THE INFLUENCE OF PRESSURE ON (Ga In) (As P) QUATERNARY SEMICONDUCTOR LASERS

BY

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A thesis submitted to the Physics Department at the University of Surrey for the Degree of Doctor of Philosophy

Department of Physics, University of Surrey. October 1983
Results are presented of high pressure studies of some optical, electrical and band-structure characteristics of the quaternary semiconductor alloy $\text{In}_x \text{Ga}_y \text{As}_z \text{P}_{1-y}$. The first pressure measurements on lasers with a 1.3 µm ($\text{In Ga}) (\text{As P})$ active layer have been made in order to determine the cause of the extreme temperature sensitivity of the threshold current in these devices.

The threshold current in 20 µm stripe $(\text{In Ga}) (\text{As P})$ lasers, operating at 1.3 µm wavelength, decreases with increasing pressure, whereas the opposite effect occurs in $(\text{Ga Al}) \text{As}$ lasers. At high temperatures the threshold of quaternary lasers shows a more marked decrease with pressure than at room temperature. The temperature sensitivity parameter $T_Q$ increases from about 65 K at atmospheric pressure to over 100 K at about 7 kbars.

In order to interpret these results a high pressure photoconductivity technique was used in determining the pressure coefficient of the direct energy band-gap, $\frac{dE_0}{dP}$, across the alloy composition. The samples were grown on InP at 659°C. The resulting epitaxial layers were 5-10 µm thickness and had mid $10^{16}$ cm$^{-3}$ carrier concentration. The first measured values of $\frac{dE_0}{dP}$ for the quaternary alloy was found to vary from $8.5 \pm 0.5$ meV kbar$^{-1}$, at $y = 0$, to $12.5 \pm 0.5$ meV kbar$^{-1}$ near $y = 1$ alloy composition. Good theoretical agreement was obtained with these rather surprising results. From the calculated pressure dependence of the band structure, in addition to the $\frac{dE_0}{dP}$ values, the variation of the effective masses of electrons and holes were also calculated. Hence the presence of alloy scattering rather than space charge scattering was determined from the pressure dependence of the mobility.
Analysis of the first pressure measurements of the quaternary lasers, indicates that the results can best be interpreted in terms of an intervalence band absorption loss mechanism that decreases with increasing pressure. Since $T_0$ increases with increasing pressure it may reasonably be assumed that the mechanism responsible for the decrease in threshold current with pressure is the loss mechanism causing the extreme temperature sensitivity of the lasers.
The author wishes to thank Dr. A.R. Adams for his invaluable help and guidance throughout this work. A CASE studentship with Standard Telecommunication Laboratories (STL) was financially supported by the Science Research Council.

It is a pleasure to acknowledge the industrial supervisor Dr. P.D. Greene of STL, especially for the use of the Liquid Phase Epitaxy (LPE) growth facility and his interest and advice during this work.

The author wishes to also acknowledge Dr. C.N. Ahmad, Mr. B.J. Gunney, Mrs. V. Hinton, Dr. N.G. Emerson, and Mrs. S. Wheeler (STL), for their technical assistance.

Finally, the author would like to thank Mrs. P. Wakelam for typing this thesis.
PUBLICATIONS

The following papers, based on this work, have been published in the scientific literature.

(i) 'High pressure photoconductivity technique and their application to semiconductor alloy systems.' Proc. 8th AIRAPT conf., Uppsala, (1981).

(ii) 'The temperature and pressure dependence of the electron and hole mobilities in $\text{Ga}_x \text{In}_{1-x} \text{As}_y \text{P}_{1-y}$ alloys.' J. Elect. Mater., 11, 1, (1982).

(iii) 'Pressure dependence of threshold current in $\text{Ga}_x \text{In}_{1-x} \text{As}_y \text{P}_{1-y}$ lasers.' Electron. Lett., 18, 12, (1982).

(iv) 'The influence of pressure on the temperature sensitivity of $\text{Ga}_x \text{In}_{1-x} \text{As}_y \text{P}_{1-y}$ lasers.' Electron. Lett. 18 21, (1982).

(v) 'The effect of pressure and active layer doping on the threshold current of (Ga,In) (As,P) lasers.' Gallium Arsenide and Related compounds, (1982).
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REFERENCES
1.1 The importance of the quaternary as a Laser material

The loss in an optical fibre consisting of a germanium-doped-silica core and a borosilicate cladding is shown in Fig. 1.1. The low loss region of 1 to 1.6 \( \mu m \) has attracted considerable amount of interest over the past few years for a major application \(^1\). For the telecommunication purposes there are two wavelengths that are attractive, the 1.3 \( \mu m \) wavelength and the 1.55 \( \mu m \) wavelength with possible losses \(^2(2,2a)\) of 0.5 and 0.2 dB/km respectively, in silica based optical fibres.

The choice of semiconductor material, with the correct range of wavelengths, is important for communication systems using silica based optical fibres. In Fig. 1.2 the relationship between the energy band gap and the lattice constant is shown for III-V alloy systems. In the diagram, if the region of low loss is added, as shown by the cross-hatch, then the possible systems using a binary as a substrate can be determined. The possible contenders for the quaternary system are \((\text{In Ga})(\text{As P})\) and \((\text{Al Ga})(\text{As Sb})\) \(^3\), lattice-matched to In P and Ga Sb respectively.

The quaternary alloy offers flexibility in selecting both energy band gap and lattice constant independently. Such flexibility is important for growing high quality materials. For the quaternary alloy \(\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}\) grown lattice matched to \(\text{InP}\ y \approx 2.1x\), where only \(y\) is quoted in this thesis. The high degree of lattice matching allows crystals to be grown relatively free of dislocations and produces high quality interfaces for heterostructures. This is only
possible if the energy band gap can be changed without altering the lattice constant.

The advantages (3) of using (In Ga) (As P) over the (Al Ga) (As Sb) compound are: the absence of Al in the system allows easier processing; the physical characteristics of InP substrate such as hardness, conductivity and thermal expansion coefficients are superior to those of Ga Sb; and there is no miscibility gap region or it is small.

1.2 Objectives and Summary of Contents

A major disadvantage of the lasers made from In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ quaternary alloy is that their threshold current is extremely sensitive to temperature. The experimentally measured threshold current density, $J_{th}$ (Amp m$^{-2}$), of (In Ga) (As P)/InP quaternary lasers is usually approximated by $J_{th}(T) \propto \exp(T/T_0)$ (within a limited temperature range), where $T$ (K) is the temperature and $T_0$ (K) is the temperature sensitivity parameter. The parameter, $T_0$, is generally found to be in the range 60 to 70 K within a limited temperature range (3) near or just above room temperature. In contrast, the (Ga Al)As/Ga As lasers show a much lower temperature sensitivity, as characterised by a much higher value of $T_0$ (160 - 200 K (12)) which remains constant through a wider range of temperatures. Hence, the low T problem indicates the extent of the temperature sensitivity of the quaternary lasers. Besides $T_0$ being low, the quaternary laser can have up to three different $T_0$ values over the 77-400K temperature range, namely, $T_0 \approx 100K$ for $T_0 < 260 - 300K$, $T_0 \approx 60K$ for $260-300K < T < 340K$, and $T_0 \approx 33K$ for $T > 340K$. 
Several primary causes have been suggested in the literature to explain the temperature sensitivity of the quaternary lasers:

(1) intervalence band absorption \(^{5,6}\),

(ii) Auger recombination \(^{7-10}\),

(iii) loss of carriers over heterojunction barriers \(^{25-28}\), or

(iv) recombination at impurity centres \(^{11,13}\).

There is considerable controversy as to which of these is the dominant loss mechanism and combinations of their effects have also been suggested. The bulk of the work on these loss mechanisms considers only temperature measurements on the quaternary lasers in order to distinguish between the losses.

The study (iii) of laser characteristics as a function of pressure has been considered here for the first time as a method for identifying the dominant loss mechanism. The effect of pressure is an attractive method because a few kilobars of pressure can produce a significant and reversible change in the relative positions of the bands in III-V semiconductors. This is ideal because all the mechanisms listed above are very sensitive to the band gap. The effect of hydrostatic pressure on lasers offers a non-destructive technique and perhaps more important is that pressurisation of a single sample may provide data of greater reliability than the comparison of several samples of different compositions, since uncontrolled variation of other parameters such as doping or interface abruptness are avoided.

Pressure is normally employed as a variable parameter, together with temperature, in experiments to determine band structures. The effect of pressure shifts bands of different symmetry at different characteristic rates from which they can be identified. Hydrostatic pressure can also simulate the effect of varying the alloy
composition. The relative shifts amongst the energy bands can also have direct consequence on the transport properties. Besides the shift in band gap, pressure can lead to transfer of free carriers from one set of band edge points to another. Changes in the effective masses affects other parameters and can be prominent in the pressure dependence of mobility. The conventional use of pressure involves electrical and optical measurements for detailed band structure parameters for a given semiconductor.

The first pressure measurements on the 1.3 μm quaternary lasers are reported here and they distinguish clearly the behaviour from that of (Ga Al) As/Ga As lasers indicating the presence of a pressure dependent loss mechanism. A review of laser diode theory which includes the relationships between spontaneous emission, stimulated emission, absorption and the threshold current have been derived in Chapter 2. The theory also includes loss mechanisms and how they affect the threshold current of the quaternary lasers. The effect of pressure on the threshold current depends on the changes in band structure of the quaternary active layer. Thus the band structure of $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}/\text{InP}$ alloy and its pressure dependence is given in Chapter 3. The calculations of the band structure which include energy bands and the effective masses have been based on Phillips (32) and Van Vechten (35) quantum dielectric theory. Initial characterisation of the $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}/\text{InP}$ alloy which include the determination of parameters such as the pressure coefficients of the direct energy band gap were obtained from samples grown using the Liquid Phase Epitaxy (LPE) growth facility available at the Standard Telecommunication Laboratory. The LPE growth system where the epitaxial layers were grown at 659°C on InP substrates has been described in Chapter 4.
A brief review of other important systems suitable for III-V compounds, in particular the quaternary, have been summarised and include vapour phase epitaxy (VPE) and molecular beam epitaxy (MBE). In chapter 5, the high pressure measurement techniques have been described including the piston and cylinder apparatus used here. A photoconductive technique was used here for pressure coefficient measurements and Hall measurements for mobility data. A pulsed technique was used for threshold current measurements near and above room temperatures and to measure the shift in operating wavelength as a function of pressure of the quaternary lasers.

The first measurements of the pressure coefficient $dE_0/dP$ on LPE $\text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y}/\text{InP}$ have been made and are presented in Chapter 6. The observed increase in $dE_0/dP$ from $y = 0$ to $y = 1$ composition is then compared with the calculated values obtained using the dielectric theory (Chapter 3). The influence of pressure on mobilities in quaternary alloys has been studied in Chapter 7 in order to resolve the ambiguity between Alloy scattering and space charge scattering. The study is also useful for testing the effective mass parameters determined in Chapter 3. The first results of the pressure measurements on the 1.3µm quaternary lasers have been presented in Chapter 8. The results, which distinguish clearly the behaviour of quaternary from (Ga Al) As lasers have been discussed for the first, time in terms of the four loss mechanisms introduced earlier. From the measurements, the effect of pressure on the important $T_0$ parameter can also be determined. Although these studies were mainly on 1.3 µm oxide-stripe quaternary lasers, interesting measurements have also been made on two other quaternary laser structures, (a) with $n^+$ active layers (b) inverted rib-waveguide structures.
Fig. 1.1 Transmission (loss) spectrum for an optical fibre

Fig. 1.2 Energy & lattice constants for III-V alloy systems. Low loss regions of optical fibre is indicated by cross-hatch
CHAPTER 2
LASER THEORY

2.1 Introduction

The low $T_0$ problem of the quaternary lasers has attracted a considerable amount of research. In this chapter the semiconductor laser theory has been summarised with reference to 1.3 $\mu$m (In Ga) (As P) lasers. The theory includes spontaneous emission, stimulated emission, absorption and also the threshold current relations. Although the fabrication of the 1.3 $\mu$m (In Ga) (As P)/In P double heterostructure (DH) lasers will be described in the growth chapter, some properties of the stripe geometry lasers have been presented in this chapter.

The four models presented here have been reported in the literature and claim to explain the origin of the $T_0$ problem. Each model represents a different loss mechanism that is believed to be present in these quaternary lasers giving rise to the high temperature sensitivity of their behaviour. The controversy is centred around the four loss mechanisms: Intervalence band absorption, Auger recombination, loss of carriers over the heterostructure barrier, and recombination at impurity centres. Each of these mechanisms will be considered in this chapter and its effect on the threshold current derived.

Although these loss mechanisms are discussed mainly with reference to the quaternary lasers, in-plane Superluminescence (15) and IVBA (16) are believed to be responsible for the non-linear light-current characteristics of quaternary light emitting diodes (LEDs).

These studies on the quaternary LED's are also important in understanding the characteristics of the quaternary alloy for its use.
in optical fibre communication\(^{(18)}\). An example is the fabrication of the surface emitting (In Ga) (As P)/In P LED, where the transparency of the In P substrate allows the light to be extracted through the substrate.

2.2.3 Blackbody Radiation and Einstein Relations

The interaction of light radiation and free carrier electrons in a semiconductor can be interpreted using Einstein relations. The continuous nature of the allowed electron energy bands in a semiconductor demands the use of Fermi-Dirac statistics to determine the occupation of the states.

A blackbody radiation or thermal radiation (equilibrium emission within a cavity at a uniform temperature) analogy is used to derive various relations describing the absorption and emission processes. The derivation of the photon density distribution is reported in a number of books\(^{(12,24,127)}\). The photon density distribution \(P(E)\) can be written as

\[
P(E) = \frac{8 \pi m_e^3 E^2}{h^3 c^3} \left[ 1 + \frac{E}{\langle n \rangle} \frac{d\langle n \rangle}{dE} \right] \frac{1}{\exp(E/kT) - 1}
\]  

The units \((12)(127)\) of \(P(E)\) at energy \(E\) are the number of photons per unit volume and unit energy interval. The refractive index is \(n\), the bracketed term in the denominator is \(\langle n \rangle\), the average number of photons per state given by Bose-Einstein distribution law. The bracketed term in the numerator is the dispersion term which is often assumed to be unity\(^{(12)}\).

The relationship between the spontaneous emission, stimulated
emission and absorption probabilities can be obtained by considering the semiconductor in thermal equilibrium. These are the Einstein relations. By considering absorption, spontaneous and stimulated transitions between a state in the valence band 1 and a state in the conduction band 2, the density of photon $P(E)$ of energy $E$ can be derived. This derivation can be found in Casey and Panish. The expression for $P(E)$ is

$$P(E) = \frac{A_{21}}{B_{12} \exp \left[ \frac{(E_c - E_v)/kT}{B_{21}} \right]} \quad (2.2)$$

where $B_{12}$ and $B_{21}$ are the probabilities of the absorption and stimulation transitions, while $A_{21}$ is that of the spontaneous transition.

Comparing this equation with equation (2.1), leads to

$$B_{12} = B_{21}$$

and

$$A_{21} = \frac{8\pi \hbar^2}{\hbar^3 c^3} B_{21} \quad (2.3)$$

with $[1 + (E/\hbar)(d\bar{n}/dE)]$ equated to unity. These equations are Einstein's relations and show that the spontaneous emission probability is related to stimulated emission and absorption probabilities.

The necessary condition for gain is that a photon is more likely to cause another downward electron transition between energy states.
2, 1 with another photon emitted than it is to be absorbed. Written in transition rates

\[ r_{21} > r_{12} \]  

(2.4)

where \( r_{12} \) is the absorption rate. Using Einstein relations and the transition rate equations given in Casey and Panish, this is simplified to

\[ F_2 - F_1 > E_2 - E_1 \]  

(2.5)

For the stimulated emission rate to exceed the upward absorption rate the separation of the quasi-Fermi levels, \( F_2 - F_1 \), must exceed the photon emission energy \( E_2 - E_1 \).

The relationship linking the spontaneous emission rate with the stimulated emission rate and the absorption rate are dealt with in detail by Casey and Panish (12) and Thompson (127) and will not be repeated here. However, as an example, the spontaneous emission rate for states in the conduction and valence band of semiconductor are given (12) as

\[
 r_{\text{spon}}(hv) = \frac{4mne^2hv}{m^2E_0h^2c^3} \int_{-\infty}^{\infty} \rho_c(E_c) \rho_v(E_c - hv) \\
 \times |M|^2 f_c[1 - f(E_c - hv)] \, dE_c
\]  

(2.6)

The definition of the density of states, fermi functions and the momentum matrix can be found in the literature. Similar expressions can be derived for the stimulated emission \( r_{\text{stim}}(hv) \) and the absorption coefficient \( a(hv) \).
It is necessary to determine $\alpha(h\nu)$ to obtain the stimulated emission and spontaneous rates. In order to determine $\alpha$, (normally obtained experimentally) the transition probability $B_{12}$ has to be calculated. The derivation of $B_{12}$ requires quantum mechanical arguments using time dependent perturbation theory. The result of this sort of analysis \((12)\) gives

$$B_{12} = \frac{e^2\hbar}{2m_e^* \varepsilon_o \hbar^2 n^2} |M|^2$$ \hspace{1cm} (2.7)

The momentum matrix $M$ was considered initially by Lasher and Stern \((21)\) and is now present in many texts. Using the momentum matrix for band-to-band transitions when $k_c = k_v$, $B_{12}$ is given \((127)\) as

$$B_{12} = \frac{e^2\hbar}{6m_e^* \varepsilon_o \hbar^2} \left\{ \frac{1 + \Delta_o/E_o}{1 + 2/3.\Delta_o/E_o} \left[ 1 - \frac{m_e^*}{m} \right] \right\}$$ \hspace{1cm} (2.8)

where $m$ is the free electron mass, $m_e^*$ is the effective mass of the electron in the conduction band, $E_o$ is the band gap and $\Delta_o$ is the spin orbit splitting.

2.4 Linear Gain

The absorption rate is the difference between the upward transition rate and the downward transition rate. Therefore, a positive $\alpha(E)$ represents net absorption, while a negative $\alpha(E)$ means the net stimulated emission rate exceeds the absorption rate.

A negative absorption coefficient represents gain. The necessary condition for the stimulated emission rate to exceed the absorption rate was given in equation (2.5) on the condition that the
quasi-Fermi levels separation exceed the photon energy. However, to obtain lasing, the gain must overcome the device losses such as free carrier absorption, scattering, and radiations from the mirror faces which are discussed in greater detail below.

For a lightly doped crystal (the radiative transition from the conduction to valence band with momentum conservation) the linear gain, assuming parabolic states and Fermi-Dirac distribution functions is given (22)(23) as

$$a = \left[ \frac{\mu}{\epsilon} \right]^{\frac{1}{2}} \frac{\omega}{\mu} |M|^2 \int_{E_0}^{\infty} \frac{E_{cv}(E_{fc} - E_{fv})}{(\omega - E_{cv})^2 + (h/\tau_{in})^2} \left[ \frac{\hbar}{\tau_{in}} \right] dE_{cv}$$

(2.9)

where $E_{cv} = E_c - E_v$.

The permeability and the dielectric constant are represented by $\mu$ and $\epsilon$ respectively. The angular frequency of light is $\omega$, while $\tau_{in}$ is determined from the intraband relaxation time of electrons and holes, and hence by scattering mechanisms.

$$\frac{2}{\tau_{in}} = \frac{1}{\tau_c} + \frac{1}{\tau_v}$$

(2.10)

where $\tau_c$ and $\tau_v$ are determined approximately from the electron and hole mobilities. The remaining terms are given in reference (6). The quasi-Fermi level for the electrons $E_{fc}$ and for holes $E_{fv}$ in lightly doped p-type material are determined (20) from the injected electron density and the total hole density.
2.5 Threshold Current

The two cleaved ends of the laser chip provide parallel reflecting surfaces and the waveguide between these two mirrors forms a Fabry-Perot resonator. The oscillation can be analysed by considering the plane wave reflections between the parallel and partially reflecting surfaces separated by a distance L.

The radiation intensity grows exponentially with position Z along the laser axis according to

$$I(Z) = I(0) \exp \left[ (g - \alpha)Z \right] \quad (2.11)$$

where \( g \) is the optical gain provided by stimulated emission.

The lasing threshold condition requires the waves to propagate one round trip \((Z = 2L)\) of the cavity with the gain exactly matched by the loss. If the reflection coefficients are \( R_1 \) and \( R_2 \) for the two cleaved facets then

$$\frac{I(2L)}{I(0)} = R_1 R_2 \exp \left[ (g - \alpha)2L \right] \quad (2.12)$$

Thus at threshold

$$1 = R_1 R_2 \exp \left[ (g - \alpha)2L \right] \quad (2.13)$$

therefore with equal reflection coefficients the gain is

$$g = \frac{1}{L} \ln \left( \frac{1}{R} \right) + \alpha \quad (2.14)$$

The absorption coefficient \( \alpha \) in equation (2.14) is the optical loss per cm from processes not directly associated with the gain.
mechanism, such as diffraction, scattering, and free carrier absorption.

The various loss mechanisms in the (In Ga)(As P)/InP laser are considered in section 2.10.

The current density \( J \) in Am/cm\(^2\) for an active layer of thickness \( d \) with no non-radiative recombination and no stimulated emission is given by

\[
J = e d r_{\text{spon}}
\]  

(2.15)

A nominal current density \( J_{\text{nom}} \) is often used where \( d \) is set equal to 1 \( \mu \)m and the quantum efficiency is set equal to unity. To relate \( J_{\text{nom}} \) to the gain, first \( r_{\text{spon}} \) has to be calculated and hence \( J_{\text{nom}} \) is found using (2.15). The gain, which takes into account the difference between the upward and the downward transition rates is obtained from equation (2.9). The gain peaks at some energy \( E_m \) between \( E_0 \) and the quasi-Fermi level separation \( \Delta E_F \).

For a range of injected carrier density, a curve of maximum gain, \( g_m \), versus \( J_{\text{nom}} \) is produced. For low currents \( g_{\text{max}} \) may be written as

\[
g_{\text{max}} = \beta (J_{\text{nom}} - J_o)^2
\]  

(2.16)

where \( J_o \) is the value of \( J_{\text{nom}} \) at which \( g_{\text{max}} \) goes to zero. The factor \( \beta \) is a gain constant (cm/A mp) and is different for different materials.

2.6 Differential Quantum Efficiency

Besides threshold current 'density', differential quantum efficiency measurements are sometimes reported for semiconductor lasers.
The total external quantum efficiency is simply the ratio of the detector current to the laser drive current. The differential quantum efficiency $\eta_D$, is defined (12) as the differential change of emission intensity $F$ with laser drive $I_L$,

$$\eta_D = e \frac{dF}{dI_L} \tag{2.17}$$

The spontaneous emission saturates at threshold and the total emission intensity above threshold may be represented as

$$eF = F_{\text{spon}} \eta_{\text{spon}} I_{\text{th}} + F_{\text{stim}} \eta_{\text{stim}} (I - I_{\text{th}}) \tag{2.18}$$

where $F_{\text{spon}}$ and $F_{\text{stim}}$ are the photon escape probabilities for spontaneous and stimulated emission, respectively. Factors $\eta_{\text{spon}}$ and $\eta_{\text{stim}}$ are the internal quantum efficiencies for spontaneous and stimulated emission, respectively, and are taken as constant for currents above the threshold current.

By combining equations (2.17) and (2.18).

$$\eta_D = \eta_{\text{stim}} F_{\text{stim}} \tag{2.19}$$

where the photon escape probability for stimulated emission $F_{\text{stim}}$ is the ratio of the external optical power to the total optical power generated internally by stimulated emission,

$$F_{\text{stim}} = \frac{P_{\text{ext}}}{P_{\text{ext}} + P_{\text{abs}}} \tag{2.20}$$
From equation (2.47) the gain at threshold is the sum of the internal and external losses, where \((1/L)\ln(1/R)\) represents the mirror loss. If the losses are only at the mirrors and/or can be incorporated within the absorption coefficient \(a\)

\[
F_{\text{stim}} = \frac{(1/L) \ln(1/R)}{a + (1/L) \ln(1/R)} \tag{2.21}
\]

and the differential quantum efficiency \(\eta_D\) is given by

\[
\eta_D = \frac{\eta_{\text{stim}}}{1 + aL \ln(1/R)} \tag{2.22}
\]

Before the threshold current relation is deduced the confinement factor, \(\Gamma\), has to be introduced. Because the propagating mode spreads outside the active layer, the active layer absorption coefficient is reduced by the confinement factor \(\Gamma\). The fraction of propagating mode \((1 - \Gamma)\) is within the confining layers, and thus the absorption coefficient in the confining layer is reduced by \((1 - \Gamma)\).

Therefore, an expression for the threshold current density can be written as

\[
J_{\text{th}} (A/cm^2) = J_{nd} \frac{d}{\eta_D} + \frac{d}{\eta_D} \left[ \frac{1}{\Gamma \beta} \left( q_1 + \frac{1}{L} \ln \left( \frac{1}{R} \right) \right) \right] \tag{2.23}
\]

where \(q_1\) includes all the absorption losses.
2.7 Stripe-Geometry Laser

Most heterostructure lasers, intended for use commercially are stripe geometry lasers for reasons described below. Stripe widths are typically 5-30 μm. The stripe geometry restricts the current along the junction plane. This lateral confinement serves several purposes: (1) reduction of the cross-sectional area which also reduces the operating current; (2) single filament operations and fundamental mode emission for stripe widths of \( \approx 20 \mu \text{m} \); and (3) improved laser operation by enclosing the waveguide in the slab structure. (If stimulated emission takes place in localised regions, then these are called laser filaments.)

The growth and fabrication of the quaternary stripe geometry laser has been presented in Chapter 4. From equation (2.23) the threshold current is inversely proportional to the quantum efficiency and the stimulated emission is proportional to the optical density. Thus for low threshold current, good optical and carrier confinement is necessary. This is provided in the stripe geometry laser by doping and composition discontinuities which create index of refraction and potential discontinuities.

In the DH lasers the recombination region is bounded by two higher band gap regions to confine the minority carriers and the radiation. The higher band gap regions provide optical barriers because of their reduced index of refraction at the lasing photon energy of the recombination region.

2.8 Far-field Pattern

The active region of stripe-geometry lasers is smaller than that of the broad-area lasers and so the output powers are also lower. For a
typical 20 μm stripe width and 300 μm length quaternary laser, the far-field emission pattern is illustrated in Fig. 2.1. with 0.2-0.3 μm active layer thickness. The thickness ensures fundamental mode emission. The full angle between the half-power points are 50° in the direction perpendicular to the junction plane and 10° along the junction plane.

The effect of cavity length L on the (Ga In) (As P) lasers will not be considered. Experimentally the J_\text{th} is relatively insensitive to changes in length above 200 μm. Lasers of shorter length show a steep rise in J_\text{th}.

2.9 The T_0 Problem

The threshold currents of (In Ga)(As P)/In P DH lasers depend strongly on temperature in the temperature range of greatest interest (20 - 70°C). It is experimentally found (11)(17)(13)(9) that the threshold current density J_\text{th} of Ga As and (Ga In) (As P) based DH lasers varies with the temperature T as J_\text{th} \propto \exp(T/T_0) (within a limited temperature range) where the parameter T_0 describes the temperature sensitivity. Figure 2.2 illustrates the dependence of J_\text{th} on T for Ga As - (Ga Al) As (18) and (In Ga) (As P)/In P (54) DH lasers. The value of T_0 is 60 - 70K for T > 250K and T_0 \approx 110K for T < 250K for (Ga In) (As P)/In P DH lasers. For comparison, the T_0 values of (Ga Al) As/Ga As DH lasers can reach 300K. Thus the low T_0 value of the (Ga In) (As P)/In P DH lasers is a major problem and imposes several limitations for the use of the laser in, e.g., optical communication, at high ambient temperature.

Several reasons have been proposed in the literature to explain the complicated temperature dependence of the threshold current:
Fig. 2.1  Far-field emission of a stripe geometry laser
Fig. 2.2 Temperature dependence of the threshold current of the quaternary laser. Inset compares it with (GaAl) As laser.
(i) Intervalence band absorption; (ii) Auger recombination; (iii) Carrier leakage over the In P cladding layers; and (iv) recombination through impurity centres.

2.10 Losses

2.10.1 Intervalence Band Absorption

The absorption coefficient $a_i$ is the total loss in the laser at threshold current.

$$a_i = a_{in} + a_{ac} + \frac{a_{ex}(1-\Gamma) + \ln(1/R)}{L\Gamma} \quad (2.24)$$

where $a_{in}$ is the product of the slope of peak linear gain versus injected carrier density and the injected carrier density at zero gain. Physically $a_{in}$ is the residual internal absorption loss in the active layer. It is worth emphasising, that the value of $a_{in}$ is not the actual absorption loss at the lasing wavelength, but is the residual absorption at zero injection level.

The second absorption term in equation (2.24) is $a_{ac}$ and represents the loss in the active region. A possible loss mechanism was proposed by Adams et al (5) to explain the absorption $a_{ac}$. The mechanism involved intervalence band absorption (IVBA). Figure 2.3 shows schematically the absorption $a$, due to electronic transitions from the split-off band into holes which have either been injected into the heavy hole band by forward bias or arise from thermally excited acceptors. Transitions to the partially empty acceptor levels $E_A$ are also possible in IVBA and are represented by $a_2$. 


The absorption coefficient $a_1$ is directly proportional to the hole density available at $E_1$, (Fig 2.3), hence

$$a_1 \propto \exp \left[ \frac{(E_{FV} - E_1)}{kT} \right] \quad (2.25)$$

Due to the large heavy hole effective mass and usually light p-doping, the hole quasi-Fermi level $E_{FV}$ does not enter the valence band even at the high injection levels obtained at the laser threshold current. Therefore equation (2.25) can be approximately written (6) as

$$a_1 = B_1 n \left( \frac{2m^*}{m_v} \right) \frac{kT}{2} \exp \left( \frac{-E_1}{kT} \right) \quad (2.26)$$

Similarly the absorption coefficient $a_2$ is written (6) as

$$a_2 = B_2 \left[ 1 + \left( \frac{1}{2} \right) \exp \left( \frac{[E_A - E_{FV}]}{kT} \right) \right]^{-1} \quad (2.27)$$

where $B_1$ and $B_2$ are constants of proportionalities. These two absorptions make up the intervalence band absorption $a_{ac} = a_1 + a_2$.

The remaining two absorptions in equation (2.24) represent the loss in the cladding layer and loss at the mirrors respectively.

2.10.2 Auger Recombination

A considerable amount of literature has been published on the problem of temperature dependence of the threshold current in (In Ga)(As P)/In P lasers proposing that Auger (7-10) recombination can account for the low $T_0$ problem.

The theory of Auger recombination has been introduced for semiconductors by Beattie and Smith (29) while Lochman (30), for example,
Light Absorption by Intervalence Band Absorption

Fig. 2.3 Schematic diagram of the intervalence band absorption in the band structure of quaternary
modified it for phonon assisted Auger recombination. Auger recombination as well as intervalence band absorption are intrinsic loss mechanisms and suggests that it may not be possible to reduce the high temperature sensitivity of these 1.3 \textmu m (In Ga)(As P)/In P lasers.

A detailed study of Auger processes in the 1.3 \textmu m quaternary laser has been given by Dutta et al. The main band-to-band Auger transitions are CCCH, CHHS, and CHHL. (The notation C, H, L, and S represent the conduction band, the heavy hole band, the light hole band, and the split-off band respectively.) The three band-to-band processes shown in Fig. 2.4 are characterised by a strong dependence on both the band gap, $E_Q$, and the temperature, $T$. The exponential dependence of the Auger transition rate $R_A$ on $E_Q$ and $T$ was approximated as

$$R_A \propto \exp \left(-\frac{X}{kT}\right)$$  \hspace{1cm} (2.28)

Where the energy $X$ is derived by considering the conservation of momentum and energy, for the CCCH process

$$X = E_Q \frac{m_e^*}{m_e^* + m_h^*}$$  \hspace{1cm} (2.29)

for the CHHS process

$$X = \frac{m_s^* (E_Q - \Delta_Q)}{(2m_h^* + m_e^* - m_s^*)}$$  \hspace{1cm} (2.30)

and for CHHL process

$$X = E_Q \frac{m_e^*}{(2m_h^* + m_e^* - m_l^*)}$$  \hspace{1cm} (2.31)
Fig. 2. Schematic diagram of the three band-to-band Auger processes. The electrons (closed circles) & holes (open circles) transitions involves the conduction, heavy-hole, light hole, & split-off band
The conduction-band, valence band, and the split-off band effective masses are $m_e^*$, $m_h^*$, $m_l^*$, and $m_s^*$. The total spontaneous radiative recombination rate in a uniformly excited layer, say 1 µm thick, determines the radiative component of injected current $I_R$. If $I_A$ is the non-radiative Auger recombination current, the threshold current is given by

$$I = I_R + I_A$$

The Auger component of the current $I_A$ is proportional to $\alpha/\tau_A$ where $\tau_A$ is the Auger lifetime. The lifetime, $\tau_A$, can be derived from the Auger transition rates.

2.10.3 Loss over the Heterojunction Barrier

An alternative reason for the low $T_o$ value of the 1.3 µm (In Ga)(As P)/In P laser has been given by Yano (25). Carrier leakage from the quaternary active layer into the In P confining layers is an extension of the loss mechanism reported (26) in (Ga Al) As lasers.

The dominant carrier leakage (25, 27) is of electrons loss over the P-In P layers. The leakage current can be approximately written (25) as

$$I \propto N_c(T) \exp \left[ \frac{(E_F - \Delta E_o)}{kT} \right]$$

where $N_c(T)$ is the conduction band density of state, $E_F$ is the Fermi-energy, and the difference in the band gaps between the quaternary and the In P confining layer is $\Delta E_o$. 
2.10.4 Loss through Impurity Centres

The model attributing the temperature sensitivity of the threshold current to non-radiative recombination centres at 0.3 eV from the band edge was proposed by Horikoshi et al (11). The importance of possible impurity centres responsible for the temperature sensitivity was also emphasised by Nahory et al (13). A suggestion of the existence of an electrically active recombination centre has been proposed to explain the temperature sensitivity of the threshold current in (In Ga)(As P)/In P lasers, and a short discussion is presented in chapter 8.
CHAPTER 3
BAND STRUCTURE OF THE QUATERNARY ALLOY

3.1 Introduction

In this chapter the emphasis is placed on why the quaternary alloy has become one of the new materials for optoelectronic devices and its development from the binary III-V compounds. Phillips (32) proposed a quantum dielectric theory on which Van Vechten (35) formed the basis for the calculation of the energy band parameters. These calculations can be described using a number of prescriptions. The main parameters the theory uses are the electronegativity, $C$, the homopolar energy gap, $E_h$, $D_{av}$ the term introduced to account for d-core states, and nearest neighbour distance parameter, $d$. This later parameter is particularly useful for analysis of high pressure experiments since it can be directly related to pressure through compressibility. The prescriptions, as used for the binary $A^N B^{8-N}$ compounds, were adjusted for the quaternary alloy, including the effect of d-core states. A five-level k.p analysis, as developed by Lawaetz for the binary III-V semiconductors, was used for the calculation of the effective mass parameters. Again the appropriate adjustment for the quaternary alloy being obtained.

The development of the energy band pressure coefficient from dielectric theory for some group III-V, II-VI and IV semiconductors was carried out by Camphausen et al (37). From these the calculation of the direct energy band gap pressure coefficient, $\frac{dE}{dp}$ for the quaternary alloy was possible. The calculation of the effective masses using k.p theory was then used in conjunction with the Van Vechten theory in determining the effective mass pressure dependences.
The pressure analysis in this chapter was possible by expressing the energy band gap and the effective mass parameters as a function of nearest neighbour distance and hence compressibility.

3.2 Characteristic Band Structure of the Quaternary Alloy

The characteristic band structure of the elemental and binary semiconductor have been well documented in the literature. Hence only a summary is presented here. Most of the III-V compounds crystallise into zinc-blende structure, each atom being surrounded by four nearest neighbour atoms of a different species forming a regular tetrahedron as shown in Fig.3.1. The diamond and zinc-blende structures can be described by two inter-penetrating face centred cubic lattices.

The Brillouin zone and the symmetry points for the zinc-blende (diamond or face centred cubic) lattice is shown in Fig.3.2. The principal symmetry points are the Γ point at the zone centre, the L and X points are at the zone boundary and along the [111] and [100] axes respectively.

The band structure of III-V compounds is basically similar to that of the group IV elements, including Si and Ge, with differences due to lack of inversion symmetry. A typical band structure of a III-V compound is shown on Fig.3.3. The conduction band minima are at the zone centre and approximately at the L and X points along the [111] and [100] directions respectively. The valence band has a more complicated structure having a maximum at the Γ point that is degenerate. The maxima consists of two bands having very different curvatures which are hence called the heavy and light hole bands.

Initially Glisson et al (38) provided plots of $E_0$ and $a_0$ versus composition for many quaternary alloys.
Fig. 3.1 Zincblende structure

Fig. 3.2 Brillouin zone boundaries for a face-centred cubic lattice
Fig. 3.3 Band structure of GaAs
These diagrams are extremely useful in the design of devices for specific applications. The general approach of interpolation was first suggested by Moon et al.\(^{(39)}\) in determining \(E_0\) as a result of the deviation from linearity across the alloy composition observed by Thompson and Wooley\(^{(40)}\). Although empirical results of the bowing parameters\(^{(41-3)}\) have been reported their physical significance is still not clear. The quaternary (In Ga)(As P) material has become the focus of interest, however, there are few parameters that have been measured. Hence, an interpolation procedure must be adopted between the measured parameters of the binary constituents.

The interpolation technique applied here involved weighting each individual parameter by the fractional amount of binary material present in the quaternary \(Ga_x\) \(In_{1-x}\) \(As_y\) \(P_{1-y}\). For example, the contribution due to In P would be a fraction \((1 - x) (1 - y)\) of the In P parameter \(\Theta_{In\ P}\) as given in equation (3.1)

\[
\Theta_Q = (1 - x) \left[ (1 - y) \Theta_{In\ P} + y \Theta_{In\ As} \right] + x \left[ (1 - y) \Theta_{Ga\ P} + y \Theta_{Ga\ As} \right]
\]

The condition for lattice match with In P imposes the condition, to a first order, of \(y = 2.1x\). The interpolation allows estimates of the compositional dependence of material constants.

3.3 Energy Band Gap Parameters

The method of calculating the band structure of tetrahedrally co-ordinated semiconductors can be summarized as a number of steps or prescriptions\(^{(37)}\). The direct energy band gap of a compound, provided there are no d-core states in any of the elements, is given by
\[ E_i = E_{h,i} \left[ 1 + \left( \frac{C}{E_{h,i}} \right)^2 \right]^{\frac{1}{2}} \]  

(3.2)

where \[ i = 0, 1. \]

Phillips (32) separated the average gap into homopolar and heteropolar parts, \( E_h \), and \( C \). The homopolar gap \( E_{h,i} \) is usually assumed to be a function of nearest neighbour distance, \( d \), only and is expressed as

\[ E_{h,i} = E_{h,i} |_{Si} (d/d_{Si})^{\delta_i} \]  

(3.3)

Thus for a given compound the homopolar gap is a function of the homopolar gap of silicon and the ratio \( (d/d_{Si}) \) raised to the logarithmic derivative \( \delta_i \). The experimental determination of \( E_{h,i} \) for two group IV elements \( (C = 0) \) give \( \delta_i \) and therefore \( E_{h,i} \) for the other materials.

Values of the logarithmic derivatives and other parameters required in the determination of band structure calculation of III-V compound are given in Table 3.1

The heteropolar energy \( C \), also defined as the ionic energy, for a binary compound, is a measure of the electronegativity difference between the elements. The heteropolar energy \( C \) can also be defined as the change in gap produced by the antisymmetric potential in a binary compound. The value of \( C \) for a compound under consideration would be deduced by measuring its dielectric constant \( \epsilon_0 \). The determination of \( C \) from \( \epsilon_0 \) is discussed by Camphausen et al (37).

This method of determining \( C \) from \( \epsilon_0 \) was not employed for the quaternary (In Ga)(As P) alloy. Instead, the measured energy band gap of the alloy was used to deduce \( C \) across the alloy composition, as discussed in Chapter 6.
### Table 3.1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value for Si</th>
<th>Logarithmic derivative</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP</td>
<td>5.17</td>
<td>-1.3077</td>
</tr>
<tr>
<td>$V_{AC-X_4}$</td>
<td>8.63</td>
<td>-1.43</td>
</tr>
<tr>
<td>$E_{0,h}$</td>
<td>4.1</td>
<td>-2.75</td>
</tr>
<tr>
<td>$E_{1,h}$</td>
<td>3.6</td>
<td>-2.22</td>
</tr>
<tr>
<td>$E_{2,h}$</td>
<td>4.5</td>
<td>-2.3821</td>
</tr>
<tr>
<td>$\Delta E_0$</td>
<td>12.8</td>
<td>-5.07</td>
</tr>
<tr>
<td>$\Delta E_1$</td>
<td>4.976</td>
<td>-4.97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>$d(\AA)$</th>
<th>$C$(eV)</th>
<th>$D_{AV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>4.444</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>Ge</td>
<td>4.630</td>
<td>0</td>
<td>1.267</td>
</tr>
<tr>
<td>GaAs</td>
<td>4.626</td>
<td>2.90</td>
<td>1.235</td>
</tr>
<tr>
<td>GaP</td>
<td>4.460</td>
<td>3.30</td>
<td>1.152</td>
</tr>
<tr>
<td>InSb</td>
<td>5.302</td>
<td>2.30</td>
<td>1.417</td>
</tr>
<tr>
<td>InAs</td>
<td>4.940</td>
<td>2.74</td>
<td>1.354</td>
</tr>
<tr>
<td>InP</td>
<td>4.802</td>
<td>3.339</td>
<td>1.270</td>
</tr>
<tr>
<td>AlP</td>
<td>4.460</td>
<td>3.135</td>
<td>1.0</td>
</tr>
</tbody>
</table>
The expression given in (3.2) is solely for the compound with no d-core state elements, however, the quaternary alloy has d-core states. Thus the energy band gap expression is changed to account for the d-core states and is rewritten (37) as:

\[ E_i = [E_{h,i} - (D_{av} - 1)\Delta E_i] \left[ 1 + \left( C/E_{h,i} \right)^2 \right]^{\frac{1}{2}} \] (3.4)

The direct energy band gap, \( E_0 \), will be considered which corresponds to \( \Gamma_{25'} - \Gamma_{15} \) or \( \Gamma_{2'} - \Gamma_{1} \) band transitions. In the expression (3.4) \( \Delta E_0 \) is not the spin-orbit splitting but is a factor which scales as the nearest-neighbour distance. The factor \( (D_{av} - 1) \Delta E_0 \) is associated with the presence of d-core electrons.

Physically (35), d-core levels interact with the sp\(^3\) hybridized valence and conduction bands. This interaction is non local i.e., the interaction with s-like states is greater than with p-like states. (The s-like states penetrate the d-core and are therefore less screened from the nuclear potential than p-like states.) Therefore, s-like valence and conduction band states are lowered in energy relative to the p-like levels. This splitting of the s-like and p-like states weakens the energy of the sp\(^3\) covalent bond. It also reduces the energy of the particular band gap which corresponds to transitions from predominantly p-like valence states to predominantly s-like conduction-band states - in this case \( E_0 \).

Direct experimental determination of \( D \) is made difficult (35), and may be subject to large errors. Thus Van Vechten (I) used a semi-empirical approach to determine \( D \) of a binary crystal AB say;

\[ D(AB) = A(A)A(B) - [8(A)8(B) - 1] (Z_A - Z_B)^2 \] (3.5)
where \( Z \) values are the valence of elements and parameters \( \delta \) are functions of covalent radii. These parameters are given in Table II of Van Vechten (33). The value of \( D_{av} \) is a weighted average of factors \( D \) for skew compounds and is equal to \( D \) for atoms from the same row. (ie. If elements A and B do not appear in the same row of the periodic table, then the average \( D \) value \( D_{av} \) differs from the factor \( D \).)

Continuing with the binary AB, for the moment, Van Vechten (35) proposed

\[
D_{av}(AB) = \frac{1}{8} \left[ (8 - Z_A) D(Z_A, r_A) + (8 - Z_B) D(Z_B, r_B) \right]
\]  

(3.6)

where \( D(Z_A, r_A) \) is the value of \( D \) for the "horizontal compound" containing element A. The derivation of \( D_{av} \) for the quaternary \( \text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y} \) alloy can be described by first considering the value of \( D_{av} \) for \( \text{InP} \). For the binary \( \text{InP} \), the constituent elements \( \text{In} \) and \( \text{P} \) belong to different rows, thus an average has to be taken. According to (3.6) \( D_{av} \) for \( \text{InP} \) is given by

\[
D_{av}(\text{InP}) = \frac{5}{8} D_{\text{InSb}} + \frac{3}{8} D_{\text{AlP}}
\]

(3.7)

where all the group III lattice sites have Indium atoms and all the group V lattice sites have Phosphorus atoms. By introducing Gallium to the \( \text{InP} \) crystal a ternary alloy \( \text{In}_{1-x} \text{Ga}_x \text{P} \) is formed. Where the fraction of Gallium \( x \) reduces the Indium content to a fraction \( (1 - x) \). Thus the \( D_{av} \) value of \( \text{In}_{1-x} \text{Ga}_x \text{P} \) is given by

\[
D_{av}(\text{InGaP}) = \frac{5}{8}((1 - x)D_{\text{InSb}} + x D_{\text{GaAs}}) + \frac{3}{8} D_{\text{AlP}}
\]

(3.8)
In the ternary In\textsubscript{1-x} Ga\textsubscript{x} P introduction of Arsenic will lead to the formation of the quaternary In\textsubscript{1-x} Ga\textsubscript{x} As\textsubscript{y} P\textsubscript{1-y} alloy. Hence the fraction of Arsenic \( y \) reduces the content of Phosphorus to a fraction \((1 - y)\).

Thus for the quaternary In\textsubscript{1-x} Ga\textsubscript{x} As\textsubscript{y} P\textsubscript{1-y} alloy which is of interest here, the weighted average value \( D_{av} \) can be written as:

\[
D_{av} = \frac{5}{8} [D_1(1 - x) + D_2x] + \frac{3}{8}[D_2y + D_3(1 - y)]
\]  

(3.9)

where \( D_1, D_2, \) and \( D_3 \) are the D values for In Sb, Ga As and Al P respectively as given in Table 3.1.

For completeness, the following can be used to build up the band structure of a crystal. The ionization potential \( IP \), i.e., the energy difference between the top of the valence band at \( \Gamma_{25} \) or \( \Gamma_{15} \) and the vacuum level, is given by

\[
IP = IP_h [1 + (C/IP_h)^2]^{\frac{1}{2}}
\]  

(3.10)

where \( IP_h \) is the homopolar contribution which scale as \( d \) similar to that of \( E_{h,i} \) with appropriate logarithmic derivative \( \delta_1 \).

The splitting of the conduction-band X levels, \( X_1 \) and \( X_3 \), is proportional to \( C \),

\[
E_{X_3} - E_{X_1} = \text{Const.} \cdot XC
\]  

(3.11)

where the constant value \((37)\) is 0.07.1.

The absolute value of the maximum valence-band energy of the X point \( X_4(X_5) \) is argued to be a property of the row only, and
specifically independent of the value of $C$ the electronegativity.

Thus,

$$E_x = E_x \left|_{sl} \right. \frac{(d/d_{sl})}{\delta x}$$

(3.12)

However Camphausen et al (37) modified this and describes $E_{X_4}$ ($E_{X_5}$) by a similar expression,

$$E_x = E_{X,h} \left[ 1 + \frac{(C/E_{X,h})}{2} \right]^{1/2}$$

(3.13)

where $E_{X,h}$ scale as $d$ similar to that of $E_{h,i}$ with approximate logarithmic derivatives.

The energy of the top of the valence band at the symmetry point $L$, the $L_3^r (L_3)$ state, is set equal to a constant fraction of the energy separating $L_{25}^r$ and $X_4$. Van Vechten arbitrarily set $t = 0.5$. However Camphausen et al (37) used $t = 0.4$ which corresponded to the ratio of the shifts of $L_3^r$ and $X_4$ with respect to $L_{25}^r$.

### 3.4 Effective Mass Parameters

The introduction above of lattice parameter $d$, ionicity $C$, and the effect of $d$-electron shells in the cores in describing the calculation of the energy band gap structure is now followed by effective mass calculations.

The effective mass $m_e^*$ of electrons in the $\Gamma$ conduction minimum may be related to the direct energy band gap $E_0$ using a simple formal expression of the second-order $k.p$ perturbation theory.

$$\frac{m_o}{m_e} = 1 + \frac{M^2}{3} \left[ \frac{2}{E_0} + \frac{1}{E_0 + \Delta_0} \right]$$

(3.14)
The free electron mass is denoted by \( m_0 \), while the spin-orbit splitting is \( \Delta_0 \) and \( M \) is the appropriate momentum matrix element.

Cardona (45) used a five level \( k.p \) model to calculate the effective mass of electrons and holes (light and heavy). Lawaetz (46) used a similar approach but has derived the band-gaps and momentum matrix elements for individual compounds using the quantum dielectric theory of Van Vechten and Phillips described above. The semi-empirical approach was also adopted by Herman et al (47) using \( k.p \) theory, where emphasis was placed on the matrix elements.

After Dresselhaus, Kip and Kittel (48) parameters can be introduced for the valence band edge at the \( \Gamma \) point

\[
F = -2 \frac{|\langle x | P x | \Gamma_2^+ \rangle|^2}{m \left( E_{\Gamma_2^+} - E_{\Gamma_2^-} \right)} \tag{3.15}
\]

\[
H_1 = -2 \frac{|\langle x | P x | \Gamma_{15}^+ \rangle|^2}{m \left( E_{\Gamma_{15}^+} - E_{\Gamma_{25}^-} \right)} \tag{3.16}
\]

\[
G = -2 \frac{|\langle x | P x | \Gamma_{12}^+ \rangle|^2}{m \left( E_{\Gamma_{12}^+} - E_{\Gamma_{25}^-} \right)} \tag{3.17}
\]

\[
H_2 = -2 \frac{|\langle x | P x | \Gamma_{25}^- \rangle|^2}{m \left( E_{\Gamma_{25}^-} - E_{\Gamma_{25}^-} \right)} \tag{3.18}
\]

and spin-orbit splitting \( \Delta_0 \) of the \( \Gamma_{15} \) states yield the additional parameter

\[
q = 4 \frac{|\langle x | P y | \Gamma_{15}^+ \rangle|^2 \Delta_0^4}{9m \left( E_{\Gamma_{15}^+} - E_{\Gamma_{25}^-} \right)^2} \tag{3.19}
\]
These parameters have been considerably simplified by ignoring all but the terms closest in energy, i.e. where the denominator is smallest. From the above it is possible to further define the Luttinger valence band parameters;

\[
y_1 = - \frac{1}{3} (F + 2G + 2H_1 + 2H_2) - 1 + \frac{1}{2} q \quad (3.20)
\]

\[
y_2 = - \frac{1}{6} (F + 2G - H_1 - H_2) - \frac{1}{2} q \quad (3.21)
\]

\[
y_3 = - \frac{1}{6} (F - G + H_1 - H_2) + \frac{1}{2} q \quad (3.22)
\]

In the above equations, F is equivalent to (-Ep/Eo) and H_1 is (-Ep^l/Eo^l). Ep and Ep^l are the principal interband momentum matrix elements and Eo the fundamental direct p-s energy gap and Eo^l is the p-p gap at \Gamma.

Thus

\[
F = - \frac{E_p}{E_o} \quad (3.23)
\]

\[
H_1 = - \frac{E_p^l}{E_o^l} \quad (3.24)
\]

and q in equation (3.19) can also be simplified to give

\[
q = - \frac{2}{9} \frac{H_1 \Delta^l_o}{E_o} \quad (3.25)
\]

Ep, Ep^l, H_2 and G are affected by d-core states and these are included in defining these matrix elements.
\[ E_p = E_p \big|_{Si} \delta [\beta + (1 - \beta) Z] \quad (3.26) \]

\[ E_p^l = E_p^l \big|_{Si} \delta [\beta + (1 - \beta) Z] \quad (3.27) \]

\[ H_2 = H_2 \big|_{Si} Z \delta \quad (3.28) \]

\[ G = G \big|_{Si} Z \delta \quad (3.29) \]

The normalised values of \( E_p, E_p^l, G \) and \( H_2 \) to Si are determined from experimental valence-band parameters for Ge. Thus (46)

\[ E_p \big|_{Si} = 21.6 \text{ eV}, \quad E_p^l \big|_{Si} = 14.4 \text{ eV} \]

\[ H_2 \big|_{Si} = -0.19, \quad G \big|_{Si} = -0.75 \]

\[ \delta = [1 + a(D_{av} - 1)] (d_{Si}/d)^2 \quad (3.31) \]

where \( a \) is a constant of order unity. Lawaetz (46) showed that \( a \) has a value of 1.23. This value of \( a \), 1.23 is greater than the average value of unity, this is not surprising since the influence of the d-core electrons is stronger for the highest symmetry point \( \Gamma \) in the Brillouin zone.

The definition of \( Z \) is given as

\[ Z = \frac{E_p^l + E_p - h}{2E_p^l} \quad (3.32) \]
where \( E_{0,h}^l = 3.4 \left( d/d_{si} \right)^{-1.92} \) \hspace{1cm} (3.33)

and \( E_0^l = (E_{0,h}^l + C^l)^{1/2} \) \hspace{1cm} (3.34)

is the energy band gap between \( \Gamma_{13v} \) and \( \Gamma_{15c} \) states. The value of \( C^l \) was taken to be equal to that of \( C \) by Van Vechten \((34)\), but stated later that somewhat larger values should be used for p–p gaps. However, Lawaetz used

\[ C^l = 1.25 \, C \] \hspace{1cm} (3.35)

which can be estimated from equation (3.4).

The nature of \( \beta \) is zero for no d-core electrons, 1 for isoelectronic compounds with d electrons, and somewhere in between otherwise. Thus a value of 0.5 has been used.

Having described the parameters for the band-structure calculations, the relative effective masses can be deduced. The conduction-band mass is given \((46)\) by

\[
\frac{m}{m_e^c} = 1 - F \left( 1 - y^1 - x \right) + F^l \hspace{1cm} (3.36)
\]

where the second term results from the interaction with the valence bands \( \Gamma_{25}^l \),

\[
y^1 = \frac{\Delta_0}{3(c_E + \Delta_0)} \hspace{1cm} (3.37)
\]
while the $x$ stands for the contribution from the $\Gamma_{15c}$ band and is approximately,

$$x = \frac{\beta}{\beta + (1 - \beta)Z} \frac{E_0 - E_l}{E_0 - E_{0,h}} \frac{E_{0,l} - E_{0,h}}{2E_0}$$ (3.38)

And the third term, in the $m_0/m_0^*$ equation, is the contribution from higher-lying states. The value of $F^l$ is usually assumed to be $-2$.

Expressions for the light-hole mass $m_{lh}^*$ and heavy-hole mass $m_{hh}^*$ can be written as

$$m_{lh}^* = (\gamma_1 + \overline{\gamma})^{-1}$$ (3.39)

and

$$m_{hh}^* = (\gamma_1 - \overline{\gamma})^{-1} [1 + 0.05 \gamma_h + 0.0164 \gamma_h^2]^{2/3}$$ (3.40)

where

$$\overline{\gamma} = (2\gamma_2^2 + 2\gamma_3^2)^{1/2}$$ (3.41)

$$\gamma_h = 6(\gamma_3^2 - \gamma_2^2)/(\gamma_1 - \overline{\gamma})$$ (3.42)

The calculations given above for the effective mass-parameters are semi-empirical and include the effect of d-core states.

The calculation of the effective mass parameters is usually in reasonable (46) agreement with experimental values. However, for the quaternary (In Ga) (As P) alloy the lack of experimental values is not a difficulty since the above calculations have been extended for the alloy.
Using the expressions given above, effective masses, $m_e^*$, $m_l^*$ and $m_h^*$ were calculated for the In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ alloy lattice matched to InP. The effective masses vary linearly across the alloy and are shown in Fig. 3.4 for the composition range $y = 0$ to $y = 1$. These calculations of the effective masses were particularly useful in calculating transport properties.

3.5 Effect of Pressure on the Band Structures of Quaternary Alloys

3.5.1 Effect of Pressure on the Energy Bands

A theoretical treatment of the effect of pressure on the band structure can be carried out on the basis of the band structure calculations shown in this chapter. This is important in understanding the observed variation in the electrical and optical properties of semiconductors under pressure. Hydrostatic pressure as opposed to uniaxial stress is usually the technique employed. Although hydrostatic pressure on a semiconductor retains the symmetry of the crystal axis, uniaxial stress (49) can cause the lifting of the degeneracy of the valence band maximum thus destroying the cubic symmetry of the crystal.

Paul and Drickamer (50-1), from the changes in the electrical properties of semiconductors, have shown that the pressure coefficients (relative to the valence band) were 12, 5, and -1.5 meV kbar$^{-1}$ for the $\Gamma$, L, and X points respectively as shown in Fig. 3.5. From their results they formulated a semi-empirical rule that was sufficient to explain the change in the electrical properties and was relatively independent of material. Since this early work there has been considerably more investigation of the properties of III-V compounds under pressure refining the earlier conclusions of Paul and Drickamer.
Fig. 3.4 Calculated composition dependence of the effective mass ratio of a) electrons, b) heavy-holes, and c) light-holes.
Fig. 3.5  Approximate pressure coefficients of $\Gamma$, $L$, & $X$ points
The pressure coefficients of the energy minima have now been measured to greater accuracy and also do in fact show a difference from compound to compound as shown (52) in Table 3.2, nevertheless, the relative magnitudes given by Paul and Drickamer remain unchanged.

The theoretical pressure coefficients can be obtained by differentiating, with respect to pressure, the expressions obtained for the energy band gaps. To explain the results of the pressure measurements on the quaternary laser in terms of the movement of the direct energy band gap, the pressure coefficient of the direct energy band gap is presented in chapter 6.

3.5.2 Variation of Effective Mass $m^*_e$ with Pressure

The parameters involved in calculating the effective masses $m^*_e$, $m^*_l$, and $m^*_h$ included the nearest neighbour distance, the energy band gap and the $D_{av}$ terms. These three parameters can be calculated as a function of pressure as discussed above and so the variation in the effective masses $\frac{m^*_e}{m_o}$ and $\frac{m^*_h}{m_o}$ with pressure were also accessible.

The effective mass $m^*_e$ of electrons in the conduction $\Gamma_{1c}$ band minimum, was given by equation (3.36). In the formula, $\Delta_o$ can be regarded as a relatively small correction to $E_o$ and its value can be safely regarded as a constant with pressure and equal to that obtained by linear interpolation of $\Delta_o$ for the binary constituents of the alloy. $M$ is the momentum matrix element coupling the conduction to the valence band. This is found to vary little from one III-V compound to another and may therefore be regarded as
Fig. 3.6 Normalized variation of electron effective mass with pressure

Table 3.2

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \frac{dE}{dP} )</th>
<th>( \frac{dE_{PL}}{dP} )</th>
<th>( \frac{dE_{RX}}{dP} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>14.2 ± 1.2</td>
<td>5</td>
<td>-1.5</td>
</tr>
<tr>
<td>GaAs</td>
<td>11.2 ± 0.5</td>
<td>-</td>
<td>-2.7</td>
</tr>
<tr>
<td>GaP</td>
<td>10.7</td>
<td>-</td>
<td>-1.1</td>
</tr>
<tr>
<td>InP</td>
<td>9.8 ± 0.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(ref. Martinez, G. 52)
constant over the small changes in lattice constant induced by pressure. The momentum matrix, \( M \), was determined using the experimentally measured values of \( m^* \) (53) and the measured direct energy band gap \( E_0 \) (54). The assumptions made to determine \( dm^*/dP \) are supported by direct measurements of \( dm^*/dP \) in GaAs using the magneto phonon effect (55). The calculated variation of electron effective mass with pressure is shown in Fig. 3.6 for two alloy compositions up to 10 kbars.

3.5.3 Variation of Effective Hole Masses with Pressure

In Section 3.4 the heavy-hole mass and light-hole masses were calculated for the quaternary \( \text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y}/\text{InP} \) across the alloy composition. The parameters involved in the calculations included the terms which were pressure dependent. These parameters were related in turn to the nearest neighbour distance and hence compressibility.

The Luttinger valence band parameters \( \gamma \), \( \gamma_2 \) and \( \gamma_3 \) given by (3.20), (3.21), and (3.22) were defined by combination of \( F \), \( G \), \( H \), \( H_2 \), and \( q \) which can be expressed in terms of the interatomic spacing. Thus the variation of Luttinger parameters with pressure, were accessible. Having established the variation of the Luttinger parameters with pressure, the changes in the effective masses of the valence band were possible from the relation (3.39) and (3.40). Using these expressions the calculated values for \( m^* \) and \( m^* \) are shown as a function of pressure in Fig. 3.7 for \( y = 0.64 \), and \( y = 0.9 \).

The calculation of the effective masses are particularly useful in studying their dependence on scattering mechanisms as shown in
Fig. 3.7a Normalised variation in the heavy-hole mass with pressure

Fig. 3.7b Normalised variation light-hole effective mass with pressure
Chapter 7. The values of the various effective masses together with their pressure dependence are also useful in Chapter 8 for the analysis of the effect of pressure on the 1.3 μm quaternary laser.
4.1 Introduction

Although several III-V quaternary alloys may be grown on binary semiconductors \(^{(12)}\), for longer wavelength heterojunction lasers \(\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}\) grown lattice matched to \(\text{InP}\) is at present the most important. This quaternary alloy can also be grown lattice matched to \(\text{GaAs}\). The attainable energy band gap range of \((\text{Ga In})\text{(As P) quaternary on GaAs is comparable to that of the (Ga Al) As ternary, and is of interest for visible lasers. The quaternary alloy (Al Ga) (As Sb) can also be used to fabricate\(^{(56)}\) lasers in the 1.0 – 1.7 \(\mu\text{m}\) wavelength range, but the (In Ga)(As P) laser is preferred because it employs \(\text{In P}\) confining layers whereas the (Al Ga) (As Sb) requires quaternary alloys for confinement.

Various growth techniques have been developed including liquid-phase epitaxy \(^{(57)}\) (LPE), vapour-phase Epitaxy (VPE), organometallic chemical vapour deposition (OM-CVD), and also molecular beam epitaxy (MBE). The LPE technique is at present the most successful in terms of better quaternary (In Ga) (As P) heterostructure laser characteristics \(^{(2)}\), than some of the other growth processes. This is followed by VPE \(^{(56)}\) while OM-CVD and MBE growth techniques are relatively new for the synthesis of the lasers.

The \((\text{Ga In})(\text{As P})\) quaternary alloy was grown by the author using the LPE technique only. The other growth techniques described here are for comparison only. Thus here emphasis is placed on LPE growth of \(\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}\) alloys on \(\text{In P}\) substrates, and indicating the parameters controlling the lattice matching, energy band gap and also the surface morphology. The temperature at which epitaxial layers are grown is one of the main factors in controlling the above properties.
However, there are reports of limitations on the growth temperatures which (63, 64) indicate presence of immiscibility domain. The possibility of the existence of an immiscibility domain is also discussed in this chapter.

4.2 Liquid phase Epitaxy (LPE) of (In Ga)(As P)

There are a number of advantages of growing III-V compound semiconductors using the LPE technique over the other growth techniques such as VPE, MBE, etc. The simplicity of the LPE growth apparatus is an advantage. The LPE technique is less hazardous than VPE and MBE which often make use of highly toxic, explosive or corrosive materials. The LPE technique does not require a low pressure chamber and has the ability to produce higher growth rates.

One of the disadvantages of LPE was the lack of accurate reproducibility, especially for complex compounds. However, with the improvement in technology, where automatic furnaces have been introduced (58), very complicated structures are being grown with a high degree of consistency. As the LPE growth can be achieved over a large temperature range, the homogeneity of the epitaxial layer can vary in the direction of growth. However, the difficulties in obtaining very thin layers have, to a certain extent, been overcome by the automation of the LPE furnaces.

The first basic LPE growth technique (59) was the "tipping" furnace in which the layer is grown when, by tipping the furnace, the solution-substrate contact is obtained. The next stage in the development of the LPE growth technique was the introduction of the vertical furnace, in which the substrate is "dipped" into the solution.
Using the vertical furnace heterostructures can be grown in which the substrate is dipped for subsequent layers. The most important improvement in the LPE growth system has been the introduction of the horizontal slider technique which makes use of a graphite boat. This was the system used in the present work and will be described in more detail.

4.2.1 The horizontal slider technique

The quaternary alloy Ga$_x$ In$_{1-x}$ As$_y$ P$_{1-y}$ across the composition (57) were grown on semi-insulating Fe-doped (100) In P using the horizontal furnace containing Pd-diffused H$_2$ and a graphite boat with a single-well slider. The slider (Fig. 4.1), in addition to the single well, incorporated a recess underneath it which housed a large In P cover slice for the In P substrate during the heating-up period. The purpose of the cover slice was to limit the amount of thermal erosion of the substrate and thus neither a buffer layer nor an In etch melt was necessary. In order to reduce substrate defects and contamination, the substrate was etched in 1% Br-CH$_3$OH solution, and washed in solvent before loading into the boat. A fixed hopper above the slider held slightly more In P than was required for saturation. The other two source materials In As and Ga As and the In metal were loaded into the well in the slider. As the furnace was heated up the In As and Ga As dissolved and subsequently a small displacement of the slider allowed the In P to fall into the melt. The melt was step cooled from 679°C to a growth temperature of 659°C and the slider was moved so as to bring the supersaturated melt over the substrate, and left for 10-15 mins which resulted in 5-10 µm of epitaxial layer. After growth the melt was moved off and left to cool.
Fig. 4.1 Single well graphite boat for LPE growth of quaternary alloy
4.2.2 Cooling Techniques for LPE Growth

There are four main LPE growth techniques \((60, 61)\): step-cooling, equilibrium cooling, supercooling, and the two-phase-solution technique. Each of these techniques governs the thickness of the LPE layers and this is dependent on growth time, temperature, cooling rates, etc. The analysis of the four techniques is based on the assumption that the growth rate is determined by the rate of solute diffusion toward the substrate-melt interface.

The growth of the quaternary \((n = 4)\) alloy \((\text{In Ga})(\text{As P})\) from an In rich solution requires \((n - 1)\) three diffusion equations given by

\[
\frac{\partial x^i_s}{\partial t} = D^i \frac{\partial^2 x^i_s}{\partial s^2} \tag{4.1}
\]

where \(x^i_s\) stands for the particular liquid composition of Ga, As, or P, in the melt at position \(s\) at time \(t\). \(D^i\) is the diffusion coefficient of each component. The assumption before growth is that the melt is homogeneous, i.e., \(x^i_s(s, 0)\) is a constant and thereafter the boundary conditions are dependent on the growth techniques.

The growth rate of the epitaxial layer can be calculated using the conservation of mass where the atoms lost from the melt are gained by the solid at the melt-substrate interface. Hence,

\[
D^i \left| \frac{\partial x^i_s}{\partial s} \right|_{s=0} + |x^i_s(o, t) - x^s(o, t)| \frac{de}{dt} = 0 \tag{4.2}
\]

where \(x^i_s(o, t), x^s(o, t)\) are the liquid and solid concentrations respectively at \(s = 0\) (interface). The epitaxial thickness and the
growth rate are \( e \) and \( \frac{de}{dt} \) respectively. The solution of these equations with the appropriate boundary conditions for the four cooling techniques results in the determination of the epitaxial layer thickness.

### 4.2.3 Step Cooling

For the step-cooling growth technique the growth temperature \( T_g \) is given in equation (4.3)

\[
T_g = T_1 - \Delta T_0
\]  

(4.3)

and \( x_1^i(o,t) = \text{constant} \), where \( T_1 \) and \( \Delta T_0 \) are the liquidus temperature and the temperature step from \( T_1 \) respectively.

The thickness of the epitaxial layer grown is given by

\[
e = K \cdot \Delta T_0 \cdot t^{\frac{1}{2}}
\]  

(4.4)

where

\[
K = \frac{2}{\sqrt{\pi}} \cdot x_1 \int_{-1}^{1} \frac{\partial T}{\partial x_1^i} \left[ x_1^i(o,t) - x_1^i(o,t) \right]^{-1} \left[ x_1^i(o,t) - x_1^i(o,t) \right] \left[ x_1^i(o,t) - x_1^i(o,t) \right] dt
\]

(4.5)

### 4.2.4 Equilibrium-Cooling

For the equilibrium cooling technique the growth temperature is

\[
T_g = T_1 - R t
\]

and

\[
x_1^i(o,t) = x_1^i(s,o) - \left[ \frac{R}{m} \right] t
\]

(4.6)

where \( R \) is the cooling rate and \( \frac{1}{m} = \partial x_1^i(o,t)/\partial T \).
The thickness of the epitaxial layer grown by equilibrium cooling technique is

\[ e = \frac{2}{3} K \cdot R \cdot t^{3/2} \]  

(4.7)

where \( K \) is given by equation (4.5).

4.2.5 Supercooling

The growth temperature for the supercooling technique of LPE growth is given by

\[ T_g = T_1 - \Delta T_0 - R \cdot t \]  

(4.8)

Thus the supercooling technique is a combination of equilibrium-cooling and step-cooling techniques. Hence the epitaxial layer thickness grown by supercooling techniques is given by

\[ e = K(\Delta T_0 t^{1/2} + \frac{2}{3} R t^{3/2}) \]  

(4.9)

4.2.6 Two-phase-solution

The two-phase-solution technique is similar to the equilibrium-cooling method, except for the excess piece of In P on top of the melt. Growth is initiated after a temperature is reached far enough below \( T_1 \) for precipitation to occur (thus there are two phases in the melt-substrate system). As there are a number of parameters, size, shape, etc. of the precipitates it is not possible to predict a theoretical expression for the thickness of the epitaxial layer.

Typical thickness as a function of time of growth are given in [75] Fig. 4.2 for the step, equilibrium and the supercooling methods of
Fig. 4.2  Thickness versus time for three different growth cycles, as in the insets. (after de Cremoux 75)

Fig. 4.3  Isothermal sections of quaternary at three temperatures (immiscibility domains). Dotted lines represent the quaternary lattice matched to InP & GaAs. (after de Cremoux et al 64)
LPE growths. The inset against each curve indicates the temperature cycle used in the growths.

4.3 Other Characteristics of Quaternary LPE growth

The growth of a quaternary layer with a particular dopant can also be achieved. This is usually obtained by adding a small quantity of the elemental impurity or the impurity alloyed with Indium. However, the addition of the dopant results in changes in the distribution coefficients of the Ga, As and P. (Distribution coefficient is the atomic fraction in the solid to that in the liquid.) This effect changes both the energy gap and the lattice constant of the (Ga In) (As P) epitaxial layer for a given melt composition.

Lattice mismatch has considerable influence on device properties such as reliability, quantum efficiency etc. The amount of lattice mismatch for the quaternary alloy corresponds to the ratio of the difference in the lattice constants \( \left( a_Q - a_{InP} \right) / a_{InP} \).

Lattice mismatch for ideal LPE layers are less \((24)\) than \(\pm 1\%\), measured by x-ray diffraction patterns \((62)\).

A growth temperature of 659°C was used successfully to grow the \(In_{1-x}Ga_xAs_yP_{1-y}\) across the alloy composition. However, as a result of lower growth temperatures of 590°C, perhaps to eliminate the effect of meltback, there is reported \((64)\) to be considerable difficulty in growing LPE layers around the 1.3 \(\mu m\) to 1.4 \(\mu m\). This region expands if the growth temperature is further decreased to 570°C. The region of quaternary alloy, in which growth difficulty is experienced for a given growth temperature, is the immiscibility region. Fig. 4.3 shows the possible immiscible domain \((65)\) in the (Ga In) (As P) alloy for three temperatures. It is the region
of the domain between the intersection of the isotherm and the straight line of compositional lattice matching to In P and Ga As. Takahei et al. (65) found that the immiscibility is not so large as that de Cremoux et al have predicted. Takahei et al. found that the LPE growth of the quaternary is limited (65) at 580°C due to the low solubility of P, while at 750°C there was decomposition of In P substrate.

4.4 LPE Growth of Double Heterostructure (Ga In) (As P)/In P

Multilayer structures for double heterostructure lasers for use in this work (14, 66), were grown with a five-well graphite sliding boat Fig. 4.4 similar to the one used for the single quaternary layer growth Fig. 4.1.

The growth preparation was similar to that for the single layer growth with additional features including an etch melt used to remove about 20 µm in 20s, and excess In P in the quaternary melt to ensure two-phases of In P during growth. The temperature cycle for the LPE growth of a three layer structure is shown in Fig. 4.5. The temperature at which In P layers are grown does not influence the composition. The quaternary layers were grown at 659°C. The n-passive layer, and the p-passive layer were doped with Sn and Zn respectively, while the quaternary active layer was nominally undoped.

Broad contact DH lasers were usually cut initially to characterise the structure before stripe lasers were fabricated. The fabrication of the stripe-geometry laser by STL was usually carried out from a heterostructure slab that showed good broad contact laser characteristics. The Oxide-defined stripe contact is obtained by depositing SiO₂ on the p-In P confining layer (or on a p⁺ quaternary contact layer - as sometimes used) and opening 20 µm-wide stripes using
Fig. 4.4  Multiwell graphite boat for laser structures

1. In etch melt
2. In + InP + Sn
3. In + InAs + GaAs
4. In + InP + Zn
5. In + InAs + GaAs + Zn (all optional)
6. InP cover slice
7. InP in hopper for melt 3
8. InP substrate

Fig. 4.5  Temperature cycle for growth of laser structure
In_{1-x}Ga_xAs_{1-y}P_{y} for C.W. operation at \( \lambda = 1.3 \) \( \mu \)m

**Fig. 4.6** Schematic diagram of the 1.3 \( \mu \)m quaternary stripe laser structure
standard photo lithographic procedures. The slices are then reduced in thickness to 100 μm by etching and polishing the substrate. The thinned slices are then contacted by alloying evaporated Au/sn and Au/zn into the n- and p-sides respectively. Further Au deposition layers are made on both sides before being cleaved and sawn into laser chips of 250 - 500 x 100 μm. A typical stripe-geometry laser is shown in Fig. 4.6 with a 20 μm stripe.

4.5 Vapour Phase Epitaxy

Typical VPE technology uses open tube systems (Fig. 4.7) in which some source chemicals are gaseous at room temperature. This is an added advantage since this allows high flexibility in introducing dopants into the material as well as control of composition gradients by accurate flow metering. For n-type III-V material H₂Se is used for Se doping for example, while using elemental Zn for p-type doping. Heterostructures with the n or p-type of doping can be grown simply by shifting from one gas flow to another with appropriate valves without removing the material from the reactor. Many of the III-V binary compounds are grown by this technique, however one of the difficulties encountered is the preparation of Al containing alloys because of the adverse reaction the vapours have on standard equipment used.

The hydride VPE (56) growth of (Ga In)(As P) alloy may involve the chemical reaction HCl + Ga + AsH₃ + In + PH₃ + H₂. The metal chlorides are formed by passing HCl over In and Ga metals (which are held at high temperatures). The chlorides would then be mixed in the 'mixing zone' with the Arsine and phosphine brought in through a separate tube (56). P-type doping can be achieved by passing H₂ over heated Zn, while n-type doping can be achieved by introducing, for
example H$_2$S or H$_2$Se to the group V line. The growth on the In P substrate, is initiated after preheating of the substrate to a few degrees below growth temperature in a phosphine atmosphere (in order to minimise decomposition effects). The substrate, after loading into the mixing zone, would be rotated continuously during growth in order to smooth out any non-uniformities in temperature or gas flow. The growth is terminated by withdrawing the substrate from the mixing zone. Growth of heterostructures is achieved by isolation of the substrate away from the growth zone while the subsequent layer reactant flows are adjusted, before the substrate is reloaded and growth is initiated. This is repeated until the desired multilayer structure is obtained. The task of VPE multilayers is of course simplified and improves reproducibility due to the automation.

The In P substrate defect density governs to some extent the defect density of the VPE layers since substrate defects can propagate into the epitaxial layers. Thus the In P substrate surface morphology is extremely critical in the VPE growth of In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ alloy since the final epitaxial surface will be of no higher quality than the initial starting surface. Good quality VPE (In Ga)(As P) quaternary alloys have been grown by Olsen et al (56) using growth temperatures between 650°C and 700°C and with a variety of gas flow conditions.

4.6 Organometalic Chemical Vapour Deposition

Although the OM-CVD is a relatively new technique it has been reported (67) to be used in the growth of In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ alloys.
Fig. 4.7 Sketch of a VPE growth system

Fig. 4.8 Sketch of an MBE growth system for GaAs (GaAl)As heterostructure
The lasers produced from these OM-CVD alloys show comparable \((67)\) device characteristics to LPE devices. \((2)\) In this OM-CVD technique decomposition of organometallic compounds are used as a source of group III elements and arsine and phosphine hydrides as the sources of group V elements. Most of the organometallic compounds are moderately volatile liquids at room temperature and decompose at several hundred degrees centigrade. The compounds are transported into the reaction chamber in dilute vapour by bubbling \(H_2\) through at \(0^\circ C\), and the walls of the chamber do not require heating. However, the substrate is heated between \(550-700^\circ C\) for epitaxial growth as a result of the decomposition of both sets of organometallic and hydride elements. As in VPE, doping can be introduced into the reactant gas streams, (e.g. Organometallic \(Zn(C_2H_5)_2\), or hydride \(H_2S\)).

The \((\text{In Ga})(\text{As P})\) lasers grown by Hirtz et al \((67)\) using low pressure MO-CVD obtained a value of \(80K\) for \(T_o\) in the threshold temperature dependence \(\exp(T/T_o)\), which is slightly better than the \(60-70K\) values obtained with LPE. However, the test of long lifetime of these lasers grown by MO-CVD has to be proven to be reasonable compared to those lasers grown by LPE.

4.7 Molecular Beam Epitaxy (MBE) of \((\text{In Ga})(\text{As P})\)

The MBE growth technique, like the MO-CVD, is a relatively new technique for growing the quaternary \((68)\) \((\text{In Ga})(\text{As P})\) lasers. The technique has capabilities of preparing complex multilayer heterojunction structures with extreme control.

The main feature of the MBE growth technique is the growth of epitaxial layers by impinging thermal beams upon a heated substrate
under ultra-high vacuum conditions. As the growth is carried out using individual atoms or molecules impinging on the surface of the substrate the epitaxial growth rate are relatively slow in comparison to the other growth techniques, and varies from less than 0.1 to 2 μm/hr. However this slow growth actually allows very precise layer thickness control over a large area.

The molecular and atomic elemental beams are generated by heating the source, usually in separate effusion ovens (Fig. 4.8). The MBE reactor has a number of features that allow detailed as-grown characteristics to be studied and as a result real time adjustments to the conditions can be obtained for the desired growth.

During MBE growth of the (In Ga)(As P) heterostructure, a difficulty is reported \(^{(68)}\) in reference to the p-doping of the In P confinement layer. The typical p-type dopants used for In P, viz, Cd and Zn do not stick on the In P surface during MBE growth, however a limited success is obtainable with Be, Mg as p-dopants. This difficulty can be overcome by post diffusion after MBE growth, but this is an added process that the other growth techniques do not suffer from.
CHAPTER 5
HIGH PRESSURE EXPERIMENTS

5.1 Introduction

In this chapter the pressure system and the measurement techniques are presented. The hydrostatic pressure apparatus used for this work was a piston and cylinder system designed for pressures up to 8 kbars. Greater pressures can be obtained with a larger piston diameter (16 kbars) similar to the piston of the equipment sited at STL. Greater pressures can be obtained by using solid pressure transmitting media such as epoxy or Na Cl etc. These systems produce non-hydrostatic stresses below about 15 kbars but the media then begins to flow and produce a good approximation to hydrostatic pressures allowing pressures greater than 100 kbars to be achieved. For the 8 kbar piston and cylinder system modifications were carried out to allow optical measurements and high temperature measurements.

The effects of pressure on the 1.3 µm quaternary lasers require knowledge of the effect of pressure on the band structures of the alloy. Hence the programme for experimental study included the measurement of the effect of pressure on the band gap using the photoconductivity technique. The effect of pressure on the transport properties were examined by Hall measurements. And the effect of pressure on the lasers was obtained from the measurements of the light-current characteristics and the shift in their operating wavelength with pressure. All these measurements required different sample preparation, and in the case of laser measurements, a laser mount was designed to be installed inside the pressure chamber.
5.2  The Piston And Cylinder System

5.2.1  The Piston and Cylinder

Figure 5.1 shows schematically the piston and cylinder apparatus used for the pressure dependence study. The cylinder was made of hot-worked die steel and was pressed into a steel ring on a tapered angle. The outer ring was held down by steel straps to prevent it rising on unloading. Safety spacers were also placed between the ring and die to prevent crushing if sudden leakage of the pressure transmitting fluid occurred.

The two pistons were of 2.5 cm in diameter, as shown in Fig. 5.2 and were made out of hardened tool steel. Electrical leads to contact terminals at the end of each piston were passed out of the pressure chamber via hardened silver steel terminals ground into the ceramic sleeves and then through a hole in each piston. Although the paths of the electrical leads through the piston provide regions of stress concentrations nearby reducing the pistons compressive strengths, it was expected that the extrusion of the silver steel terminals down the hole would be the most serious limitation of this design at high pressures. Each piston face was capable of accommodating eight silver steel terminals which were evenly distributed around the piston face. To the bottom piston a manganin gauge was installed, at the centre, occupying two of the eight terminals, and a heating coil with power distributed over four terminals because of the miniature cables used in the piston. The heating coil inside the piston and cylinder pressure chamber had to be insulated by a PTFE sheath to avoid shorting problems. Typical power consumption of the coil was about 30W and the maximum increase in temperature above room temperatures was 50°C. A secondary heating source was available in the form of a
Fig. 5.1  Schematic diagram of the piston & cylinder hydrostatic pressure system

Fig. 5.2  Detailed diagram of thrust piston
heating tape around the outside of the cylinder which would allow temperatures to be raised to about 100°C inside the pressure chambers. However, considerable care has to be taken when pressurizing at high temperatures, as there is increased possibility of leakage at lower pressures. One possible remedy was to use two 'O' rings instead of the single one employed under room temperature operation. The top piston also houses eight silver steel terminals of which two are occupied by the thermocouple and a small toroidal magnetic field system occupy another pair. The four remaining terminals are available for clover leaf samples used in the Hall measurements.

5.2.2 Optical Window

The thrust piston described above is suitable for electrical measurements such as Hall measurements. However, when optical measurements are required a window has to be created for light to pass through the piston and into the pressure chamber. Figure 5.3 shows schematically the thrust piston with such an optical window. A 1 cm diameter sapphire crystal is sealed to the piston end face using a single layer of aluminium foil and held in position by a small cylindrical frame. Pilkington optical fibres were used to guide the light to and from the window.

Five single optical fibres with 0.5 mm diameter were fitted into the 1.5 mm diameter hole in the piston. The ends of the fibres were cleaved in order to achieve better transmission properties. However, attempts to increase the area of the optical fibre bundle using a large number of fibres of smaller core diameter 0.08 mm posed considerable difficulty due to breakages and loss in fibre flexibility. A system now being developed for use in the piston and cylinder
Fig. 5.3 Piston & cylinder system with optical light path through the top piston.
device. consists of a single optical fibre emerging directly from
the pressure chamber without the need for the sapphire crystal. This
will allow samples to be butted directly to the end of the fibre.

Another modification from the conventional piston was the
introduction of coaxial cable into the piston rather than the single
core cables. Thus either DC or fast (n-sec) electrical pulse
measurements were possible.

5.2.3 Pressurization

The pressure transmitting medium (69) used here for the 8 kbar
pressure range was castor oil although 1:1 mixture of amyl alcohol
and castor oil medium is an alternative.

The sealing between the piston and cylinder is accomplished by
the combination of a neoprene 'O' ring and a phosphor bronze ring.
Up to a pressure of 4 kbar sealing is due to the 'O' ring. At higher
pressures the 'O' ring becomes redundant and sealing is due to the
expansion of the bronze ring. Leakage is sometimes observed between
4-6 kbars. This is the region where the operation of both rings is
at its most inefficient. A possible method to avoid this is to
accelerate the operation of the bronze ring by increasing the pressure
quickly past the 4-6 kbar pressure range. Once the seals have been
brought into operation without leakage pressure can be decreased or
increased. A backing pad, with a 'U' groove milled in it to accommo­
date the electrical leads is used on top of the piston. The
possibility of air traps is minimised by over filling the cylinder
and allowing the excess of the liquid to leak out when the piston is
lowered. Each pressure increment is accompanied by a change in
temperature. This can be monitored by the thermocouple inside the
pressure chamber, and it is found that thermal equilibrium is achieved within 15-20 minutes and only then are any measurements carried out. Loading was achieved by a 60 ton hydraulic system or more recently a hand operated bench top hydraulic system which consisted of an expanding ram against another fixed die set. The two forms of loading are shown schematically in Fig. 5.4. Both methods produced a linear load against pressure curve as shown in Fig. 5.4. The pressure was monitored by a manganin gauge located inside the pressure chamber and attached to the bottom piston. The manganin wire has a \((\text{抵抗} \cdot \text{压强}) = 0.2743 \text{kbar}^{-1}\) pressure dependence of resistance and hence pressures within the cell can be accurately measured. The pressure as given by the manganin gauge was found to agree with experimental error with the ratio load/area of the piston indicating minima loss of load to frictional forces.

Although most of the pressure measurements were obtained using the piston and cylinder systems, for pressures in excess of 8 kbars the opposed Bridgeman anvil apparatus shown in Fig. 5.5 can be employed. The high pressure cell was based on the MgO loaded epoxy anulus described by Pitt \((70)\) but various adaptations were employed. To obtain hydrostatic conditions at low loads and to facilitate retrieval of the sample for further measurements the sample was sometimes simply surrounded by liquid uncured epoxy. A further adaptation was the use of smaller diameter gaskets with dimensions of 9mm outer diameter, 3mm inner diameter and 1.2mm thickness. With these, pressures of 33 kbars were obtained using a bench top apparatus and a hydraulic hand pump. The most important development was again the introduction of optical fibres. Single optical fibres were sometimes introduced through the circumference of the cell but for the system developed here a permanent optical path through an optical
Fig. 5.4  Calibration curves for two different loading system
a) 60ton loading system as shown in inset  b) bench top hydraulic pump as shown in inset
fibre bundle passing through the lower anvil was preferable as shown in Fig. 5.5.

5.3 High Pressure Photoconductivity Measurements

The pressure coefficient of the band gap is of considerable importance because it can be related to the pressure dependence of the threshold current of the quaternary laser. It can also be used in the analysis of scattering mechanisms in the LPE quaternary material. The LPE In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ quaternary alloy grown on semi-insulating InP used in this work was described in Chapter 4. The sample configuration used for photoconductivity measurements was usually a clover leaf prepared for Hall measurements as described below. The crystals were thoroughly cleaned in warm Methanol to dissolve any grease and then transferred into warm Trichloral Ethylene to remove any other deposits that may have accumulated prior to preparation. Indium contacts to the epitaxial layer were made using a hot soldering iron. The contacts were then alloyed in a hydrogen atmosphere at a temperature just above the melting point of the contact material for approximately two minutes. Most of the samples studied had carrier concentrations of $10^{16}$ cm$^{-3}$ with epitaxial layers of 5-10 μm thickness. The sample would then be placed in front of the sapphire window with electrical leads soldered on to the contact pins located around the piston. All the photo-conductivity measurements were carried out at room temperature.

The concept of photoconductivity has been reported (71-2) by many authors. The use of the photoconductivity method used here for the pressure measurements is shown as a block diagram in Fig. 5.6 (a). A tungsten lamp was an adequate light source for the spex grating monochromator which had an accuracy of ±1nm.
Fig. 5.5 Opposed Bridgman apparatus with an optical fibre window
Fig. 5.6a Experimental set up for photocoductivity measurements under pressure.

Fig. 5.6b Monochromator output (measured by a flat Unicam detector) versus wavelength using diffraction gratings blazed at 1 μm & 2 μm.
Using grating blazed at 1 μm and at 2 μm the effective range of the monochromator is 0.5 to about 2.5 μm. Figure 5.6 (b) shows the characteristic output of the monochromator using 1 and then 2 μm grating as measured by an IR (Unicam IR 50) detector. The monochromator had a facility that allowed continuous wavelength scan and hence the photoconductivity spectra were obtained, at each pressure, with a constant scan rate.

As with most photoconductors (73) an external bias of some kind is required. Hence a small constant electric field was applied across the sample while AC photoconductivity spectra were recorded by detecting the changes in voltage across a series resistor. The incident light radiation from the grating monochromator was chopped at a fixed frequency in the range 15-200 Hz and the subsequent AC photo-signal generated in the sample was detected on a Brookdeal preamplifier phase sensitive detector. No dependence of the shape of the spectra upon the electric field nor upon the chopping frequency was detected and they were only adjusted to obtain the best signal to noise ratio. It was necessary to take considerable care to eliminate higher-order radiation from the grating by the use of IR filters. Photoconductive spectra were recorded at each pressure increment and the shift in the photoconductive edge was used to determine the pressure coefficient \( \frac{dE_0}{dp} \). The configuration of the \((\text{In Ga})(\text{As P})/\text{InP}\) sample with respect to incident light, from the monochromator was an important factor. Light incident on the quaternary epitaxial layer produced a single photoconductive edge. Light incident on the InP substrate resulted in two edges. First there was the rise in photoconductivity at the band gap of the quaternary followed by a swift decrease at higher photon energies corresponding to the absorption edge of the InP.
5.4 Sample Preparation

The clover leaf samples were either cut by a standard photoresist and etching technique or by an ultrasonic cutting tool. Briefly, the former etching process involves coating the epitaxial layer with a positive photoresist (Shipley AZ B50H). After pre-baking, the sample is exposed to ultra-violet light with the negative clover leaf mask on the sample. On developing, the unexposed resist is removed. The remaining photoresist is further hardened by baking before the sample is etched in $H_2SO_4$, $H_2O_2$ and $H_2O$ in the ratio 1:1:7 at 50°C to remove the epitaxial layer and some of the substrate around the leaf. The sample, after etching, is washed and the photoresist removed with acetone to reveal the clover leaf pattern.

The ultrasonic technique involves cutting a clover leaf shape sample with a cylindrical tool made out of brass and mounted on an ultrasonic vibrator. The sample slice is fixed with the substrate face down on a transparent slide with shellac wax. Cutting is carried out with an abrasive mixture of fine tungsten carbide granules and water brushed on the area to be cut. Considerable care is required when using this method, especially monitoring the distance the tool travels before cutting past the sample and into the slide holder, causing breakage of the sample. Breakage also results from cutting at high speed.

Contacts to the samples were carried out by a metallic evaporation process with a fine aluminium foil mask which exposed only the pin holes on each lobe. On n-type material a layer of Au with 5% Sn was evaporated followed by a thin film of Ni to ensure that the contacts would stick to the surface before alloying at 450°C for about five minutes to produce good ohmic contacts. A similar process was used for p-type material with Au + 5% Zn alloy contacts. To overcome the
depletion of phosphorus from the samples due to its high vapour pressure at high temperatures, alloying was carried out in a glass capsule lined with InP. The epitaxial layer had an InP cover slice also to compensate any depletion of phosphorus.

A special problem exists for Mn-doped quaternary alloy in that the contacts do not remain ohmic at low temperatures. Although low temperature and pressure measurements are not the subject of study in this work it is of some importance in making contacts to quaternary alloys. A process similar to that used for InP and Ga As involves ion implantation and laser annealing to overcome the non-ohmic contact behaviour. Briefly, the procedure involves irradiating the contact area on the sample, with appropriate masking, with a dose of $1 \times 10^{15}$ cm$^{-2}$ of 150 keV Zn-ions at 80° to the surface normal to avoid channelling. Because of the possibility of disordered material produced at a depth of about 3μm by the implantation process, samples can be laser annealed with energy density of about 0.8 J cm$^{-2}$ of Q-switched Ruby laser. Contacts made using this technique remained ohmic down to liquid nitrogen temperature.

5.5 High Pressure Hall Measurements

Pressure dependent measurements of the electron and hole mobilities were carried out on the $\text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y}$ alloy lattice matched to InP. The standard Van der Pauw (74) technique was used for both resistivity and Hall voltage measurements. The clover leaf sample configuration and the circuit used for these measurements are shown in Fig. 5.7. A constant current was passed through the sample and a 10 kΩ resistance box in series. A standard 1Ω resistor is also incorporated in the circuit with a digital multimeter across it to
Fig. 5.7  
(a) Resistivity & Hall measurement circuit  
(b) Clover leaf sample configuration
monitor the sample current. The output from the sample was measured by a Keithley digital multimeter. A 4-port/12 terminal switch was introduced in the circuit, which allowed measurements to be made across different lobes around the clover leaf with forward and reverse current.

The Hall voltage, $V_H$, was measured in the presence of a magnetic field. The magnetic field was supplied by a coil wound around a toroid of high quality mild steel and fixed on the thrust piston end as shown in Fig. 5.2. The coil was made of 870 turns of 0.18mm enamelled copper wire, with a resistance of 23.4 Ω. A current of 55mA produced a magnetic field of $B = 1 + 0.03$ k Gauss across the 0.75 mm toroid gap. At this low current heating effects on the coil resistance were negligible. The field was assumed to be uniform at the centre of the pole faces, which has an area of $(2.0 \times 1.8)$ cm$^2$. The effect of pressure on the toroid magnetic field has been reported to be negligibly small, and not more than 0.4%.

The Hall constant, $R_H$, and the carrier density, $n$, were determined from the relation

$$R_H = \frac{V_H t}{B I} \approx \frac{1}{ne} \quad (5.1)$$

where $t$ is the sample thickness, $I$ is the sample current. The average of four Hall voltage readings, with the reversal of sample current and magnetic field was taken to cancel out the extraneous voltages due to any contact effects. For resistivity measurements the average of eight readings, with current reversal, was taken without the magnetic field and the resistivity was then calculated by the formula
\[ P = \pi t \left[ \frac{V_{AB, CD} + V_{BC, DA}}{\ln(2)} \right] f \left[ \frac{V_{AB, CD}}{V_{BC, DA}} \right] \] (5.2)

where \( V_{AB, CD} \) is the voltage across CD due to the flow of current between A and B, Fig. 5.7. The factor \( f \) is called the non-uniformity function and is a function of the ratio \( [V_{AB, CD} / V_{BC, DA}] \). The magnitude of \( f \approx 1 \) is accurate to within 1\% for ratio less than 1.5. The Hall mobility, \( \mu_H \), was then calculated by the relation

\[ \mu_H = \frac{R_H}{\rho} \left( \text{cm}^2 \text{v}^{-1} \text{s}^{-1} \right) \] (5.3)

5.6 Pressure Measurements on (In Ga)(As P)/InP Lasers

5.6.1 Laser Mount

The laser is an optoelectronic device with cleaved ends acting as parallel reflecting surfaces. Therefore the most important factor in handling these laser chips is the possible damage to the facets. The usual technique of handling the chip is by hypodermic needle pump. However, with considerable care and attention the lasers can also be handled with a fine pair of tweezers, avoiding any contacts with the mirror end of the laser devices. Emphasis is also placed on the tweezer and the laser mount (described below) being clean and dry.

From the far field emission pattern of the stripe lasers the end of a laser chip has to be pointed towards the sapphire window for the light to be transmitted down the optical fibres and detected externally. The laser mount, built here for its use in the high
Fig. 5.8  Schematic diagram of the laser mount for use in the high pressure system.
pressure piston and cylinder apparatus, is shown in Fig. 5.8. The laser was held in position by a sprung metal tab to the base plate. The metal tab and the base plate also served as the two electrical contacts to the laser. The mount was then fitted around the sapphire crystal by a ring base. The screws allowed any adjustment in the position of the laser with respect to the optical window and also reduced any possibility of mis-alignment during pressurisation.

5.6.2 Laser Light Detectors

The choice of semiconductor detectors employed in detecting the laser radiation, whether quaternary or (Ga Al)As, depends on the operating wavelength of the laser. Fig. 5.9 shows the absorption coefficient ($\mu\lambda$) against photon energy for (In Ga)(As P), (Ga Al)As, Ge and Si materials. It can be seen that beyond about 1 $\mu$m wavelength region, appropriate for the quaternary lasers, a germanium detector is suitable. However, at the wavelength of (Ga Al)As lasers a silicon detector is more favourable. Hence, the detectors adopted for the work presented here involved large area Ge and Si detectors for the 1.3 $\mu$m quaternary and (Ga Al)As lasers respectively. For lifetime measurements avalanche photodiodes would be more appropriate, with their fast responses.

5.6.3 Threshold Current

The light current characteristic of the semiconductor laser was measured as a function of pressure. A block diagram of the experimental layout is shown in Fig. 5.10 (a). The measurements were carried out under pulse operation with a generator with up to 50 ns pulse width and
Fig. 5.9 Absorption coefficient verses energy for 
(GaAl)As, (GaIn)(AsP) alloys, & the choice of Ge & Si 
detector range
Fig. 5.10a Block diagram of the apparatus employed in the measurement of the laser threshold current with pressure.

Fig. 5.10b Block diagram of the apparatus used in measuring the shift in the operating wavelength of the laser with pressure.

piston & cylinder

pressure

optical fibres

chamber

lens

spectrometer
detector

Ge or Si

pre-amp

pulse generator

phase shifter

phase sensitive detector

chart recorder

storage oscilloscope

x-y recorder

current probe

current pulse generator

fast low noise amp.
repetition rate of 1 kHz. The laser signal light, detected by the Ge detector, was fed into a dual beam storage oscilloscope via a fast low noise amplifier. The injected current pulse was detected by a Tektronix current probe and fed into the oscilloscope. The appropriate reference/trigger source from the pulse generator completed the inputs into the oscilloscope. With the two inputs, the storage oscilloscope was used to display the light-current characteristic of the laser. Hard copies of the characteristics were obtained on an x-y recorder.

The measurements of the light-current characteristics in these lasers, at each pressure, were obtained with increasing current. For consistency the current pulse amplitude on the pulse generator was increased automatically at a constant speed. The pressure system was sufficiently stable at most pressures to enable accurate determination of the threshold current from the light-current curves. Although, the laser was immediately inside the sapphire window with the optical fibre bundle conveying part of the laser emission outside to the detector, the fraction of the emission reaching the detector was not determined, hence the incremental quantum efficiency could not be assessed.

The measurement of the shift in the operating wavelength of the quaternary laser with increasing pressure was also carried out. The laser was pulsed with a constant excitation current just above the threshold current and the laser light output was detected via the spex spectrometer (used as a monochromator in photoconductivity measurements) with a 1 μm blazing. The optimum signal to noise ratio was obtained by chopping the laser light and feeding the output of the Ge detector through the Brookdeal pre-amplifier and phase
sensitive detector system as used for the photoconductivity measurements. The remaining experimental set up was as employed in the threshold current measurements.
CHAPTER 6

PRESSURE COEFFICIENT \( \frac{dE_0}{dP} \) of \( \text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y} \text{ALLOY} \)

ACROSS THE ALLOY RANGE \( y = 0 \) to \( y = 1 \)

6.1 Introduction

Pressure measurements are very useful in determining the band structure of semiconductors. Although a piston-cylinder device, described in Chapter 5, was used for the present work, Bridgman anvils and, more recently, diamond anvil systems have been used to study semiconductors under very high pressures. Various measurements have been reported for looking at the band structure under hydrostatic pressure. For example, absorption, photoluminescence, resistivity, and electroreflectance studies have been performed. The most direct and perhaps the simplest method of probing the band structure is by measurement of the absorption coefficients. The absorption measurements can be used to study a number of different transitions, for example band-to-band, band to impurity, exciton etc. Absorption measurements in semiconductors often require very thin samples (few microns). Absorption measurements would also require optical paths for both the incident beam and the transmitted beam.

In the past very little work has been carried out on the pressure dependence of the energy band gaps of semiconductor alloys. In an investigation of \( \frac{dE_0}{dP} \) for \( \text{Al}_x \text{Ga}_{1-x} \text{As} \) up to \( x = 0.5 \) aluminium composition, an interesting discontinuity has been reported by Lifshitz et al. They observed a steady increase in \( \frac{dE_0}{dP} \) up to \( d = 0.25 \) at which point there appears to be a discontinuous decrease.

In this chapter the pressure coefficient, \( \frac{dE_0}{dP} \) of the direct
band gap of quaternary In$_{1-x}$ Ga$_x$ As$_y$ P$_{1-y}$ lattice matched to InP has been determined from photoconductivity measurements. The photoconductivity technique exploits the change in conductivity in a crystal due to changes in the number of charge carriers caused by illumination. The magnitude of increase in conductivity due to photon absorption depends on the rate of generation and the lifetime of the carriers. The increase in conductivity is generally sufficient for direct band gap measurements, however difficulties arise when measuring deep level photoconductivity where often a decrease in temperatures is required to resolve the spectral peaks.

$dE_0$ was obtained from the shift in the photoconductive edge with pressure, for a given quaternary alloy composition and this is described in Section 6.2. The determination of $dE_0$ for quaternary and InP simultaneously is presented in Section 6.3. The latter procedure was extended for other alloy compositions and is described in Section 6.4.1. The measured $dE_0$ is compared, in Section 6.4.2, with interpolated values from binary $dE_0$ and calculated $dE_0$ values using the quantum dielectric theory presented in Chapter 3. A study of deep levels is presented in Section 6.5.

6.2.1 Measured Photoconductive Response

Using the experimental set up and the technique of photoconductive measurement described in the earlier chapter, one obtains a typical photoconductive response as shown in Fig. 6.1. This spectrum is of a quaternary with an alloy composition of $y = 0.11$. Other characteristics of this sample and some of the other samples
used are given in Table 6.1. With the experimental set up used here the horizontal scale displayed wavelength while the vertical scale gave the photoconductive response in arbitrary units. For the purpose of determining the shift in the absorption edge there was no need for absolute photoconductivity measurements. However, possible movements of the optical fibres, or fluctuations in the monochromator's output intensity could lead to misinterpretations.

The photoconductive spectrum in Fig. 6.1 was obtained with increasing wavelength. Thus, for energies above the lowest energy band gap (e.g. at A) the sample absorbs producing a photoconductive response. The photoconductivity edge B, is considerably sharper than any other structure observed. The sharp drop off in photoconductive signal at B can be used to estimate the energy band gap of the semiconductor. Alternatively the intersection of a straight line through the photoconductive edge and the wavelength axis as shown by Point C is sometimes used.

However, the shape of the photoconductivity response with pressure was found to be constant with pressure giving an accurate determination of \( \frac{dE_0}{dP} \) independent of the point A, B, or C chosen. Some aspects of the band tailing with respect to deep levels will be given in a later part of this chapter.

6.2.2 \( \frac{dE_0}{dP} \) of \( y = 0.11 \)

In determining the direct energy band gap pressure coefficient,
Photoconductive response

Fig. 6.1  Photoconductivity edge of InGaAsP/InP (y=0.11)

<table>
<thead>
<tr>
<th>Sample no</th>
<th>Alloy (y)</th>
<th>Mobility (cm²V⁻¹s⁻¹)</th>
<th>Dens. (cm⁻³)</th>
<th>Thickness (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF380</td>
<td>0.11</td>
<td>58</td>
<td>14.3 x 10¹⁶</td>
<td>6.8</td>
</tr>
<tr>
<td>5LE771</td>
<td>0.32</td>
<td>48</td>
<td>270</td>
<td>6.8</td>
</tr>
<tr>
<td>GW166</td>
<td>0.40</td>
<td>61</td>
<td>13</td>
<td>4.0</td>
</tr>
<tr>
<td>5LE821</td>
<td>0.50</td>
<td>75</td>
<td>3.4</td>
<td>4.9</td>
</tr>
<tr>
<td>GW86</td>
<td>0.64</td>
<td>77</td>
<td>3.4</td>
<td>4.0</td>
</tr>
<tr>
<td>GW167</td>
<td>0.80</td>
<td>117</td>
<td>6</td>
<td>8.4</td>
</tr>
<tr>
<td>SF325</td>
<td>0.96</td>
<td>109</td>
<td>0.71</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 6.1
the shift in the photoconductive edge was observed with increasing pressure up to 8 kbars. The method used to vary the pressure and the photoconductive technique were described in an earlier chapter.

A common procedure (84) for observing changes in the energy gap is to observe the variation of the photon energy at which the absorption edge reaches an arbitrary level. This was the technique employed but rather than observe an arbitrary level of absorption spectrum the energy at half maximum photoconductive peak of edge was used.

The shift in the photoconductive edge with hydrostatic pressure for a typical quaternary alloy is shown in Fig. 6.2. These photoconductive measurements were carried out at room temperature. It must be emphasised that as semiconductors are temperature sensitive with a typical temperature coefficient (85), \( \frac{dE_o}{dT} \), of \(-4 \times 10^{-4}\) ev K\(^{-1}\) for the quaternary alloy, changes in temperature within the pressure cell are important. In the piston and cylinder device the changes in temperature which accompanied each increment of pressure could be considerable (86). However the temperature was monitored using a thermocouple and it was found that the equilibrium room temperature was usually regained within a few minutes after loading.

The value of \( \frac{dE_o}{dP} \) was obtained by plotting the shift in energy of a particular point on the photoconductive edge against pressure. The slope represented the direct energy pressure coefficient of the quaternary alloy. The slope of the line was obtained by a least square fit. This is
Fig. 6.2  Photoconductivity edge of the quaternary at three pressures ($y=0.11$)

Fig. 6.3  Shift in photoconductivity edge of a quaternary with pressure. The line is a least square fit.
shown in Fig. 6.3. for a typical quaternary alloy where the solid line is by least square fit.

6.3.1 Simultaneous measurement of the Photoconductive Spectra of Epitaxial layer and InP Substrate

Chapter 4 gives an account of the liquid phase epitaxial (LPE) technique used in growing the $\text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y}$ quaternary epitaxial layer on a semi insulating InP substrate. The energy band gap and lattice constant contours of the $(\text{In, Ga})(\text{As, P})$ quaternary is shown in Chapter 1. As shown, the quaternary alloy grown lattice matched to InP has a smaller energy band gap than InP at all alloy compositions. This allows simultaneous observation of the photoconductivity edge of the quaternary epitaxial material and the absorption edge of the InP.

An example of the photoconductive spectra is given in Fig. 6.4. The spectrum was obtained using the configuration shown in the inset where light first passed through the InP substrate and the signal was detected by the contacts made on the quaternary epitaxial layer. For energy greater than the InP energy band gap, no photoconductive signal was observed since the substrate was opaque. As the incident photon-energy approached the InP band gap energy, and so began to transmit through to the quaternary, a photoconductive edge was detected corresponding to the InP energy band gap. As the photon energy band continued to decrease and approached the band gap energy of the quaternary a sharp decrease in photoconductivity was observed corresponding to the quaternary energy band gap. Although the sample with an alloy composition $y = 0.6$ resulted in photoconductive edges which were well defined, the quaternary samples with alloy compositions
Fig.6.4 Simultaneous observation of photoconductive edge of quaternary & substrate using the configuration in the inset. The dotted spectrum is at 8 kbar pressure.

Fig.6.5 Shift in photoconductivity edge of quaternary & InP with pressure. The lines represents the least square fit.
near the InP, because of small differences in $E_0$ (Chapter 1), required careful attention. Care had to be taken when measuring the photoconductive edges of the sample with composition near the ternary (Ga In)As where often a change in grating was required due to the larger difference between the two band gaps.

6.3.2 The Variation $\Delta E_0^Q / \Delta E_0^{\text{InP}}$ with Pressure

The purpose of the sample configuration adopted here was to enable the determination of the pressure coefficient of $dE_0$ of the quaternary alloy with respect to the pressure coefficient of InP. As will be discussed in connection with the pressure dependence of the heterojunction barrier in quaternary lasers, the relative pressure coefficients are of particular importance. The pressure coefficient of InP has been measured by many authors by different techniques. The pressure coefficient of InP obtained here by photoconductive technique was $8.5 \pm 0.5$ meV/kbar. This agrees, within the accuracy, with those values published elsewhere.

Having established the pressure coefficient of InP, the pressure coefficient of the quaternary alloy was determined knowing that the pressure calibration was correct and also removing any doubts about the effect of pressure on the interface between the substrate and the epitaxial layer.

In Section 6.3.1 a typical photoconductive spectrum of the InP and the quaternary layer was shown at two pressures. For the purpose of determining the two pressure coefficients a number of spectral traces were recorded at various pressures for a given sample. The shift in the band gaps with pressure for both the InP and quaternary
were measured by observing the movement of a point on each photoconductive edge. These shifts are plotted on an energy against pressure curve as shown on Fig. 6.5. From these \( \frac{dE}{dP} \) values of 8.5 \( \pm \) 0.5 meV kbar\(^{-1} \) and 9.4 \( \pm \) 0.5 meV kbar\(^{-1} \) were obtained for InP and In\(_{.69} \) Ga\(_{.31} \) As\(_{.67} \) P\(_{.35} \) respectively.

Besides the photoconductive edges of InP and the quaternary, the spectrum shows other structure. The interesting peaks between the photoconductive edges were due mainly to the characteristic of the grating and so remain fixed with pressure. The structure below the photoconductive edge, for transitions involving energies below the smallest direct band gap, may be due to the existence of deep levels. Section 5 has been devoted to the subject of energy levels within the band gap of the quaternary alloy and which might also be present in the quaternary laser.

6.4.1 Compositional dependence of \( \frac{dE}{dP} \)

The measurement of \( \frac{dE}{dP} \) of the direct energy band gap of the quaternary given in the above section was extended across the alloy composition and is shown in Fig. 6.6. The measured \( \frac{dE}{dP} \) varied from 8.5 for InP to 12 meV kbar\(^{-1} \) near the ternary (In Ga)As. The samples used for the photoconductivity measurements, shown on Table 6.1, were grown by LPE, mainly for general characterisation of the quaternary material for device applications.

The pressure coefficient \( \frac{dE}{dP} \) of the quaternary showed a gradual increase with increasing alloy composition, \( y \), with no indication of any deviation as seen by Lifshitz et al (81) for
Fig. 6.6 Measured pressure coefficient of the direct band gap. The dotted curve is derived by linear interpolation of the coefficients of the binary compound constituents. The full curve is calculated using the quantum dielectric theory of Phillips & Van Vechten.
Ga$_{1-x}$ Al$_x$ As. Lifshitz et al studied the direct energy band gap pressure coefficient of Ga$_{1-x}$ Al$_x$ As and observed an initial increase in $dE_o/dP$ up to $x = 0.25$ composition where there was a sudden decrease until at $x = 0.35$ a steady value was established up to $x = 0.5$ composition. Since the direct-indirect, $\Gamma$-X, band crossover appears around $x = 0.45$ composition, the absorption edge becomes somewhat ill defined at higher values of $x$. The quaternary In$_{1-x}$ Ga$_x$ As$_y$ P$_{1-y}$ lattice matched to InP is a direct band gap compound across the whole alloy composition (Chapter 1) and hence the photoconductive edge was well defined.

One of the characteristics of the measured values of $dE_o/dP$ especially near the $y = 1$ alloy composition is their large values in comparison with the values (52) of the binary compounds InP, In As, Ga As and Ga P given (52) in Table 3.2. The interpolated values of $dE_o$ from the binary constituents is shown as a dotted curve in Fig. 6.6, and shows the disagreement at higher alloy compositions. To explain this the analysis carried out in Chapter 3 using Phillips and Van Vechten's dielectric theory can be elaborated to calculate a theoretical $dE_o/dP$ curve for the quaternary alloy.

6.4.2 Theoretical determination of $dE_o/dP$

The interband energy separation at the $\Gamma$-point, $E_0$, including the effect of d-core states is defined from equation (3.4) as

$$E_0 = [E_{h,0} - (D_{av} - 1)\Delta E_0][1 + (C/E_{h,0})^2]^{1/2}$$  \hspace{1cm} (6.1)

where most of the terms depend on the nearest neighbour distance.
For example the homopolar part of the energy gap

\[ E_{h,0} = E_{h,0} \bigg|_{Si} (d/d_{Si})^{-2.75} \]. And since the quaternary alloy was lattice matched to InP the value of \( E_{h,0} \) was assumed to be equal to \( E_{h,0} \) of InP across the alloy range at atmospheric pressure.

The value of \( \frac{dE_{Q}}{dP} \) can be determined by differentiating the expression for \( E_{O} \) given in equation (6.1). This is given by Camphausen et al (37) as

\[
\frac{dE_{Q}}{dP} = \left[ 1 + \left( \frac{C}{E_{Oh}} \right)^2 \right] \frac{dE_{Oh}}{dP} - \frac{\Delta E_{O} \cdot d(D_{av} - 1) - (D_{av} - 1) \cdot d\Delta E_{O}}{dP} \\
+ \left[ 1 + \frac{E_{O}}{(E_{Oh}/C)^2} \right] \left( \frac{1}{C} \frac{dc}{dP} - \frac{1}{E_{Oh}} \frac{dE_{Oh}}{dP} \right)
\]

(6.2)

The atmospheric values of \( C, E_{O,h}, \Delta E_{O} \) and \( D_{av} \) for the quaternary \( \text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y} \) alloy was calculated using equations (6.1), (3.3), (as 3.3) and (3.9) respectively.

The magnitude of \( C \) at atmospheric pressure across the alloy composition for the quaternary alloy is shown in Fig. 6.7 (a). The compositional dependence of \( C \) was determined directly from the measured (54) value Fig. 6.7 (b) of the direct energy band gap \( E_{O} \), using equation (6.1). The pressure variation of \( C \) was assumed to be zero, i.e. \( \frac{dC}{dP} = 0 \). This assumption was shown to be justified by Camphausen et al (37) and Martinez (52) indicated that it is in any case negligible compared to other variables in equation (6.2).

To account for the d-core states Van Vechten (36) introduced the \( (D_{av} - 1)\Delta E_{O} \) term in inter band gap equation (6.1). However Camphausen et al (37) modified the expression for \( (D_{av} - 1) \), which isolated the pressure dependent factors as given by

\[
(D_{av} - 1) = R \left( \frac{d/d_{Si}}{Y} \right)^{X} \left( 1 - f_{1} \right)^{X}
\]

(6.3)
Fig. 6.7a  Electronegativity difference ($\delta$) versus composition ($y$)

Fig. 6.7b  Measured composition dependence of direct band gap
where $d_{\text{Si}}$ is the nearest neighbour distance in Silicon and the ionicity factor $\xi$ is given by

$$\xi = \frac{c^2}{E_{\text{oh}}^2 + c^2} \quad (6.4)$$

The factor $R$, assumed to be pressure independent (37), recognises the particular d-core state involved. Camphausen et al (37) obtained 13 and 2.4 for the values of $Y$ and $X$ respectively, by fitting the pressure coefficient $\frac{dE_0}{dP}$ of Ge. However, by fitting the pressure coefficients of Ge, InP, ZnS and Ga As values of 13.3 and 2.1 were obtained for $Y$ and $X$ respectively.

To determine $\frac{dE_{0,h}}{dP}$, $\frac{d\Delta E_0}{dP}$ and $\frac{d(D_{av} - 1)}{dP}$ knowledge of the compressibility $K$ was required. Unfortunately to date, no measurements of the compressibility for the quaternary alloy have been reported so the linear interpolation procedure was used to calculate $K$ from the binary compound values. The compressibilities of the binaries that form the quaternary $\text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y}$ were tabulated by Camphausen et al (37) and are listed in Table 7.1.

The pressure dependence of $E_{0,h}$, $\Delta E_0$ and $(D_{av} - 1)$ are derived in Appendix A and the results are given as

$$\frac{dE_{0,h}}{dP} = 3.578K \left( \frac{d}{d_{\text{Si}}} \right)^{-2.75} \quad (6.5)$$
Having established the pressure dependence of all the parameters in equation (6.2), a theoretical curve of the pressure coefficient \( \frac{dE^0}{dP} \) was obtained. The solid curve in fig. 6.6 represents the calculated pressure coefficient for the quaternary alloy across the \( y = 0 \) to 1 composition. With the exception of the anomaly near the reported miscibility gap (Chapter 4) the agreement with the measured values is reasonable. The curve also predicts the slightly higher values of \( \frac{dE^0}{dP} \) measured near the \( y = 1 \) alloy composition.

6.5.1 Deep energy levels

Deep energy levels are known to influence semiconductor properties and to affect the characteristics and operation of devices. One of the undesirable effects which may be attributed to their presence is the reduction in LED and laser operational lifetime. This may be due to the movement or formation of deep levels in the active layer during operation.

Deep levels can result from defects in the crystal produced during growth, subsequent processing or even during device operation. These levels are usually characterised by the charge, the activation energy \( E^0 \), and their capture-emission rates.
Standard optical methods can be used to study deep levels. It is possible to observe deep levels using photoconductivity even at room temperatures.

6.5.2 Techniques of characterising deep levels

A relatively new technique developed recently (89) is deep-level transient spectroscopy (DL TS). It is capable of displaying the spectrum of traps in a semiconductor crystal and this involves transient capacitance measurements as a function of temperature. The spectrum takes the form of positive and negative peaks depending on whether the traps are near the conduction or valence band. The height of the peak is proportional to the trap concentration and the position, in temperature, of the peak is uniquely determined by the capture cross section of the trap. In addition, by proper choice of experimental procedures, it is possible to measure the thermal emission rate, activation energy $E_T$, concentration profile, and the capture rate of each trap.

One of the principles on which DL TS is based is the influence the traps have on the capacitance (90) of a depleted region and hence the space charge density in the material. The use of these conventional transient capacitance measurements are important in studying the effect of pressure on deep levels and can reveal (91) information such as the pressure coefficient of the level and can identify the particular band with which the level makes transitions.

The transient capacitance technique employs reverse bias pulses by which the traps are emptied and filled resulting in varying
capacitance. A new analysis of the C-V characteristics was carried out by Majerfeld et al (92) which yields the position of the trap $E_T$.

6.5.3 Applications

The technique used by Majerfeld et al (92) was to apply a large reverse bias at room temperature; at this temperature the deep levels are fully ionized. The temperature is then reduced to a low temperature (240-120K). A C-V profile is recorded as the reverse bias is reduced until, at a forward bias, all the trap levels are occupied. A second C-V profile is then obtained as the reverse bias is increased. The rate at which the reverse bias is increased may have important consequences (93) on the results. At the lower temperature the traps remain charged everywhere in the space charge region.

The difference between the two C-V profiles can be analysed, Appendix B, to give the energy trap depth $E_T$ and its concentration $N_T$. Although Ga As showed the presence of a deep level, LPE quaternary $\text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y}$ showed no difference in the C-V profile between 300K and 77K. This may indicate that the concentration of traps are smaller than the measurable $10^{14} \text{ cm}^{-3}$ by this technique.

The presence of deep levels in the binary compounds Ga As (94), InP (95), GaP (96) and (Ga In) As (97) suggest the possibility of deep levels in the quaternary (98) (In Ga)(As P) alloy. Although both the quaternary alloy and the quaternary laser resulted in featureless DLTS spectra, the presence of deep levels in this alloy cannot be completely dismissed without a more comprehensive study of deep levels.
6.6 Summary

Results of pressure measurements on $\text{In}_{1-x} \text{Ga}_x \text{As}_{y} \text{P}_{1-y}/\text{InP}$ were presented. Photoconductivity was measured to determine the band gap, $E_0$, and its pressure coefficient $\frac{dE_0}{dP}$.

Although it is possible to determine the band gap $E_0$ from the photoconductivity edge and then deduce $\frac{dE_0}{dP}$ by measuring the shift in the edge with pressure, the method employed in obtaining $\frac{dE_0}{dP}$ was based on the observation that the photoconductive edge moved without altering its shape. This method allowed the determination of $\frac{dE_0}{dP}$ to a much greater accuracy than one can measure the absolute value of $E_0$.

A brief study on the detection of deep levels was made. The photoconductivity technique used has failed to detect any deep levels below the band gap, and more sensitive methods such as DLTS and transient capacitance measurements, carried out on a quaternary alloy and a quaternary laser also proved negative.

The LPE quaternary alloy lattice matched to InP was used to measure the photoconductive edge of the quaternary alloy and the absorption edge of the InP substrate simultaneously. This enabled $\frac{dE_0}{dP}$ for the alloy to be measured with respect to InP. $\frac{dE_0}{dP}$ showed a general increase in measured value from InP to the composition near the ternary $\text{In}_{1-x} \text{Ga}_x \text{As}$. The values of $\frac{dE_0}{dP}$ near the ternary were found to be slightly larger than the values obtained by interpolating between the binaries.

Using the quantum dielectric theory of Phillips and Van Vechten, a
theoretical curve of $\frac{dE_o}{dP}$ was calculated. The advantage of interpreting
the band structure in terms of the interatomic distance was that the
calculation of $\frac{dE_o}{dP}$ was possible assuming knowledge of the compress-
ibility.

Whereas the interpolated values failed to predict the measured
$\frac{dE_o}{dP}$ for the quaternary at the higher alloy compositions, a theoretical
analysis produced a $\frac{dE_o}{dP}$ curve which was in reasonable agreement with
measured values. Despite the agreement obtained, measurements of
compressibility of the quaternary alloy need to be made before firm
conclusions are drawn.
7.1 Introduction

The low field electrical mobility is one of the fundamental electrical properties of III-V Semiconductors that is frequently studied. The mobility parameter is used as a measure of the transport characteristic of the crystal. Perhaps the most widely studied III-V semiconductor has been GaAs including its transport properties under hydrostatic pressure. The effect of pressure on the ternary Ga$_{1-x}$Al$_x$As has been carried out by Lifshitz et al (99) from Hall measurements.

The electrical transport properties of the In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$/InP quaternary are presented in this chapter. The various scattering mechanisms present in the III-V semiconductor are also reviewed. The scattering rate equations were obtained from references given by Hayes et al (100). The analysis of the electron and hole mobility have to be considered separately. The hole mobility introduces complications due to degeneracy of the valence band maximum. An ambiguity was found by Hayes et al (100) from analysis of the temperature dependence of both the electron and hole mobility in the (In Ga)(As P) quaternary alloy. Therefore pressure measurements on the mobilities were made. The results are analysed in terms of the scattering mechanisms to distinguish between alloy scattering and space charge scattering.
7.2 Electrical Transport in III-V compounds

7.2.1 Introduction

The transport characteristics of semiconductors can be interpreted in terms of the scattering mechanisms which the carriers suffer under the influence of a low electric field. As the material in question is the quaternary In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ alloy, in addition to the usual phonon and ionized impurity scattering mechanisms, two other mechanisms are considered. These are alloy scattering and space charge scattering.

7.2.2 Acoustic Phonon Scattering Mechanisms

The acoustic phonon frequency increases almost linearly with wave vector, $k$, reaching a maximum at the zone edge. Acoustic phonons can scatter the electrons in two ways as identified by deformation potential and piezo-electric scattering.

The deformation potential scattering is a result of fluctuations introduced in the conduction and valence band energies. The resulting mobility limit of this mechanism is given by (128)

$$
\mu_{AC} = \frac{2^{3/2} \pi^{1/2} e \hbar^4}{3m^* \frac{3}{2} \frac{u^2}{k_B T}} \frac{1}{E_{AC}^2} \frac{2^{-3/2}}{T} \tag{7.1}
$$

where $i$ is the mass density, $u$ is the average sound velocity, and $E_{AC}$ is the deformation potential. A typical value ($^{101}$) of 18 eV for $E_{AC}$ has been reported which is high enough to possibly influence low field $\mu_e$ for the In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ quaternary of low alloy $y$ composition.

The piezo-electric scattering results from redistribution of
charge and hence a change in the potential. The mobility limit due to this mechanism is given by (129)

\[
\mu_{PE} = \frac{16/2\pi}{3} \frac{h^2 \varepsilon_0}{m_e^{3/2} \epsilon K^2 k_B} \frac{1}{T^{\frac{3}{2}}}
\]  

(7.2)

where \(\varepsilon_0\) is the low frequency dielectric constant and \(K\) the electro-mechanical coupling constant.

Although PE scattering may influence the mobility in pure polar crystals at very low temperatures, the mobility in polar semiconductors with \((130)\) impurities is probably dominated by ionized impurity scattering. Hence over the temperature range considered PE scattering can be safely ignored.

7.2.3 Optical Phonon Scattering

The optical phonon frequency has a fairly constant value around the centre of the Brillouin zone tending to a smaller value at the zone boundary. The mobility limit associated with the scattering of electrons by optical phonons \(\mu_{po}\) is given by (100),

\[
\mu_{po} = 2.6 \times 10^{51} \frac{T}{300} \left[\frac{e^*}{e}\right]^{\frac{1}{2}} \left[\frac{m_e}{m_e^*}\right]^{3/2} \Omega \theta \frac{\exp(z)-1}{G(z)}
\]  

(7.3)

where \(e^*\) is the Callen effective charge, \(M\) is the reduced ion mass, \(\Omega\) is the volume of the primitive cell, \(\theta\) is the polar phonon temperature and \(z = \frac{\theta}{T}\). The function \(G(z)\) is given graphically by Ehrenreich (102) and depends on the electron density. In the
temperature range considered here the measured mobility is most affected by polar optical phonon scattering.

As with acoustic phonons, optical phonons produce another scattering mechanism as a result of potential perturbation. The mobility limit for this non-polar optical phonon scattering is given by

\[ \mu_{NPO} = 6.345 \times 10^{-5} \rho u^2 \left( e\left(\frac{\theta}{T}\right) - 1 \right) T^{-1/2} S\left(\frac{\theta}{T}\right) \]  

(7.4)

where \( u \) is the longitudinal sound velocity, \( E_{NPO}^* \) the non-polar optical deformation potential and \( S(\theta/T) \) tends to \( T^{-1} \) at high temperatures.

7.2.4 Ionized Impurity Scattering

The substitution of an impurity on a lattice site alters the periodic potential and thus results in scattering. The electrons have small energies at low temperatures and hence they can be scattered by the ionized impurities. However, at high temperatures the electrons have higher energies and therefore they are not as strongly scattered. The mobility limit of the ionized impurity scattering is given by

\[ \mu_{II} = 3.28 \times 10^{15} \frac{E_o^2 T^{3/2}}{\left[ \frac{m^*}{m_o} \right]^{1/2} N_i} \left[ \ln(1 + b) - \frac{b}{1 + b} \right]^{-1} \]  

(7.5)

where \( b = 1.29 \times 10^{14} \frac{k_s m^* T^2}{m_o n^*} \)  

(7.6)
and \[ n' = n + (N_D - N_A - n)(n + N_A)/N_D \] (7.7)

where \( n \) is the electron density, \( N_D \) and \( N_A \) are the density of donors and acceptors respectively.

### 7.2.5 Space Charge Scattering

In studying the effect of impurities, it is usually assumed that the impurity distribution is uniform. However, it is possible that inhomogeneities may exist due to, for example, clustering of impurities, causing regions to have a charge different to that of the surrounding crystal. Space charge regions form around the inhomogeneities resulting in distortions of the conduction and valence band. The space charge mobility to be given as

\[
\mu_{sc} = \frac{10^4 e}{\sqrt{2} N_S A k_B T^{1/2}} m_e^{* -1/2} T^{-1/2} \]  

(7.8)

where \( N_S \) is the concentration of space charge regions and \( A \) the effective scattering area of the space charge regions.

### 7.2.6 Alloy Scattering

The alloy scattering process arises, in III-V semiconductor alloys, from the random arrangement of the alloy constituent atoms on the lattice sites. The work of Brooks has been quoted by many authors in relation to alloy scattering in III-V ternary and quaternary alloys. A derivation of the mobility limit for alloy scattering was
recalculated by Littlejohn et al (106) and is given by

\[ \mu_{Al} = 8 \times 10^4 \sqrt[2]{\frac{h^4 m^*_{e} - 5/2}{e}\frac{T^{\frac{1}{2}}}{3\pi \Omega k_B^{\frac{3}{2}} S(\omega)(\Delta U)^2}} \]  

(7.9)

where \( s(\omega) \) refers to the degree of randomness, being unity when there is total disorder and becoming zero on a perfectly ordered structure. \( \Delta U \) is the alloy scattering potential in eV and is a measure of the magnitude of the fluctuations caused by the atom's distribution variation. Alloy scattering is the question of further discussion later on in this chapter.

7.2.7 Hole Mobility

The analysis of hole mobility is considerably more complicated than that of electron mobility, due to the degeneracy and p-like symmetry of the valence band. The hole mobility in III-V materials was initially considered to be dominated by polar optical phonon scattering, at high temperature. Eventually this assumption was disproved (104) and mechanisms including non-polar optical phonon scattering and acoustic phonon scattering had to be taken into account.

A detailed theory of hole mobility has been given by Wiley (104). For the calculations involving III-V compounds, transport at the top of the valence band is complicated by the fact that there are both light and heavy holes. Equations for the scattering mechanisms given above for electron mobility has to be further modified by the p-like symmetry of the wave functions. These points have been dealt with in detail by Wiley et al (104) and his approach is followed by writing
\[ \mu_{PO} = 2K_H \mu_{PO} \]  
\[ \mu_{II} = 1.5 \left( \frac{r^{3/2} + r^{3}}{1 + r^{3/2}} \right) \]  
\[ \mu_{SC} = \frac{r^{5/2} (1 + r^{3/2})}{1 + r^{3/2}} \]  
\[ \mu_{AL} = \frac{r^{5/2} (1 + r^{3/2})}{1 + r^{3/2}} \]

and

\[ \mu_{\text{AC/NPO}} = 3.17 \times 10^{-4} \frac{r^{5/2} (1 + r^{3/2})}{(1 + r^{3/2})^2} \frac{\rho u^{-2}}{(m_h^*/m_0)^{5/2}} \]

\[ S(\Theta, \gamma, T)T^{-3/2} \]

\[ E_{\text{AC}}^2 \]

Here \( \mu_{PO}, \mu_{AL}, \mu_{SC} \) and \( \mu_{II} \) are obtained using the equations for electrons but substituting the heavy hole effective mass \( m_h^* \).

The factor \( r = m_h^*/m_1^* \). In equation (7.10) and (7.11) the factors 2 and 1.5 take into account \( p \)-like symmetry of the hole wave functions.

\( K_H \) is a correction factor for the light holes and is given by Kranzer (105). The values of \( \rho, u, E_{\text{AC}} \) are given in Table 7.1 \( \gamma = \left( \frac{E_{\text{NPO}}}{E_{\text{AC}}} \right)^2 \)

and \( S \) is a function also given graphically by Wiley and Di Domenico (104). No attempt has been made to correct \( \mu_{AL} \) and \( \mu_{SC} \) for the \( p \)-like symmetry of the holes.

7.3 Temperature and Compositional dependence of \( \mu_e \)

7.3.1 Compositional dependence of \( \mu_e \)

Measurements have been made of low field hall mobility in
Table 7.1 Values of physical parameters of binary compounds used as a basis for interpolated estimates of the parameters in quaternary alloy

<table>
<thead>
<tr>
<th>Parameter</th>
<th>InAs</th>
<th>InP</th>
<th>GaAs</th>
<th>GaP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K \times 10^6 \text{(bar}^{-1})$</td>
<td>1.72</td>
<td>1.38</td>
<td>1.34</td>
<td>1.13</td>
</tr>
<tr>
<td>$e^*/e$</td>
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<td>0.27</td>
<td>0.20</td>
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</tr>
<tr>
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<td>0.85</td>
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<tr>
<td>$m^*_l/m_o$</td>
<td>0.027</td>
<td>0.089</td>
<td>0.074</td>
<td>0.14</td>
</tr>
<tr>
<td>$\theta \text{(K)}$</td>
<td>350</td>
<td>498</td>
<td>420</td>
<td>582</td>
</tr>
<tr>
<td>$M \cdot 10^{26} \text{(kg)}$</td>
<td>7.4</td>
<td>3.99</td>
<td>5.92</td>
<td>3.515</td>
</tr>
<tr>
<td>$k_s$</td>
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<td>12.35</td>
<td>12.9</td>
<td>11.1</td>
</tr>
<tr>
<td>$\bar{u} \text{(ms}^{-1})$</td>
<td>3090</td>
<td>3810</td>
<td>3900</td>
<td>4760</td>
</tr>
<tr>
<td>$\rho \text{(kgm}^{-3})$</td>
<td>5667</td>
<td>4787</td>
<td>5307</td>
<td>4130</td>
</tr>
<tr>
<td>$E_{\text{AC}} \text{(eV)}$</td>
<td>3.2</td>
<td>3.6</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>$E_{\text{NPO}}$</td>
<td>5.7</td>
<td>6.3</td>
<td>6.5</td>
<td>6.7</td>
</tr>
<tr>
<td>$\Delta_o \text{(eV)}$</td>
<td>0.38</td>
<td>0.13</td>
<td>0.34</td>
<td>0.08</td>
</tr>
</tbody>
</table>
LPE n-type quaternary In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ lattice matched to 100 InP substrate by Greene et al (57). The compositional dependence of the electron mobility, $\mu_e$, at room temperature, measured with electron concentrations in the low 10$^{16}$ cm$^{-3}$ range are shown in Fig. 7.2. They span the entire alloy range except for the region $y = 0.65$ to $y = 0.8$ which, as stated in the previous chapter, is of relatively little technological importance. However, a value of $\mu_e$ at the $y = 0.72$ alloy composition is included for completeness in the Fig. 7.2. as measured by Enda (100). Overall, the electron mobility measurements indicate a downward bowing from $y = 0$ composition to a minimum near $y = 0.25$ composition prior to a steep rise in mobility up to $y = 1$ composition with $\mu_e$ reaching about 11000 cm$^2$ v$^{-1}$ s$^{-1}$.

7.3.2 Temperature dependence

The measured temperature dependence of $\mu_e$ in some representative alloy compositions is shown in Fig. 7.3. As can be seen, $\mu_e$ increases with decreasing temperature to below 100 K indicating that impurity scattering is not very significant at room temperature. In order to analyse the temperature dependence of the mobility two important assumptions have been made. These assumptions are concerned with the measured Hall mobility, $\mu_H$, and the method of combining the various scattering mechanisms.

It is assumed that the low field $\mu_H$, is equal to the drift mobility, which is not true for most semi-conductors, particularly when ionized impurity scattering is important. However, independent experimental investigations (57) of the mobility to high magnetic fields, between room temperature and 77K, indicated values of $\mu_H/\mu_D$
Fig. 7.2  Compositional dependence of the room temperature electron mobility

Fig. 7.3  Temperature dependence of the electron mobility in some representative alloy compositions. The solid line through the experimental points is the sum of a-c theoretical curves.
to be unity.

Matthiessen's rule was assumed in combining the mobility limits, \( \mu \), to account for the measured mobility

\[
\frac{1}{\mu} = \sum \frac{1}{\mu_i} \tag{7.15}
\]

The application of Matthiessen's rule is shown in Fig. 7.3 which allows a clear graphical display of the scattering mechanisms to be made. In the analysis, the use of Matthiessen's rule to obtain numerical parameters for the individual scattering mechanisms at one temperature gave good agreement across the whole temperature range. The calculated curve of mobility limit, \( \mu_{\text{PO}} \), imposed by polar optical phonon scattering was given by equation (7.3).

Some of the parameters were obtained by linear interpolation of the values for the binary constituents of the quaternary alloy which are listed in Table 7.1. The ionized impurity scattering mobility limit, \( \mu_{\text{II}} \), as given by equation (7.5) was then added using equation (7.15). Polar optical phonon and ionized impurity scattering mechanisms alone cannot explain the measured temperature variation of \( \mu_e \), a conclusion shared by Greene et al (57).

In order to obtain good fits to the measured \( \mu_e \), an additional scattering mechanism is required which has a \( T^{-\frac{1}{2}} \) temperature dependence. The additional mobility limit \( \mu_{\text{AI}} \) imposed by alloy scattering was used to obtain good fits to \( \mu_e \) throughout the temperature range. As has been pointed out (107), space-charge scattering mobility, \( \mu_{\text{SC}} \), as given by equation (7.8) has the same temperature dependence.
In addition to these three scattering mechanisms, deformation potential and piezo-electric scattering, lead to further refinement which at present is within the experimental uncertainty of \( \mu_e \).

7.4 Compositional and Temperature Dependence of \( \mu_p \)

7.4.1 Composition Dependence

The measured compositional dependence of the hole mobility, \( \mu_p \), at room temperature is presented in Fig. 7.4 for the quaternary alloy with hole concentration in the low \( 10^{16} \text{ cm}^{-3} \) range and also for \( 1 - 2 \times 10^{18} \text{ cm}^{-3} \) range. As with \( \mu_e \), the hole mobility shows downward bowing which is even more pronounced than in \( \mu_e \). The hole mobility near the \( y = 0 \) composition is about \( 140 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1} \) in agreement with accepted values for InP (104) with carrier concentration in the \( 10^{16} \text{ cm}^{-3} \) range. The \( \mu_p \) value near the \( y = 1 \) ternary composition rises steeply similar to the value of \( \mu_e \) but with a maximum of about \( 300 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1} \).

7.4.2 Temperature Dependence

To understand the variation in \( \mu_p \) with composition, measurements of the temperature dependence of \( \mu_p \) were carried out between 77-300K. The temperature dependence of \( \mu_p \) for three typical lightly doped samples is shown in Fig. 7.5. In all the samples investigated \( \mu_p \) increased with decreasing temperature down to about 100K and then began to decrease. By considering polar optical phonon, non-polar optical and acoustic phonons, and ionized impurity scattering, the mechanisms present in p-type binary compounds, it is not possible
Fig. 7.4 Compositional dependence of the room temperature hole mobility

Fig. 7.5 Temperature dependence of the electron mobility in some representative alloy compositions. The solid line through the experimental points is the sum of a–d curves.
to fit the variation of $\mu_p$ over the temperature range for the quaternary alloy. As with the electron mobility, a $T^{-1/2}$ dependent scattering mechanism was required to obtain good fit between measured and calculated $\mu_p$. In Fig. 7.5, the line through the experimental $\mu_p$ was calculated including the additional alloy scattering mechanism.

7.5 Pressure Dependence of $\mu_e$ and $\mu_p$

7.5.1 Introduction

The variation in the transport properties with pressure is of considerable importance not only for determining band structure but also for diagnostic purposes as will be discussed below. Hall measurements at high pressures allows estimates to be made of energy gaps (Chapter 5), effective masses (Chapter 3) and hence scattering mechanisms (106). In the above sections electron and hole mobilities were measured with temperature and subsequent analysis indicated the possible scattering mechanisms present in the quaternary alloy. Since alloy scattering and space charge scattering have the same temperature dependence, pressure which changes the band gap and hence the effective mass was used as the variable parameter.

The effect of pressure on the mobilities are presented in relation to the effect of pressure on the scattering mechanisms. It is shown that alloy scattering and space charge scattering can best be distinguished through their effective mass dependence.
7.5.2 Pressure dependence of \( \mu_e \)

The temperature dependence of \( \mu_e \) was explained by polar optical phonon, ionized impurity and the additional alloy scattering mechanisms. However it is possible to replace alloy scattering by space charge scattering while retaining the agreement between theory and experiment. Alloy scattering and space charge scattering are given by (7.9) and (7.8) respectively. Both scattering mechanisms have a \( T^{1/2} \) temperature dependence. Thus, it is not possible to distinguish between the two scattering mechanisms from temperature measurements alone. Although their temperature dependence is identical, their effective mass dependence of mobility is different, \( \mu_{Al} \) being proportional to \( m_e^{5/2} \) and \( \mu_{SC} \) being proportional to \( m_e^{1/2} \). Ideally measurement of the effective mass with pressure in the quaternary alloy would distinguish between the two mechanisms. The variation in effective mass of electrons with pressure has been calculated in Chapter 3 although direct measurements of \( m_e^* \) have not been obtained. The pressure dependence of the Hall mobility was measured on several samples with \( y = 0.5 \) and one with \( y = 0.92 \) alloy composition. The experimental results are shown in Fig. 7.6.

In all the samples the effect of pressure resulted in a reproducible decrease in electron mobility \( \mu_e \) with no change in the carrier concentration. Taking the relative magnitudes of \( \mu_{PO} \), \( \mu_{Al} \) and \( \mu_{II} \) as determined from temperature dependence of the curve, and their effective mass dependence as given by equations (7.3), (7.9) and (7.5), the total variations of \( \mu_e \) with pressure was calculated assuming Matthiessen's rule and is shown by solid curve in Fig. 7.6. If, however, space charge scattering with its weak \( m_e^* \) dependence was assumed rather than alloy scattering then the dashed
Fig. 7.6A. Normalized variation of electron mobility with pressure for \( y=0.5 \). Full curve includes alloy scattering. The broken line assumes space charge scattering instead.

Fig. 7.6B. Normalized variation of electron mobility with pressure for \( y=0.92 \). Full curve includes alloy scattering. The broken line includes space charge scattering instead.
curve in Fig. 7.6 is predicted. The assumption of alloy scattering clearly gives the better agreement especially considering that the theory predicts the small bowing measured in $\mu_e$ with pressure.

7.5.3 Pressure dependence of $\mu_p$

As with the electron mobility the ambiguity in explaining the temperature dependence of the hole mobility can be resolved by studying the pressure dependence of the hole mobility. As can be seen from equations (7.12) and (7.13), the variation of the effective mass will be evident through its influence on $r$ and directly through equation (7.8) and (7.9). Thus the pressure dependent effective mass term for $\mu_p$ is different from that of $\mu_e$. Measurements of the hole mobility with pressure are shown in Fig. 7.7 for two samples with alloy compositions $y = 0.64$ and $y = 0.8$. The scatter in $\mu_p$ with pressure believed to be caused by small temperature fluctuations, although, relative to the $\mu_e$ results, the changes in $\mu_p$ are considerably smaller. The effective mass dependence of $\mu_{p0}$, $\mu_{p}^{AC} + NPO$, $\mu_{II}^p$ and $\mu_{Al}^p$ were determined as a function of pressure. In Fig. 7.7 a,b the calculated variations in $\mu_p$ with pressure at room temperature are given by the solid curves. If $\mu_{Al}^p$ was replaced by $\mu_{sp}^p$, then the fits to the experimental $\mu_{sc}^p$ were poor.

The pressure dependence of the electron mobility is completely dominated by the large change in $m_e^*$ with pressure. In the case of the pressure dependence of $\mu_p$ the change in $m_h^*$ is not as dominant although it is much larger than those of other parameters. The parameters in alloy scattering which are known to be pressure dependent are $\Omega$ and
Fig. 7.7a Normalized variation of hole mobility with pressure for $y=0.64$. Full curve includes alloy scattering. The broken line includes space charge scattering instead.

Fig. 7.7b Normalized room temperature hole mobility with pressure for $y=0.8$. Full curve includes space charge scattering instead.
It is assumed that from the physical interpretation of the alloy scattering potential, its pressure dependence will be within the accuracy of the calculations. Calculations also show that the change in $\Omega$ is very small compared to the variation of $m_n^*$ with pressure.

The parameters which are known to be pressure dependent in the space charge scattering mechanism (100) are $N_s A$ and $m_n^*$ which are similar in their pressure dependence however their relative changes are very small. Thus the pressure dependence of $\mu_{SC}$ is underestimated by considering change in $m_n^*$ alone. However, the change with pressure is not sufficient to alter the conclusion.

These results further support the conclusion reached with $\mu_e$ in that alloy scattering gives a better fit when interpreting the pressure dependence of mobility rather than space charge scattering.

7.5.4 Interpretation of Alloy Scattering

One of the parameters which has been examined in understanding the origin of alloy scattering is the scattering potential $\Delta U_e$ and $\Delta U_p$ from $\mu_{Al}$ versus temperature curves. The variation of $\Delta U_e$ in eV for the quaternary alloy across the alloy composition is shown in Fig. 7.8. The swift rise in $\Delta U_e$ from $y = 0$ composition is followed by a broad maximum of about 0.7 eV near the centre of the alloy range. Although very little work has been done on $\Delta U_p$ and its interpretation, a few suggestions have been reported for $\Delta U_e$.

An explanation for $\Delta U_e$ proposed by Brooks (108) was a variation of $x(1 - x)\Delta U$ where $\Delta U$ is the energy gap difference between the constituent binary compounds. The explanation by Harrison et al (109) involved the electron affinity difference in order to determine the
Alloy scattering potential for electrons. The broken & dotted curves represent two models. The full curve is a best fit of fluctuations in the direct energy band gap, dashed fluctuations in the atomic positions.
importance of alloy scattering. And Littlejohn et al (103) proposed a more fundamental parameter that of the electronegativity difference. Two of these are shown in Fig. 7.8. These curves, unfortunately, can be produced only too easily and it does not give a clear indication of which model is to be preferred. These theories ignore fluctuations in which could be significant.

7.6 Summary

The transport properties of the quaternary alloy In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$ have been presented. The results are important when considering the use of alloys for device fabrication. The room temperature mobility versus the alloy composition showed a decrease in the mobility from $y = 0$ to a minimum near the mid alloy composition and rose steeply towards the $y = 1$ alloy composition. This appears to be an intrinsic property of the quaternary alloy. Attempts to fit the temperature dependence of the electron or the hole mobility using the conventional scattering mechanisms as used satisfactorily for the binary III-V compounds were unsuccessful for the quaternary alloy.

Optical phonon and ionized impurity scattering mechanisms were not sufficient to explain the temperature dependence of $\mu_e$ between 300 - 77K. However, when additional $T^{-\frac{1}{2}}$ dependent scattering mechanism was included good agreement was obtained for the measured $\mu_e$. Similarly when polar optical phonon, non polar optical with acoustic phonon, and ionized impurity scattering mechanisms were used to explain the temperature dependence of $\mu_p$ an additional $T^{-\frac{1}{2}}$ dependence was required. The additional scattering mechanism was obtained from alloy scattering as proposed by Littlejohn et al (103), however, the sc scattering mechanism has the same temperature dependence.
The two scattering mechanisms can best be distinguished through their effective mass dependence and hence studies of the pressure dependence of $\mu_e$ and $\mu_p$ were carried out. The results indicated the presence of alloy scattering with its $m_e^{5/2}$ dependence rather than the weaker $m_h^{-1/2}$ dependence of space charge scattering. Alloy scattering was proposed by Littlejohn et al. (103) but its physical interpretation remains unclear. Possible explanations of the alloy scattering potential $\Delta U$ have been reported although they are far from satisfactory.
CHAPTER 8

THE EFFECT OF PRESSURE ON (In Ga)(As P)/In P LASERS

8.1 Introduction

The low value \((110)(113)\) of the characteristic temperature \(T_o\) of the threshold current \(I_{th} \propto \exp \left( T/T_o \right) \), has been attributed by other workers as due to intervalence band absorption, Auger recombination, carrier leakage over the barrier or recombination through impurity centres. (See chapter 2). The bulk of the literature on the problem has considered only the temperature dependence of the threshold current. The pressure dependence of the threshold current has been used here in an attempt to isolate the loss mechanism present in the 1.3 \(\mu m\) (Ga In)(As P) quaternary lasers. In the past, little work \((111)(112)\) has been reported on the effect of pressure on semiconductor optoelectronic devices especially the use of pressure as a diagnostic tool.

In previous chapters the effect of pressure on the band structure has been discussed, including the effect on the energy band gaps, effective masses and on the transport properties of LPE grown \(In_{1-x} Ga_x As_x P_{1-y}/In P\) alloy. These studies form the base on which the effect of pressure on quaternary lasers can be examined with respect to the \(T_o\) problem. The pressure dependence of \(I_{th}\) in 1.3 \(\mu m\) quaternary lasers at room temperature has been compared to Ga As based lasers in Section (8.2). Since the fraction of the emission reaching the detector was not determined, the incremental quantum efficiency could not be assessed but it was possible to measure the \(I_{th}\) under pulsed operation at a repetition frequency of 1 kHz. The observed variation of \(I_{th}\) with increasing pressure for the quaternary lasers has been analysed in terms of the four loss
mechanisms. The results of the pressure measurements at high temperatures have been presented in section (8.4) and discussed in terms of the losses at high temperatures and high pressures. The effect of pressure on $I_{th}$ at different temperatures, determines the pressure dependence of $T_o$, as given in section (8.5). Besides the 1.3 μm quaternary lasers with undoped active layers, lasers with n+ active layers and also inverted rib waveguide lasers were examined.

8.2 Pressure Dependence of the Threshold Current

Measurements of the pressure dependence of the threshold current in 1.3 μm (In Ga)(As P) lasers were obtained. For comparison, measurements were also made on a (Ga Al)As laser. Both types of lasers were oxide-defined stripe devices with a stripe width of 20 μm. Details of the growth, structure and fabrication of the quaternary lasers have been described in Section (4.4). The temperature characteristics of these lasers were reported by Thompson (110). These quaternary lasers were of double heterostructure type and grown by LPE (Chapter 4) with In P as the confining layers. The (Ga Al)As device had an active layer of Ga$_{0.99}$ Al$_{0.01}$ As between n and p confining layers with 0.35 and 0.38 Al composition respectively.

The variation in the threshold current, $I_{th}$, with pressure is shown in Fig. 8.1. The pressure measurements were obtained at room temperature using the piston and cylinder device (described in Chapter 5) for a number of 20 μm stripe quaternary lasers and a (Ga Al)As lasers. The results were reversible and repeatable, showing that within the pressure range used, no significant pressure-induced damage occurred. The observed decrease in threshold current with pressure is consistent for a number of quaternary lasers. The effect
Fig. 8.1  Relative threshold current as a function of pressure for (GaAl)As & (GaIn) (AsP) lasers. The theoretical curve for the (GaAl)As laser was derived by considering only the effect of pressure on radiative recombination rate.
of pressure on the threshold current for a (Ga Al)As laser produced the opposite result, with $I_{th}$ increasing with increasing pressure.

If no loss mechanism is present in a laser then the threshold current is simply given by the radiative component $I_R$, which is predicted to be proportional to the square (114) of the band-gap energy $E_0$. Hence

$$\frac{I}{I_R} \frac{dI_R}{dP} = \frac{2}{E_0} \frac{dE_0}{dP}$$

(8.1)

Assuming that the value of $dE_0/dP$ for Ga As (11.5 meV kbar$^{-1}$) is valid for the active region of the Ga$^{0.99}$Al$^{0.01}$As laser, the observed increase in $I_{th}$ with pressure could be explained simply in terms of the radiative threshold current $I_R$ without invoking additional loss mechanisms. The dashed curve (a) in Fig. 8.1 is obtained as a result of radiative threshold current, in good agreement with the experimental points and suggests that pressure-dependent loss mechanisms may be unimportant in (Ga Al)As lasers.

The shift in the lasing wavelength of a quaternary laser is shown in Fig. 8.2 at different pressure. The shift in the output wavelength corresponded to a pressure coefficient, $dE_0/dP$, of 10 meV kbar$^{-1}$. This is in good agreement with photoconductivity measurements (Chapter 6) on 1.3 μm ($y = 0.6$) In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$/In P LPE material. Whereas in the (Ga Al)As laser the increase in $I_{th}$ can be explained in terms of the known pressure coefficient, the decrease in $I_{th}$ of the quaternary laser is contrary to the change of $I_R$ alone and appears to indicate a loss mechanism which decreases markedly with increasing pressure.

In an attempt to explain the decrease in $I_{th}$ observed in the
Fig. 8.2 Shift in operating wavelength of quaternary laser with pressure. The shift corresponds to \( \frac{dE_o}{dP} = 10 \text{ meV/kbar} \)

Fig. 8.3 The effect of pressure on the E-k diagram of the quaternary active layer & intervalence band absorption
quaternary lasers, an analysis of the possible loss mechanisms introduced in Chapter 2 was carried out.

8.3.1 Pressure dependence of $I_{\text{th}}$ assuming Inter-Valence band absorption

A description of the intervalence band absorption mechanism \((5)\) was given in Section \((2.10)\). The main transition involved in the intervalence band absorption is from the split-off valence band into holes injected and thermally generated within the heavy hole band.

The total loss in the laser at threshold was given by \((2.24)\) as

$$a_1 = a_{\text{in}} + a_{\text{ac}} + a_{\text{ex}} \frac{(1 - \Gamma)}{\Gamma} + \frac{1}{\mathcal{L} \Gamma} \ln \left(\frac{1}{R}\right) \quad (8.2)$$

The main transition involved in the intervalence band absorption is proportional to the hole density available at \(E_1\) (See Fig 2.3) and was given in \((2.26)\). At threshold \((6)\), the carrier density \(n_{\text{th}}\) may be written as

$$n_{\text{th}} = \frac{1}{A_0} \left[ a_{\text{in}} + a_{\text{ac}} + a_{\text{ex}} \frac{(1 - \Gamma)}{\Gamma} + \frac{1}{\mathcal{L} \Gamma} \ln(1/R) \right] \quad (8.3)$$

where \(A_0\) is determined from the linear peak gain curves. The proportional relationship between the current \(I\) and the injected carriers \(n\) is given by

$$I \propto \frac{n}{\tau_T} \quad (8.4)$$

where \(\tau_T\) is the total carrier lifetime. In the analysis of the
experimental results, it is assumed that the carrier lifetime $\tau_T$ is inversely proportional to the total hole density. Therefore the expression for $I_{th}$, assuming intervalence band absorption as the dominant mechanism is given by

$$I_{th} \propto \left[ a_{in} + a_{ac} + \frac{(1 - \Gamma) a_{ex}}{\Gamma} + \frac{1}{L} \ln \left( \frac{1}{R} \right) \right]^2 \quad (8.5)$$

The nomenclature used in intervalence band absorption analysis is consistent with that used by Asada et al (6) including the parameters determined here. Such as $\Gamma = 0.6$, $R = 0.4$ and $a_{ex} = 20 \text{ cm}^{-1}$.

The intervalence band absorption decreases with increasing pressure. This is clearly shown in Fig. 8.3 where the effect of pressure increases the band gap separation and thus the corresponding transitions between the split-off valence band and the heavy hole must move to shorter wavelength (larger $k$ value) where the injected density of holes is smaller. Quantitatively, the effect of pressure was calculated from the band structure parameters of the conduction band, the valence band, and $dE_0/dP$, determining the absorption coefficient $a_1$. The values (as given in previous chapters) of $dE_0$, heavy-hole mass, split-off mass and the split-off band gap were 10 meV kbar$^{-1}$, 0.69, 0.13 and 0.27 eV respectively. The absorption coefficient $a_2$ involving the acceptor level is assumed to be insensitive to pressure for the temperature range considered here. The value of $a_{in}$ was calculated to be 200 cm$^{-1}$ plus the radiative recombination component.

The theoretical $I_{th}$ as a function of pressure assuming intervalence band absorption as the dominant loss mechanism is shown, as curve b, in Fig. 8.4 and is in reasonable agreement with the experimental results.
Fig. 8.4 Calculated variation of the threshold current with pressure for the 1.3 μm (GaIn)(AsP) lasers. The curves through the experimental points represent IVBA (a) & Auger recombination (c). The model assuming impurity scattering (e) (full curve) or barrier leakage (broken curve) lead to increased threshold current.
The intervalence band absorption coefficient $a_{ac}$ was 100 cm$^{-1}$ at atmospheric pressure. There has been little or no reported measurements of $a_{ac}$ for the quaternary LPE layer. Intervalence band absorption has been studied by Braunstein (115)(116) on GaAs and by Gobeli et al (117) on InSb. Attempts have been made here to measure the intervalence band absorption. However, the results will not be discussed here at the present time as there is considerable controversy as to the characteristics of the In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$/InP LPE layer required to simulate the conditions, such as the exact injected carrier density of the quaternary active layer under threshold condition. Evidence to support intervalence band absorption has been reported by Yamanishi (118) et al with measurements of current-injection induced acoustic (CIA) signals.

8.3.2 Pressure Dependence of $I_{th}$ assuming Auger Recombination

The Auger recombination model has been given in Section (2.10.2) and is often used to explain the temperature dependence of $I_{th}$ in 1.3 μm quaternary lasers. From the model it can be seen that as the effect of pressure increases the band gap separation, the probability of Auger transitions decrease and hence a reduction in $I_{th}$ is predicted. The Auger recombination model is also strongly dependent on the energy band gap and the effective masses.

The Auger recombination lifetime, $\tau_{Al}$, involving two holes interacting with one conduction band electron and leaving an energetic hole in the split-off band (CHHS process) is given by (8)

$$\frac{1}{\tau_{Al}} \propto \exp \left[ - \frac{(E_0 - \Delta_0)}{KT} \cdot \frac{m^*}{2m^* + m_e - m_s} \right] \quad (8.6)$$
The lifetime, $\tau_{A2}$, for Auger recombination involving two conduction band electrons interacting with one hole leaving one conduction-band electron with high energy (CCHC process) is given by

$$\frac{1}{\tau_{A2}} \propto \exp \left[ -\frac{E_0}{kT} \frac{m_e^*}{m_v^* + m_e^*} \right] \tag{8.7}$$

The pressure dependence of the band structure including $E_0$ and the effective masses have been measured and calculated in the previous chapters.

At atmospheric pressure the relative magnitudes of $I_R$ and $I_A$ were determined from the radiative and Auger lifetimes as measured by Thompson (110) in these lasers. Since the radiative and Auger recombination components of $I_{th}$ has been derived in terms of the pressure dependence parameter, the effect of pressure on $I_{th}$ assuming equation (2.32) was calculated from the coefficients $dI_R/dP$ and $dI_A/dP$. With lifetimes of 10 and 6 ns for radiative and Auger recombination respectively at atmospheric pressure, a decrease in $I_{th}$ with increasing pressure was calculated for the 1.3 $\mu$m (In Ga)(As P) quaternary lasers. Curve (C) in Fig. 8.4 shows the $I_{th}$ behaviour, assuming Auger recombination as the dominant loss mechanism, in good agreement with the observed pressure dependence of $I_{th}$.

### 8.3.3 Pressure Dependence of $I_{th}$ assuming Leakage over the Barrier

The feature of this model, used also to explain the temperature sensitivity of $I_{th}$ in 1.3 $\mu$m quaternary lasers, is the loss of carriers over the heterostructure barrier as described in Section 2.10. From equation (2.33) the pressure dependent terms in the barrier
loss can be reduced to

\[ I_B \propto m^* e^{3/2} \exp \left(-\frac{\Delta E_0}{kT}\right) \quad (8.8) \]

where \( \Delta E_0 \) represents the barrier height between the quaternary active layer and the In P confining layer.

The pressure coefficient of the direct energy band gap of the quaternary is greater than that of In P, hence the barrier height, \( \Delta E_0 \), has a \( \frac{d\Delta E_0}{dp} \) value of \(-1.5 \text{ meV kbar}^{-1}\) as shown in Fig. 8.5. Therefore the current associated with loss of carriers over the heterostructure barrier will increase with increasing pressure due to lowering of the barrier. Assuming the component of barrier current and the radiative current at atmospheric pressure, as given for example by Yano et al (27), the pressure dependence of \( I_{th} \) with loss of carriers over the barrier as the dominant loss mechanism is shown by curve (d) in Fig. 8.4. Clearly the loss of carriers over the barrier, in comparison with the pressure measurements, indicates that this model does not seem to be the dominant process in the quaternary lasers. It is interesting to note an important difference between a 1.2 \( \mu m \) quaternary laser and a 1.3\( \mu m \) quaternary laser lasing in the 1.2 \( \mu m \) wavelength at high pressure. In the latter case the band gap of In P confining layer has also increased, hence the heterojunction barrier is appreciably higher than in lasers grown to operate at 1.2 \( \mu m \) at atmospheric pressure.

8.3.4 Pressure Dependence of \( I_{th} \) assuming loss through Impurity centres

The remaining model attributed to the temperature sensitivity of
Fig. 8.5  Schematic diagram of the cross-section of the quaternary laser.
$I_{th}$ in 1.3 $\mu$m quaternary lasers involves non-radiative recombination centres. Although details of this model are not clear it is most likely that to explain the temperature dependence of $I_{th}$, the centres would have to be above the conduction band minima as shown schematically in Fig. 8.5. Evidence that such levels do exist in the quaternary material has been observed by Wadley, N.J. (unpublished) from very high pressure studies. However, as is usually the case with such states they exhibited an $x$-like pressure coefficient. Such behaviour would lead to an extremely steep increase in $I_{th}$ with pressure, as shown by curve (e) in Fig. 8.4. Therefore the pressure measurements indicate that it is unlikely such non-radiative recombinations play a dominant role in determining $I_{th}$ of 1.3 $\mu$m (In Ga)(As P) lasers.

8.4 **Pressure Dependence of $I_{th}$ at High Temperature**

So far it has been shown that whereas $I_{th}$ increased with increasing pressure in (Ga Al) As laser, in the 1.3 $\mu$m (In Ga)(As P) quaternary lasers it decreased with increasing pressure. This decrease in $I_{th}$ was interpreted on the assumption that the loss mechanism responsible for the extreme temperature sensitivity of the quaternary lasers decreases with increasing pressure. Of the four models considered it appears that the barrier leakage or recombination through impurity levels would give rise to an increased $I_{th}$ with increasing pressure contrary to observations. The measurements of $I_{th}$ with pressure in the 1.3 $\mu$m quaternary lasers have been extended to higher temperatures in an attempt to distinguish between intervalence band absorption and Auger recombination as the dominant mechanism.
The measurements of $I_{th}$ in quaternary lasers at high temperature and pressure is shown in Fig. 8.6. As it can be seen at higher temperature the rate of decrease in $I_{th}$ with increasing pressure is greater. This is exactly what one would expect if the loss mechanism, which increases with temperature, is being reduced by the application of pressure.

Assuming the intervalence band absorption model, the decrease in $I_{th}$ at 292K, with increasing pressure was explained in the previous section by a plausible $a_{ac}$ of 100 cm$^{-1}$ at atmospheric pressure (i.e. $p = 0$). The solid curve at 292K represents the theoretical $I_{th}$ assuming intervalence band absorption model. When the temperature was increased to 322K, the $I_{th}$ at $p = 0$ increased from 165 mA to 260 mA, corresponding to a $T_0$ value of 65K. At $p = 0$, in order to obtain the observed increase in $I_{th}$ the intervalence band absorption coefficient, $a_{ac}$, from equation (8.2) had to be increased to $a_{ac} = 200$ cm$^{-1}$. These values of $a_{ac}$ are consistent with those of Asada et al (6) the other parameters being adjusted to give an appropriate $T_0$ for a loss free laser. Thus having determined $a_{ac}$ at the higher temperature the effect of pressure on $I_{th}$ assuming intervalence band absorption model was calculated without any further adjustable parameters. The solid curve at 322K is a theoretical curve and is in good agreement with the measured $I_{th}$ in Fig. 8.6.

Similarly the results of $I_{th}$ at high temperatures and pressure were considered assuming Auger recombination as the dominant mechanism in 1.3μm quaternary lasers. As shown in Section (2.10) the model assuming Auger recombination resulted in a good fit to the curve for 292K operation assuming lifetimes of 6 and 10ns for Auger and radiative recombination respectively. This agreement is also represented in Fig 8.6 by the dashed curve. At $p = 0$, as the
Fig. 8.6 Measured effect of pressure on threshold current in quaternary lasers at two temperatures. The full line shows a theoretical curve based on an intervalence band absorption model & the broken line on a model assuming auger recombination.
temperature was increased to 322K the $I_{th}$ increased, according to $T_0 = 65K$, to 260 mA. This new $I_{th}$ was used to determine the new Auger recombination lifetime of $\tau_A = 3$ ns. Therefore, without any further adjustable parameters the theoretical $I_{th}$ at the higher temperature was calculated as shown by the dashed curve at 322K. The resulting calculated pressure variation of $I_{th}$ at higher temperature assuming Auger recombination model gives a poorer fit to experiment.

The model which assumes the loss of carriers over the heterostructure barrier as the dominant mechanism cannot explain the observed $I_{th}$ with pressure. At the high temperature and high pressure, the threshold current appears to show an increase. A possible explanation may be that at higher temperature and pressure the loss of carriers over the barrier increases considerably and becomes strong enough to compete with the intervalence band absorption. If loss of carriers over the barrier does begin to influence $I_{th}$ then not only would the $I_{th}$ saturate with increasing pressure but it should show an increasing $I_{th}$ at higher pressures.

In the analysis each possible mechanism was considered separately, whereas in practice probably more than one is operative and possibly to some extent, all four mechanisms may play a role. The results of Shah et al (119) and Yamanishei et al (120) indicate hot carriers exist in 1.3 μm (In Ga)(As P) LED's and lasers. This could be caused by either Auger recombination or by intervalence band absorption or both.

8.5 Pressure Dependence of $T_0$

The observed decrease in $I_{th}$ with increasing pressure is greater at higher temperature and supports the assumption that the loss mechanism
responsible for the pressure variation also causes the $T_0$ problem in 1.3μm quaternary lasers. From Fig. 8.6 the $I_{\text{th}}$ at 292K and 322K approach one another with increasing pressure and hence indicates the observed improvement in the $T_0$ value with increasing pressure as shown in Fig. 8.7. It is seen that $T_0$ increases from 65K at $p = 0$ to about 120K at $p = 7$ kbar and appears to be starting to saturate. Such a saturation effect is to be expected as intervalence band absorption becomes less significant and no further pressure dependent loss mechanism remains.

8.6 Pressure Dependence of $I_{\text{th}}$ for Different (In Ga)(As P) Lasers

8.6.1 Laser with $n^+$ active layer

Copeland (121) made a theoretical study of the effect of high dopant concentrations in the active layer of semiconductor lasers. The effect of p-doping on $I_{\text{th}}$ in 1.3 μm (In Ga)(As P)/In P lasers has been reported (122) (123) to show increasing $I_{\text{th}}$ with doping levels, although the temperature dependence has no relation to the dopant used (124). However, Copeland predicted that donor concentrations around $4 \times 10^{18}$ cm$^{-3}$ would significantly reduce the injected carrier concentrations required to produce inversion, without much effect on the free carrier absorption loss. This was thought likely to lead to lower, $I_{\text{th}}$, faster response and better temperature sensitivity of the $I_{\text{th}}$ in quaternary lasers.

However, measurements have been carried out here on quaternary lasers with evenmore highly doped $n$-type active layers. In particular, the effect of pressure on $I_{\text{th}}$ and its temperature dependence is compared with the corresponding data for lasers with nominally undoped active layers.
The effect of pressure on $T_0$ in 1.3 μm (GaIn)(AsP) lasers.
Trials were initially carried out by Greene on the feasibility of growing LPE 1.3 μm layers with high Se or Te doping. The conditions used were similar to those given in Chapter 4. The relationship between carrier concentration in the solid to the dopant concentration in melt is shown in Fig. 8.8 (a). Carrier concentrations exceeding $10^{19}$ cm$^{-3}$ can readily be achieved using Se as dopant. The laser structure consisted of Ge-doped n- In P, active quaternary (0.26 to 0.28 μm), Zn-doped p-In P (1.3 μm) and Zn doped p-type quaternary capping layer (0.3 μm). The active layer was grown at the same standard temperature (659°C) as for the single layer growths. The effect of varying stripe width between 5 and 30 μm for lasers made from the same growth run is illustrated in Fig. 8.8 (b). The figure includes the results for devices with Te-doped active layers with $4 \times 10^{18}$ cm$^{-3}$ carrier concentrations. In these devices the observed $I_{th}$ were only slightly greater than those normally achieved with undoped active layers.

The effect of pressure on $I_{th}$ of a 400 μm long laser with 30 μm stripe width containing a Te-doped active layer is shown in Fig. 8.9 (a) for two temperatures. The results of the pressure dependence on lasers of undoped active layer are presented again in Fig.8.9 (b) for comparison. Although direct comparison is not useful since the two types of lasers have different dimensions, the vertical axes of the two results have been scaled to permit a more useful comparison to be made.

The theoretical curves shown in Fig. 8.9 (b) represent the $I_{th}$ assuming intervalence band absorption model. For an active layer doped with Te, to $4 \times 10^{18}$ cm$^{-1}$, an intervalence band absorption model produced a good fit to the experimental points. The value of the absorption coefficient $\alpha_{ac}$ was found to be about 100 cm$^{-1}$, dictated by
Fig. 8.8.a  Relationship between carrier concentration in quaternary layer (1.3 μm) & Se or Te dopant concentration in the melt at 659°C.

Fig. 8.8.b  Threshold current as a function of stripe width for 200 μm long lasers.
Fig. 8.9a  Pressure dependence of threshold current for a laser with undoped active layer.

Fig. 8.9b  Pressure dependence of threshold current for a laser with n+ active layer.
Fig. 8.10 Pressure dependence of the temperature sensitivity, $T_0$, for undoped & n$^+$ active layer lasers.
the observed $I_{th}$ at $p = 0$. At the higher temperature, the absorption coefficient was nearly doubled, again dictated by the $I_{th}$ at $p = 0$. For these lasers the analysis was similar to the undoped lasers. In these lasers the lifetime of injected holes, which depends on the electron density, is thought to be almost independent of the injected electrons, so that the hole density and hence the intervalence band absorption becomes directly proportional to the current instead of to its square root as in normal undoped active layer lasers.

The reduction in $I_{th}$ produced by increasing the pressure is less marked for the lasers with Te-doped n$^+$ active layer. This is also evident in the values of $T_0$ with increasing pressure as shown in Fig. 8.10. Although the value of $T_0$ is over 100K at the upper end of the pressure range investigated, the significance of the lower $T_0$ value observed for the n$^+$ laser is not clear.

8.6.2 Inverted Rib Waveguide Laser

The results (110) of the temperature dependence of $I_{th}$ for 1.3 $\mu$m (In Ga)(As P) lasers showed that around 200K there is a break point ($T_{b1}$) with $T_0$ between 55 and 75K above $T_{b1}$. A second break point, $T_{b2}$, was measured by Henshall et al (125), and occurred at temperatures in excess of 273K above which $T_0$ values were typically between 30 and 50K. The lasers which exhibited these second break points were fabricated (126) with inverted rib waveguide. The process involved growing directly on a channelled substrate. The effect of low values of $T_{b2}$ is to limit the high temperature operation of these lasers and also leads to pronounced saturation of the output power. However $T_{b2}$ is not an intrinsic effect and can be controlled by fabrication for optimum high temperature operation. The low value of $T_{b2}$ is specifically
Fig. 8.11 Comparison between undoped active layer lasers & inverted rib waveguide laser threshold current.
for these inverted rib wave guide lasers and a preliminary analysis carried out by Hensall and Thompson (110) attribute a 10% of \( I_{th} \) in these lasers to the leakage of carriers over the heterojunction barrier.

The effect of pressure on the \( I_{th} \) in the inverted rib waveguide laser has been measured here and is shown in Fig. 8.11. As with undoped and n+ active layer lasers, \( I_{th} \) in the rib waveguide laser is seen to decrease with increasing pressure. However, the decrease in \( I_{th} \) is less pronounced. A possible explanation for this pressure dependence would be that an additional loss mechanism occurs which increases with increasing pressure partially cancelling the larger reducing effect on \( I_{th} \). Assuming intervalence band absorption as the dominant mechanism with an additional loss of carriers over the barrier mechanism (10% at \( p = 0 \)) good agreement was obtained between the calculated \( I_{th} \) and the observed \( I_{th} \) in these lasers.

Summary

In this chapter the first study of the effect of pressure on the 1.3 \( \mu \)m quaternary and (Ga Al) As lasers has been presented. The most interesting observation made from the measurements is the decrease in threshold current for the quaternary lasers as opposed to the increase in threshold current for (Ga Al) As laser. The decrease in threshold current with pressure in the quaternary lasers had considerable significance on the loss mechanism that is responsible for the extreme temperature sensitivity of the threshold current. Although intervalence band absorption and Auger recombination predicted a decrease in the threshold current with pressure, loss of carriers over the barrier or loss through impurity centres both predicted considerable increase in threshold current contrary to observations.
These conclusions were consistent with high temperature measurements, where the intervalence band absorption mechanism explained the results better than Auger recombination.

The temperature and pressure dependence of the threshold current enabled us to also deduce the pressure dependence of the $T_0$ parameter. It was shown that $T_0$ increased with pressure indicating the improvement in the temperature sensitivity of the quaternary laser with pressure. Its value increased to over 100K in the upper pressure range.

Lasers with different growth characteristic such as the n$^+$ active layer laser and rib waveguide laser also showed a decreasing threshold current with increasing pressure. These high pressure results were also explained by assuming the intervalence band absorption as the most dominant mechanism. In the case of the n$^+$ active layer laser the $T_0$ value also increased with pressure. In addition to the intervalence band absorption a small amount of leakage over the barrier was required to explain the pressure dependence of the threshold current in the rib waveguide laser as speculated by Henshall.
9.1 Summary

Knowledge of the cause of temperature sensitivity of quaternary lasers is of considerable importance if its influence is to be minimised. Hence the first pressure measurements have been made on the 1.3 μm wavelength (In Ga)(As P)/In P quaternary lasers and the associated quaternary alloy to examine the controversial question of the dominant loss mechanism which has been blamed for the extreme temperature sensitivity of the quaternary lasers. For the quaternary lasers, the low $T_0$ values of 60 - 70K is in contrast to 160 - 200K for (Ga Al) As lasers near room temperature. The low $T_0$ problem has been attributed, in the literature, to Auger recombination, intervalence band absorption, loss of carriers over the heterojunction or loss through impurity centres. These loss mechanisms depend on the band structure of the quaternary and In P material. Pressure produces considerable change in band structure parameters. Therefore, pressure has been used here for the first time as a diagnostic tool for the quaternary lasers.

Single layers of $\text{In}_{1-x} \text{Ga}_x \text{As}_y \text{P}_{1-y}/\text{In P}$ quaternary alloy were grown by the horizontal LPE technique at a growth temperature of 659°C. The growth conditions used here produced good quality epitaxial layers with mid $10^{16}$ cm$^{-3}$ carrier concentration and an average layer thickness of 8 μm across the range of alloy composition.
The quaternary lasers were grown by STL using a similar system. The quaternary active layer, with 0.2 to 0.3 \( \mu \text{m} \) thickness, was grown at a temperature of 659°C. The LPE quaternary samples have been used for the first pressure measurements using the shift in photoconductivity edge to determine the pressure coefficient, \( \frac{dE_0}{dP} \), across the range of alloy composition \( y = 0 \) to \( y = 1 \). The values of \( \frac{dE_0}{dP} \) increase from 8.5 ± 0.5 meV kbar\(^{-1} \) at In P composition to 12.0 ± 0.5 meV kbar\(^{-1} \) near the ternary, \( y = 1 \), alloy composition. Interpretation of the interband energy gap, in terms of interatomic distance, produces a theoretical model in good agreement with the measured \( \frac{dE_0}{dP} \) across the alloy composition. Although the theoretical model has been used in the past for binary and ternary compounds, the first application to In\(_{1-x}\)Ga\(_x\)As\(_y\)P\(_{1-y}\)/InP quaternary alloy has been made here to explain successfully the pressure coefficient results. However, despite the agreement obtained, measurements of compressibility of the quaternary alloy need to be made before firm conclusions are drawn. Besides \( \frac{dE_0}{dP} \) values, the effective masses of electrons, heavy holes, and light holes, have been calculated. These parameters have been extremely useful in the analysis of pressure measurements on lasers.

The mobility measurements in the quaternary material have been obtained with J.R. Hayes, as reported in the journal of Electronic Material 1982. The mobility measurements, as a function of pressure in the quaternary alloy, have clearly shown that alloy scattering rather than space-charge scattering is present in the quaternary alloy. Both the electron and hole mobility variation across the alloy composition pass through a minimum. The temperature variation of the electron mobility can be explained satisfactorily in terms of the polar optical phonon, ionized impurity and alloy scattering.
mechanisms. For the hole mobility, additional acoustic and nonpolar optical phonon scattering mechanism have to be considered. The pressure dependence of the electron and hole mobility in the Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$ quaternary alloy indicated the presence of alloy scattering.

The first pressure measurements on the quaternary lasers have been made where the decreasing threshold current with pressure indicates, in contrast to (Ga Al) As lasers, the presence of pressure sensitive mechanisms in the quaternary lasers. The loss mechanism, which is reduced with increasing pressure, is that responsible for the high temperature sensitivity of the threshold current. This is clearly shown by the improvement in the $T_0$ value which increases to over 100K in the upper pressure range and appears to saturate. Intervacency band absorption appears to fit best the observed results of the first pressure measurements on 1.3 $\mu$m quaternary lasers. The model assuming Auger recombination as the dominant loss mechanism cannot explain satisfactorily the pressure measurements at higher temperatures. The model assuming loss of carriers over the heterojunction barriers and the model assuming loss at impurity centres are eliminated as being the dominant loss mechanisms since each predicts increasing threshold current with pressure, contrary to observations.

In the analysis, the four loss mechanisms have been considered separately, whereas in practice probably more than one is operative and possibly to some extent, all four mechanisms may play a role. It is interesting to note that, one of the laser systems studied here seems to indicate the presence of a small amount of barrier current as well as intervacency band absorption. However, for the temperature range considered here, it is considered that intervacency band
absorption plays a dominant role in the 1.3 μm quaternary lasers. One important conclusion is that the loss mechanism appears to be intrinsic and must therefore be allowed for by system engineers.

9.2 Future Work

A number of areas of study have emerged from the work presented in this thesis. An example is the saturation of $T_0$ value at higher pressures, than obtained here. As intervalence band absorption is squeezed out perhaps barrier current begins to dominate as the heterojunction barriers are reduced with pressure. If this was the case, the value of $T_0$ would decrease since the loss over the barrier increases with pressure. Pressure measurements of quantum efficiency and lifetime, determined from observing the time delay between onset of lasing and the current pulse, will allow more quantitative analysis of the loss mechanisms. The measurement of intervalence band absorption coefficient in the quaternary alloy or possibly in the quaternary laser structure itself, is of considerable importance in understanding the role it plays in the operation of quaternary lasers. A number of interesting areas of future work are evident for applications of pressure to other semiconductor devices such as LED's, transistors etc.
APPENDIX 1

1. Derivation of $\frac{dE_{o,h}}{dP}$

\[ E_{o,h} = 4.1 \left[ \frac{d}{d_{si}} \right]^{-2.75} \]  \hspace{1cm} (1.1)

the derivative of $E_{o,h}$ w.r.t. pressure $P$ is

\[ \frac{dE_{o,h}}{dP} = -11.275 \left[ \frac{d}{d_{si}} \right]^{-2.75} \frac{1}{d} \frac{d}{dP} \]  \hspace{1cm} (1.2)

where $d_{si}$ is the nearest neighbour distance in silicon and independent of pressure. The compressibility, $k$, is defined as

\[-k = \frac{1}{V} \frac{dV}{dP} \]  \hspace{1cm} (1.3)

where $V$ is the volume of material. Assuming volume is proportional to $d^3$ then

\[-k = \frac{1}{3} \frac{d}{dP} \]  \hspace{1cm} (1.4)

Hence

\[ \frac{dE_{o,h}}{dP} = 3.758 k \left[ \frac{d}{d_{si}} \right]^{-2.75} \]  \hspace{1cm} (1.5)
2. Derivation of $\frac{d\Delta E_o}{dP}$

$$\Delta E_{o,h} = 12.8 \left[ \frac{d}{d_{si}} \right]^{-5.07}$$

the derivative of $\Delta E_{o,h}$ w.r.t. $P$ is

$$\frac{d\Delta E_o}{dP} = -64.896 \left[ \frac{d}{d_{si}} \right]^{-5.07} \frac{1}{d} \frac{d}{dP} \quad (1.6)$$

Using (1.4)

$$\frac{d\Delta E_o}{dP} = 21.63 \frac{d}{d_{si}} \left[ \frac{d}{d_{si}} \right]^{-5.07} \quad (1.7)$$

3. Derivation of $\frac{d(D_{av} - 1)}{dP}$

$$(D_{av} - 1) = R_A (1 - f_i)^X \left[ \frac{d}{d_{si}} \right]^Y$$

the derivative of $(D_{av} - 1)$ w.r.t. $P$ is

$$\frac{d(D_{av} - 1)}{dP} = R_A \left[ (1 - f_i)^X \frac{d}{dP} \left[ \frac{d}{d_{si}} \right]^Y + \left[ \frac{d}{d_{si}} \right] \frac{d(1 - f_i)^X}{dP} \right]$$ \quad (1.9)

The first term before the addition sign can be simplified as
\[ R_A (1 - f_i)^x \frac{d}{dp} \left( \frac{d}{ds_i} \right)^y = R_A^y (1 - f_i)^x \frac{d}{ds_i} \frac{1}{d} \left[ \frac{dd}{dp} \right] \]

\[ = -Y k \left( D_{av} - 1 \right) \quad (1.10) \]

The second term can be simplified as follows since

\[ f_i = \frac{c^2}{E_{o,h}^2 + c^2} \quad (1.11) \]

\[ R_A \left[ \frac{d}{ds_i} \right]^y \frac{d(1 - f_i)^x}{dp} = X R_A \left[ \frac{d}{ds_i} \right]^y (1 - f_i)^x \frac{2c^2}{E_{o,h}^2 + c^2} \frac{dE_{o,h}}{dp} \quad (1.12) \]

using (1.5)

\[ = X (D_{av} - 1) \frac{2c^2}{(E_{o,h}^2 + c^2)E_{o,h}} \frac{dE_{o,h}}{dp} \quad (1.13) \]

Hence derivative of \((D_{av} - 1)\) w.r.t. \(P\) is

\[
\frac{d(D_{av} - 1)}{dp} = k(D_{av} - 1) \left[ \frac{7.156 \times c^2}{(E_{o,h}^2 + c^2)E_{o,h}} \left[ \frac{d}{ds_i} \right]^{-2.75} \right]^\frac{Y}{3} \]
Deep Levels from Capacitance measurements

1. C - V Profil

Consider the band diagram for a Schottky barrier in reverse bias with deep trap at $E_T$ (from $\Gamma$) and $N_T$ density.

The trap energy is

$$E_T = e V_L + E_F$$  \hspace{1cm} (1.15)

From Poisson's equation, the excess voltage $V_e$ associated with the trap density $N_T$ for $0 < x < \lambda$ is

$$V_e = e \frac{N_T \lambda^2}{2 \varepsilon}$$  \hspace{1cm} (1.16)
at \( x = L \)

\[ V_L = \frac{eN_s L^2}{2\varepsilon} \]  \hspace{1cm} (1.17)

Therefore

\[ V_e^{\frac{1}{2}} = A(\frac{1}{2}\varepsilon e N_T)^{\frac{1}{2}} (C_W^1 - C_L^1) \]  \hspace{1cm} (1.18)

where \( C_W = A - \) is the measured diode capacitance, \( \frac{W}{L} \)

\[ C_L = \frac{A \varepsilon}{L}, \text{ and } A \text{ is the diode area.} \]

since \( N_s = \frac{2}{\varepsilon e A^2} \frac{dV}{dC^{-2}} \)  \hspace{1cm} (1.19)

\[ V_L = C_L^2 \frac{dV}{dC^{-2}} \]  \hspace{1cm} (1.20)

From (1.18) a plot of \( C_W \text{ vs. } V_e^{\frac{1}{2}} \) will determine \( C_L \) and hence \( V_L \) can be obtained from (1.20) and \( V \text{ vs. } C^{-2} \) curve. The trap concentration \( N_T \) can be obtained from the slope of (1.18)

The measurements and analysis of \( C - V \) Profiling can be obtained as follows: the sample is maintained under a large reverse bias at room temperature where the deep levels are fully ionized for \( 0 < x < \lambda \). The temperature is then reduced to about 120K, when a \( C - V \) (curve 1) is obtained while reducing the reverse bias until, at forward bias, all are occupied. At this
low temperature, another C - V (curve 2) is obtained until
the large reverse bias is achieved. A plot of $C^{-2}$ vs. $V$ for
curve 1 and 2, will allow $V_e$ to be determined (that is the
difference between the two curves at a given capacitance $C_u$).
A plot of $V_e^{\frac{1}{2}}$ vs. $C_w^{-1}$ results in $N_T$ from the slope and $C_L^{-1}$
is the intercept value at $V_e = 0.$
54. Greene, P.D., Private Comm.
87. See for example, Muller, H., Trommer, R., Cardona, M.,
Comm. 18, (1976).
113. Dutta, N.K., Nelson, R.J., IEEE Quantum Electron. QE-18, 3,
(1982).
118. Yamanishi, M., Suemune, I., Nonomura, K., Mikoshiba, N.,
120. Yamanishi, M., Suemune, I., Nonomura, K., Mikoshiba, N.,
122. Itaya, Y., Suematsu, Y., Katayama, S., Kishino, K., Arai, S.,
126. Turley, S.E.H., Henshall, G.D., Greene, P.D., Knight, V.P.,
127. Thompson, G.H.B., 'Physics of Semiconductor Devices'.
    Wiley Sons, (1980).
128. Wolfe, C.M., Stillman, G.E., Lindley, W.T., J. Appl. Phys, 41,
129. Rode, D.L., 'Semiconductors and Semimetals', Academic Press,
131. Bradley, C.C., 'High Pressure Methods in Solid