheffield, Sheffield. Series MR358 to MR361 were grown in 1994 to investigate hole masses in transport measurements. Series MR688, MR744, MR742 and MR738 were grown in 1996 for this work, as a result of experiments on the first series.

**MR358**

(tensile strain)

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(4) InGaAs/InP Quantum Wells

These samples are studied in chapters 5 and 6, and were grown by MOVPE at the Philips Optoelectronic Centre, Eindhoven, Netherlands in 1991. They were grown to investigate hole masses in transport measurements, and were designed such that the lowest energy quantum well transition for all four samples occurs at about 1550nm (0.8eV).

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(compressive strain)

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MOQT1444  
(compressive strain)

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<td>buffer</td>
</tr>
<tr>
<td>Substrate</td>
<td>InP</td>
<td></td>
</tr>
</tbody>
</table>

MOQT1443  
(unstrained)

<table>
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<th>500Å</th>
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<th>undoped cap</th>
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<tbody>
<tr>
<td>125Å</td>
<td>InP</td>
<td>p-doped</td>
</tr>
<tr>
<td>150Å</td>
<td>InP</td>
<td>undoped spacer</td>
</tr>
<tr>
<td>75Å</td>
<td>In$<em>{0.35}$Ga$</em>{0.65}$As</td>
<td>quantum well</td>
</tr>
<tr>
<td>150Å</td>
<td>InP</td>
<td>undoped barrier</td>
</tr>
<tr>
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<td>In$<em>{0.55}$Ga$</em>{0.45}$As</td>
<td>quantum well</td>
</tr>
<tr>
<td>150Å</td>
<td>InP</td>
<td>undoped barrier</td>
</tr>
<tr>
<td>125Å</td>
<td>InP</td>
<td>p-doped</td>
</tr>
<tr>
<td>1000Å</td>
<td>InP</td>
<td>buffer</td>
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<td>InP</td>
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MOQT1445  
(tensile strain)

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<th>undoped cap</th>
</tr>
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<tbody>
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<td>InP</td>
<td>p-doped spacer</td>
</tr>
<tr>
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<td>InP</td>
<td>undoped barrier</td>
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<td>InP</td>
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<tr>
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</tr>
<tr>
<td>125Å</td>
<td>InP</td>
<td>p-doped</td>
</tr>
<tr>
<td>1000Å</td>
<td>InP</td>
<td>buffer</td>
</tr>
<tr>
<td>Substrate</td>
<td>InP</td>
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