DEEP LEVELS IN III-V SEMICONDUCTORS
AND QUANTUM WELLS AT HIGH PRESSURE

BY

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ABSTRACT

Capacitance transient spectroscopy, frequency resolved capacitance spectroscopy and the Hall effect have been used as a function of temperature to characterise deep levels in some III-V semiconductor materials. Hydrostatic pressure has been used to move the energy bands and study the pressure dependence of the activation energy of deep levels. These experimental methods have been developed with the aim of measuring the pressure coefficients of impurity levels due to transition metals in order to establish whether their position relative to the vacuum level is fixed and independent of the host material as has been suggested by Ledebo and Ridley (1982). The pairing of the transition metal acceptor Mn with a donor from group VI has been studied in the quaternary alloy GaInAsP and shown to lend negligible carrier scattering in certain circumstances. Electron emission from quantum wells has been investigated as a function of temperature and pressure to measure conduction band-offsets and their pressure dependence.
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The following papers based on work presented in this thesis have been accepted or are to be presented for publication in the scientific literature.


"Frequency resolved capacitance spectroscopy - a new approach to measuring deep levels in semiconductors.", accepted for publication J. Phys. E (1988)

"Determination of band offsets in MBE grown GaAs/GaAlAs quantum well heterostructures: application of capacitance spectroscopy", submitted to GaAs and Related Compounds, Atlanta (1988)

"Pairing of Mn-acceptors and Te-donors in InP and In$_{1-x}$Ga$_x$As$_y$P$_{1-y}$", to be submitted to Solid State Communications.
LIST OF SYMBOLS

\( a_0 \)  lattice constant
\( A \)  junction area
\( B \)  magnetic field
\( C_r \) capture constant
\( C \) capacitance
\( C_0 \) capacitance term due to \( V_o + V_r \)
\( C' \) capacitance due to in-phase modulation
\( C'' \) capacitance due to deep level response
\( C^* \) capacitance per unit area
\( c_{n,p} \) electron and hole capture rates
\( e_{n,p} \) emission rate of electrons and holes
\( E \) electric field
\( E_a \) thermal activation energy
\( E_b \) barrier to capture
\( E_c \) conduction band energy
\( E_F \) Fermi energy
\( E_{hh} \) heavy hole band energy
\( E_g \) band gap at \( i \)
\( E_n \) binding energy
\( E_r \) energy of lattice relaxation
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>$E_{ac}$</td>
<td>activation energy of thermal equilibrium carrier conc.</td>
</tr>
<tr>
<td>$E_{opt}$</td>
<td>energy of optical absorption</td>
</tr>
<tr>
<td>$E_T$</td>
<td>absolute trap position relative to vacuum level</td>
</tr>
<tr>
<td>$E_v$</td>
<td>valence band energy</td>
</tr>
<tr>
<td>$E_{r,x,L}$</td>
<td>band gap to $\Gamma, X, L$ minima from top of valence band</td>
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<tr>
<td>$f_T$</td>
<td>probability of a level being occupied by an electron</td>
</tr>
<tr>
<td>$g$</td>
<td>degeneracy factor</td>
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<td>$G$</td>
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<tr>
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<tr>
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<td>electron effective mass</td>
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<td>heavy hole effective mass</td>
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<td>Symbol</td>
<td>Description</td>
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<td>$N_v$</td>
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<td>entropy</td>
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<td>$V_m$</td>
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<td>$V_{out}$</td>
<td>Lock-in output</td>
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<td>$\Delta E_c$</td>
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<tr>
<td>$\Delta E_v$</td>
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<td>$A_{FC}$</td>
<td>Frank-Condon shift</td>
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<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>$\Delta Z$</td>
<td>deviation of sensor function from reference function</td>
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<td>permittivity of free space</td>
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<td>$\phi_p$</td>
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<td>lattice eigenfunction</td>
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<td>$\omega$</td>
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CHAPTER 1

INTRODUCTION

Calculations of the ionization potentials of several III-V semiconductors using the quantum dielectric theory of Van Vechten (1969) have lead to the idea (Ledebo and Ridley (1982)) that the position of energy levels related to transition metal impurities are constant with respect to the vacuum level in some III-V semiconductors, irrespective of the host material. A typical case is the Chromium acceptor level which has energies relative to the valence band of 0.81, 0.94 and 1.13 eV in GaAs, InP and GaP, respectively, while its absolute position relative to the vacuum level remains almost constant as shown in figure 1.1. The position of the levels related to Fe, Cu\textsuperscript{A} and Cu\textsuperscript{B} in these materials also showed similar behaviour. Supporting evidence has been provided by Iqbal et al (1985) who obtained the position of the Cu\textsuperscript{B} level in the alloy GaAs\textsubscript{1-x}P\textsubscript{x} from optical threshold measurements. Their results are shown in figure 1.2 together with the variation of the band structure with alloy composition.
Figure 1.1 Position of Cr level in GaAs, InP and GaP
Since the variation of the Cue level is similar to that of the L and X minima it was concluded that the level follows these minima as a function of composition. However, when the position of the Cue level is plotted relative to the vacuum level assuming a linear change in ionisation potential between GaAs and GaP (figure 1.3) its position is found to be constant across the alloy range. Similar results have been reported for transition metal impurity related levels in the ternary alloy Al$_{x}$Ga$_{1-x}$As (Jansson et al (1983)). These measurements on alloys tend to confirm the hypothesis that the TM impurities are fixed with respect to the vacuum level. A theoretical explanation has been proposed by Caldas et al (1984) using a tight binding model but this contradicts a related model by Hajalmarsen et al (1980). However, measurements of the deep level activation energy as a function of composition, as performed by Jansson et al are unsatisfactory because they require theoretical calculations of the variation of ionisation potential with alloy composition in order to relate the energy level positions to the vacuum level. The ionization potentials can be calculated using quantum dielectric theory but the results obtained are in contradiction to those obtained using more recent theoretical models by Cardona and by Zawadski.

The effect of hydrostatic pressure on the position of deep levels provides complementary information to that
Figure 1.2 Energy of Cu_{B} level in GaAs_{1-x}P_{x} relative to the top of the valence band.

Figure 1.3 Position of Cu_{B} level relative to vacuum level.
of alloying and may resolve this problem. If the energy level is independent of the host lattice then it is independent of the pressure in the host lattice. The effect of hydrostatic pressure is to move the band edges in III-V compounds. Therefore, according to the model of Ledebo and Ridley the levels due to different transition metals (Cr, Fe, Cu, Ni, V, etc.) in a particular III-V compound must have the same pressure coefficient with respect to the valence or conduction band edge. This would also provide for the first time an accurate measure of the pressure coefficient of the ionization potential in GaAs.

If the different levels turned out to have the same pressure coefficients deep levels could be used as markers against which the relative positions of the band edges in different III-V semiconductors can be measured. Also the pressure coefficient of the band offset would be established. This is a very important unknown parameter in the many pressure measurements on low dimensional structures now being undertaken. Also, it would provide a direct test of the theories of Cardona and Zawadski which predict that the ionization potential decreases with pressure contrary to the predictions of the quantum dielectric theory.

In practice confirmation that the hypothesis is exactly true is not to be expected. However, since hydrostatic pressure can cause changes in band structure
similar in magnitude to those between different materials, the measurements will be able to establish how accurate the hypothesis is. It will enable direct comparison to be made between the theories of Caldas and Hajalmarson and, if correlation between theory and experiment can be established, then appropriate theoretical adjustment will be possible to subsequent measurements in other systems such as GaAlAs associated with a GaAs-AlGaAs heterojunction. Measurements of the pressure coefficients of deep levels, mainly unidentified or due to defects, in GaAs have already been undertaken. Measurements on the levels due to the transition metals Fe and Cu gave an increase in the distance between the valence band and the level of 5.5 and 5.7 meV/kbar respectively. This close similarity is very encouraging and makes clear that a wider, more systematic study is justified.

An introduction to the band structure and properties of III-V semiconductors and deep levels is given in chapter 2. The electrical techniques for the measurements of deep level activation energy used are described in chapter 3. These include Frequency Resolved Capacitance Spectroscopy, a newly developed technique particularly suited for measurements at high pressure. The implementation of these experimental methods and the high pressure systems are described in chapter 4. The activation energy of the p-type dopant Mn in InP and
GaInAsP and the pairing of Mn with Te donors has been evaluated from hole transport in LPE material. These results are presented and discussed in chapter 5. Initial measurements of the pressure dependence of the activation energy of a number of centres in III-V compounds, including the extensively reported EL2 in GaAs are reported in chapter 6.

It has been suggested (e.g. Martin et al (1983) and Hamilton et al (1985)) that the quantum well formed by the band gap discontinuities in a system such as GaAs-AlGaAs may be treated as a "giant trap". This approach, which, although it does not make reference to transition metals, provides an alternative way of measuring the band offsets. In chapter 7 the measurement of electron emission from a quantum well as a function of temperature is used to determine the conduction band offset in the GaAs-AlGaAs system. The pressure dependence of the emission from the well and the deep levels in the AlGaAs barriers is investigated, and results obtained on InP-InGaAs superlattices using three different methods are compared.

If the position of the energy levels due to the transition metals are indeed fixed with respect to the vacuum level then it is possible to predict where a level will lie in the gap of a particular material. The energy levels produced do not always fall within the forbidden gap. In the case of Vanadium, for example, it is known
that it produces a deep acceptor level 150 meV below the conduction band edge in GaAs and according to the hypothesis of Ledebo and Ridley we would expect the level to be around 160 meV above the conduction band edge in InP and thus not be detectable by conventional deep level characterisation techniques. In chapter 8 the use of hydrostatic pressure to drive a deep level in Vanadium doped InP into the gap is demonstrated.

Finally, in chapter 9, the results obtained and their implications are summarised and the recommendations for future work required are presented.
2.1 INTRODUCTION

The properties of some technologically important semiconductor materials synthesised from elements of groups III and V of the periodic table of relevance to the work carried out in this thesis are described in the following sections, with particular reference to their variation with temperature and hydrostatic pressure. The effect of impurities is outlined in section 2.3.

2.2 CRYSTAL STRUCTURE

Most crystals formed from elements of groups III and V assume the zincblende structure. The unit cell is illustrated in figure 2.1. This structure consists of equal numbers of atoms of two types occupying alternate sites on a diamond lattice such that an atom from one group has four nearest neighbours from the other. This can be thought of as two interpenetrating face centred cubic (f.c.c.) lattices of different atoms displaced by one quarter of the body diagonal distance.
Fig 2.1: Unit cell of zincblende structure.

Fig 2.2: First Brillouin zone of f.c.c. lattice, showing main symmetry points.
The three electrons in the outer shell of atoms from group III have an $s^2p'$ configuration, whereas the five electrons from the group V are in an $s^2p^3$ configuration, resulting in covalent $sp^3$ hybrid bonding with some ionic character. Figure 2.2 shows the first Brillouin zone given by the f.c.c. crystal structure. It consists of a truncated octahedron with eight hexagonal and 6 square faces. The principal symmetry points are shown: $\Gamma$ at the zone centre, $L$ at the zone boundary along the $<111>$ direction and $X$ at the zone boundary along the $<100>$ direction.

2.3 BAND STRUCTURE OF III-V SEMICONDUCTORS

2.3.1 INTRODUCTION

The band structure, that is, the dependence of electron energy on wave-number vector for the various bands, $E_n(\mathbf{k})$, is derived from the quantum mechanical treatment of electronic states in crystalline materials. The interaction of electrons with a potential (due to the negative valence electrons and positively charged ion cores) periodic with the periodicity of the lattice described in the previous section leads to regions of allowed energy states separated by forbidden energy gaps dependent on the crystal symmetry. In general, in III-V materials this leads to pronounced conduction band minima near the Brillouin zone centre, $\Gamma$, and other minima near the $L$ and $X$ points along the $<111>$ and $<100>$ directions.
Figure 2.3: Band structure of GaAs along $\langle 100 \rangle$ and $\langle 111 \rangle$ directions.
together with a more complex valence band maximum at the \( \Gamma \) point. The band structure of GaAs along the \( \langle 111 \rangle \) and \( \langle 100 \rangle \) directions, typical of most III-V semiconductors, showing the main energy gaps is illustrated in figure 2.3. Although theoretical calculations of the band structure using an assumed crystal potential at present are unable to produce results accurately enough to quantify material parameters, other methods such as \( k.p \) theory (Kane (1957, 1966)) have been used to determine the shapes of the \( E(k) \) accurately in the vicinity of the points of high symmetry within the Brillouin zone. A semi-empirical method of calculating the gaps at the extrema, based on the dielectric theory of the chemical bond developed by Phillips (1968) and Van Vechten (1969) has been shown to be particularly useful for calculating energy band pressure coefficients (Camphausen et al (1971)).

2.3.2 TEMPERATURE DEPENDENCE OF THE ENERGY GAP

The band structure will vary with temperature due to the change in lattice constant from thermal expansion. At higher temperatures the decrease in band gap with increasing temperature is mainly due to the temperature dependence of the electron-phonon interaction with a only a small contribution from the change in lattice constant. The temperature dependence of the band gaps has been
measured by several authors. Varshni (1967) found that
the results could be described by a relation of the form,

\[ E_n(T) = E_n(0) - \frac{\alpha_n T^2}{(T + \beta_n)} \]  

(2.1)

where the values of the band gap at 0 K at a particular
point, \( E_n(0) \), and the coefficients, \( \alpha_n \) (eV/K) and \( \beta_n \) (K)
have been measured and are shown for some compounds in
table 2.1. The effect of pressure on the band gap of
some of the semiconductor alloys investigated in this
thesis are referred to in the following section.

2.3.3 EFFECT OF HYDROSTATIC PRESSURE

It is apparent from the prescriptions formulated
by Van Vechten that the nearest-neighbour distance, \( d \),
plays an important role in determining the band gaps. The
application of hydrostatic pressure alters the lattice
constant via the compressibility and hence varies the
band gap without altering the symmetry of the crystal,
unlike uniaxial stress. Experimental results show that
the pressure coefficient of the energy difference between
the two states of a given symmetry is very similar in
most semiconductors (Paul (1961)) although the pressure
coefficient of the energy gaps at different points on the
Brillouin zone can be very different (Camphausen et al
(1971)). For example the pressure dependence of the direct
gap at the $\Gamma$ point, $E_\tau$, is around 10 meV/kbar in most III-Vs, whereas the coefficient of the direct gap at the L point, $E_1$, is around 5 meV/kbar. The pressure dependence of the gaps of some III-V's are shown in table 2.1.

2.4 MATERIAL PROPERTIES OF III-V SEMICONDUCTORS

The values of parameters and their pressure coefficients necessary for the analysis of experimental results on some III-V binary and alloy semiconductors are given in table 2.1. Where experimental results are not available for the alloys, values interpolated between the binary constituents are used. The sources of these are quoted in the table of references. The binary III-V compounds have a room temperature band gap in the range 0.17 eV for InSb to 2.26 eV for GaP (see figure 2.4). The commercially important binaries GaAs and InP with band gaps of 1.42 and 1.35 eV at room temperature are perhaps the most well known. The availability of high purity single crystals of these materials has enabled the range of semiconductors to be extended by the growth of epitaxial layers of semiconductor alloys of variable composition on different types of binary substrates. By careful control of the mole fraction of the constituents it is possible to produce layers of the same lattice constant as the substrate, necessary to reduce the
### Table 2.1: Properties of some III-V semiconductors

<table>
<thead>
<tr>
<th>Property</th>
<th>GaAs</th>
<th>InP</th>
<th>Ga_{0.47}In_{0.53}As</th>
<th>Al_{x}Ga_{1-x}As</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (Å)</td>
<td>5.6533</td>
<td>5.8688</td>
<td>5.8688</td>
<td>5.6533 + 0.0078x</td>
</tr>
<tr>
<td>$\varepsilon_\infty$</td>
<td>13.18</td>
<td>12.56</td>
<td>13.77</td>
<td>13.18 - 3.12x</td>
</tr>
<tr>
<td>$\frac{d\ln\varepsilon}{dT}$ ($10^{-6}$K$^{-1}$)</td>
<td>12.3</td>
<td>10.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{d\ln\varepsilon}{dP}$ (kbar)</td>
<td>-1.8</td>
<td>-1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{th}$ ($10^{-6}$K$^{-1}$)</td>
<td>6.4</td>
<td>4.56</td>
<td>5.7</td>
<td>6.4 - 1.2x</td>
</tr>
<tr>
<td>$B_r$ (eV)</td>
<td>1.522</td>
<td>1.421</td>
<td>0.822</td>
<td>1.425 + 1.155x + 0.37x$^2$</td>
</tr>
<tr>
<td>$E_x$ (eV)</td>
<td>2.010</td>
<td>2.22</td>
<td>2.16</td>
<td>1.911 + 0.005x + 0.245x$^2$</td>
</tr>
<tr>
<td>$E_l$ (eV)</td>
<td>1.840</td>
<td>1.92</td>
<td>1.67</td>
<td>1.734 + 0.574x + 0.055x$^2$</td>
</tr>
<tr>
<td>$\frac{dE_r}{dP}$ (meV/kbar)</td>
<td>10.7</td>
<td>8.5</td>
<td>9.2</td>
<td>10.7</td>
</tr>
<tr>
<td>$\frac{dE_r}{dP}$ (meV/kbar)</td>
<td>-1.5</td>
<td>-2.4</td>
<td>-1.0</td>
<td>-1.5 + 0.2x</td>
</tr>
<tr>
<td>$\frac{dE_r}{dP}$ (meV/kbar)</td>
<td>3.8</td>
<td>2.0</td>
<td>4.2</td>
<td>3.8 + 0.2x</td>
</tr>
<tr>
<td>$\alpha_r$ ($10^{-4}$ eV)</td>
<td>5.41</td>
<td>4.906</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_x$ ($10^{-4}$ eV)</td>
<td>4.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_l$ ($10^{-4}$ eV)</td>
<td>6.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$ (K)</td>
<td>204</td>
<td>327</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_e$ (m$^0$)</td>
<td>0.0665</td>
<td>0.0803</td>
<td>0.041</td>
<td>0.067 + 0.083x</td>
</tr>
<tr>
<td>$m_h$ (m$^0$)</td>
<td>0.085</td>
<td>0.12</td>
<td>0.0503</td>
<td></td>
</tr>
<tr>
<td>$m_e$ (100) (m$^0$)</td>
<td>0.465</td>
<td>0.58</td>
<td>0.465</td>
<td></td>
</tr>
<tr>
<td>$m_e$ (111) (m$^0$)</td>
<td>0.595</td>
<td>0.60</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>$\frac{1}{m_e}$ ($10^{-4}$K$^{-1}$)</td>
<td>-1.9</td>
<td>-2.2</td>
<td>-4.1</td>
<td></td>
</tr>
<tr>
<td>$\frac{1}{m_e}$ (K)</td>
<td>0.77</td>
<td>0.53</td>
<td>1.68</td>
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## Key to references for table 2.1

<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Driscoll et al.</td>
<td>1975</td>
</tr>
<tr>
<td>b Willardson and Beer</td>
<td>1966</td>
</tr>
<tr>
<td>c Adachi</td>
<td>1985</td>
</tr>
<tr>
<td>d Samura</td>
<td>1983</td>
</tr>
<tr>
<td>e Meiners</td>
<td>1986</td>
</tr>
<tr>
<td>f Takeda et al.</td>
<td>1981</td>
</tr>
<tr>
<td>g Blakemore</td>
<td>1982</td>
</tr>
<tr>
<td>h Fisher</td>
<td>1987</td>
</tr>
<tr>
<td>i Straumanis et al.</td>
<td>1967</td>
</tr>
<tr>
<td>j Bisaro et al.</td>
<td>1979</td>
</tr>
<tr>
<td>k Wolford et al.</td>
<td>1986</td>
</tr>
<tr>
<td>l Varshni</td>
<td>1967</td>
</tr>
<tr>
<td>m Forrest et al.</td>
<td>1983</td>
</tr>
<tr>
<td>n Kobayashi et al.</td>
<td>1981</td>
</tr>
<tr>
<td>o Aspnes</td>
<td>1976</td>
</tr>
<tr>
<td>p Gunney et al.</td>
<td>1982</td>
</tr>
<tr>
<td>q Shantharama et al.</td>
<td>1985</td>
</tr>
<tr>
<td>r Gell et al.</td>
<td>1987</td>
</tr>
<tr>
<td>s Wolford et al.</td>
<td>1984</td>
</tr>
<tr>
<td>t Miller et al.</td>
<td>1984</td>
</tr>
<tr>
<td>u Chamberlain et al.</td>
<td>1972</td>
</tr>
<tr>
<td>v Nicholas et al.</td>
<td>1980</td>
</tr>
<tr>
<td>w Stradling</td>
<td>1975</td>
</tr>
<tr>
<td>x Rochon and Fortin</td>
<td>1975</td>
</tr>
<tr>
<td>y Alavi et al.</td>
<td>1980</td>
</tr>
<tr>
<td>z Stradling and Wood</td>
<td>1970</td>
</tr>
<tr>
<td>α Eaves et al.</td>
<td>1971</td>
</tr>
<tr>
<td>β Shantharama et al.</td>
<td>1984</td>
</tr>
</tbody>
</table>
dislocation density and strain produced by the difference in lattice constant. The growth of alloys provides access to the band gaps between those of their binary constituents. For example the ternary alloy In\textsubscript{x}Ga\textsubscript{1-x}As, where the difference in lattice constant of its constituents InAs and GaAs is large, can be grown lattice matched to InP at x=0.53, giving a band gap of 0.73 eV at room temperature. On the other hand, alloys such as Al\textsubscript{x}Ga\textsubscript{1-x}As lattice matched to GaAs have an almost constant lattice parameter as a function of Al composition with a room temperature band gap continually variable from 1.43 eV (at x=0) to 2.16 eV (at x=1). The direct band gap in most ternary alloys has an approximately quadratic dependence on the mole fraction, x and is given by:

\[ E_g(x) = a + gx + bx^2 \]  

(2.2)

The values of these coefficients for the Al\textsubscript{x}Ga\textsubscript{1-x}As alloy are given in table 2.1.

The quaternary alloys lattice matched to a binary substrate offer a continuous range of band gap for a fixed lattice constant. The system Ga\textsubscript{x}In\textsubscript{1-x}As\textsubscript{y}P\textsubscript{1-y} can be grown lattice matched to GaAs and InP.
Figure 2.4: Band gap v Lattice constant for III-V semiconductors.
When grown lattice matched to InP the composition parameters \( x \) and \( y \) are related as follows:

\[
x (1.032 - 0.032y) = 0.47y \tag{2.3}
\]

which approximates to \( y = 2.2x \). It has a band gap ranging from 0.73 eV for \( \text{Ga}_{0.47}\text{In}_{0.53}\text{As}, \ (y=1) \) to 1.35 for InP, \( (y=0) \). The dependence of the principal band gap on composition at room temperature is given by (Pearsall (1982)):

\[
E_r \ (295K) = 1.35 - 0.775y + 0.149y^2 \ (\text{eV}) \tag{2.4}
\]

The composition dependence of the electron effective mass can be fitted to the linear expression (Nicholas et al. (1980)):

\[
m_e/m_0 = 0.080 - 0.039y \tag{2.5}
\]

The band gap dependence of the effective mass on the band gap has been measured as a function of composition by Shantharama (1986) who found that it was very different from that of the constituent compounds and appeared to follow the variation of alloy disorder.

The valence band parameters of most relevance to the work carried out in chapter 6 are the light and heavy hole effective mass. Some experimental values for these
are given in table 2.1. The light hole effective mass has been measured as a function of composition (Hermann et al. (1980)), but with only one measurement of the heavy hole effective mass in the (100) direction at a composition of $y=0.52$, it is necessary, as with the other parameters for which there are no values available, to adopt an interpolation procedure (Adachi (1982)) in order to obtain an approximate value.
2.5 IMPURITY LEVELS

2.5.1 INTRODUCTION

The band structure discussed in the previous sections assumes a perfect crystal with no impurities. This is never the case, thus it is necessary to consider the effect of impurities. Whilst intrinsic semiconductors rely on the excitation of carriers across the gap, in extrinsic materials most of the carriers are supplied by impurity atoms substituted on lattice sites. The impurities give rise to a perturbation of the atomic potential and result in energy levels, often in the gap, being produced. The impurity levels produced can be divided into two categories: shallow and deep defect states. The second part of this chapter deals with the nature of impurity levels and their relevance in semiconductor materials.

2.5.2 DEFECTS IN SEMICONDUCTORS

Any departure from the perfect periodicity of the single crystal structure can give rise to a discrete energy level separated from the free bands. There are many types of crystal defects. These are intimately related and can be of zero, one, two or three dimensions and may be called point, line, sheet and volume defects, respectively. Various theoretical methods of investigating the properties of defects in crystalline
media are available (e.g. Crocker (1985)). Point defects can be vacancies, interstitials or impurity atoms. Vacancies are empty lattice sites; for the zinc-blende structure of the III-V compounds there can be two types: one for each component atom. Interstitials are component atoms or impurities which occupy positions other than lattice sites. Impurity atoms may be interstitially or substitutionally sited. Several point defects may associate to form complexes, e.g. divacancies or vacancies close to substitutional impurity atoms. Dislocations are the only important line defect in crystals: crystals deform by a process of local slip in which a small localised displacement slowly extends giving a long range stress field around the dislocation. The direction of slip can be along the line or perpendicular to the line and produce screw and edge dislocations respectively. Arrays of dislocations can be used to explain the structure of coherent crystalline interfaces. An important form of 'sheet defect' is the quantum well. A quantum well may be treated as a giant trap and will be discussed later on.

Defects can be introduced during crystal growth and put to good use for example in conductivity control in semi insulating technology where large concentrations of deep levels pin the Fermi level at the trap level to produce "intrinsic" material (e.g. GaAs:Cr) or for lifetime control and improved switching speed for power
devices (e.g. Si: Au). Defects are not always beneficial. They can be introduced during device preparation or during device operation and can for example provide non-radiative recombination paths reducing efficiency of LED's and lasers and degrading device performance in general.

2.5.3 SHALLOW IMPURITY LEVELS

Impurities from adjacent groups in the periodic table generally produce a small perturbation of the atomic potential. The levels produced are close to the band edges (within one tenth of the gap) and the centres are thermally ionized above $\approx 40K$. A shallow donor is an atom with enough electrons to bind with its nearest neighbours and an additional electron loosely bound to the impurity. Similarly, a shallow acceptor has a loosely bound hole. A donor level is defined as being neutral if filled by an electron, and positive if empty. An acceptor is neutral if empty and negative if filled by an electron. The small binding energy means that the impurity wave function is spread over the crystal and a trapped electron or hole spends most of its time away from the impurity (a large electronic orbit could have an effective Bohr radius of about 20Å), producing only a small perturbation of the lattice sites. The impurity wave function, $\psi$, can be expanded (Jaros (1979)) in terms of the (unperturbed) host lattice eigenfunctions $\phi_{n,k}$ as follows:
where the coefficients $A_{n,k}$ associated with a band $n$ and reduced wave vector $k$ are restricted to a small fraction of the Brillouin zone near the principal band minima. The solution of the Schrödinger equation leads to a series of hydrogenic-like states. These are described well by the so-called effective mass theory (Kohn (1957)). For a simple spherical band at $k = 0$ the binding energy, $E_n$, of the energy levels obtained is

$$E_n = \frac{\langle m^*/m_0 \rangle \varepsilon_0 \varepsilon_n^{2n}}{n^2 \varepsilon_n^{2n}} \times 13.6 \text{ (eV)} \quad (2.7)$$

Refinements of this model taking into account departures of the bands from spherical symmetry lead to good agreement between theoretical values and experimental results.

2.5.4 CHARACTERISTICS OF DEEP LEVELS

Hydrogenic theory in its more advanced form can predict with precision the excited states of simple donors and acceptors. The short range effects can be incorporated so as to account for the ground state energy and its variation reflecting the chemical nature of the dopant (Pantelides (1978)). The hydrogenic theory cannot
successfully account for the behaviour of the localised states arising from impurities with higher ionisation energies which lie deeper into the forbidden gap. These deep states are not amenable to treatment using effective mass theory. Their localisation in real space, and consequent delocalisation in k-space, allowing the defect to couple to a large variety of momentum vectors or phonons, means that they tend to be non-radiative recombination centres. This delocalisation in k-space also means that any theoretical description of a deep state must involve the entire band structure, not just a single minimum of a single band.

Deep defect states or levels are often referred to as recombination centres, generation centres or traps, depending mainly on the relative magnitudes of their electron and hole capture cross-sections. Basically, a trap is a centre which traps a free carrier, and after a while this trapped carrier has a greater probability of being thermally re-excited to the nearest allowed band to become a free carrier again than of recombining with a carrier of opposite sign at the centre. The trapping centres which capture electrons only are called electron traps, and those capturing holes only are hole traps. The occupancy of these centres is determined by the thermal equilibrium interchange of the carriers of one particular sign between the centres and the allowed band. A recombination centre is a centre which also captures a
free carrier, but the captured carrier has a greater probability of recombining with a carrier of opposite sign, resulting in the annihilation of both, than of being re-excited to the nearest allowed energy band. A localised state may act as a trapping or as a recombination centre depending on its location in the forbidden energy gap (governed by the nature of impurities and temperature), the concentrations of free electrons and holes, and the capture cross-sections for capturing electrons and holes. The distinction between a trapping and a recombination centre is thus quantitative rather than qualitative and is apparent from their capture and emission kinetics.

2.5.6 CAPTURE AND EMISSION PROCESSES

We study deep levels using the electronic transitions between the level and the bands. The four basic capture and emission processes that exist at a single energy level in the band gap are illustrated in figure 2.5. The probability of a level being occupied by an electron under equilibrium conditions is given by the Fermi-Dirac distribution:

\[
f_r = \frac{1}{\frac{E_i - E_r}{k_B T} + 1 + \exp \left(-\frac{E_i - E_r}{k_B T}\right)}
\]
Figure 2.5 Capture and emission processes at a deep level $E_T$

1. Electron capture from the conduction band to an unoccupied centre.
2. Electron emission from an occupied centre to the conduction band.
3. Hole capture by an occupied centre.
4. Hole emission by an unoccupied centre.
where $E_F$ is the Fermi energy, $k_B$ is the Boltzmann constant and $T$ is temperature.

For a concentration $N_T$ of deep levels the number occupied will be $N_T f_T$ and that unoccupied $N_T(1-f_T)$. The rate at which electrons will be captured from the conduction band is proportional to the number of electrons in the band and to the number of empty levels available to receive them, so

$$\frac{dn}{dt} = -C_n n N_T (1-f_T) \quad (2.9)$$

where $n$ is the free electron density in the conduction band and $C_n$ is the electron capture coefficient which is given by the product of the root mean square capture cross-section for electrons, $\nu_n$, and their average thermal velocity, $<v_n>$:

$$C_n = \nu_n <v_n> \quad (2.10)$$

where

$$<v_n> = \left( \frac{3k_B T}{m_e} \right)^{1/2}$$

$$\quad \quad \quad (2.11)$$
where the symbols have their usual meanings. There are several mechanisms of carrier capture and these will be briefly discussed later on.

The rate at which electrons are emitted to the conduction band will be proportional to the number of occupied levels, thus

\[
\frac{dn}{dt} = e_r f_r N_r
\]  \hspace{1cm} (2.12)

where \( e_r \) is a rate constant. For dynamic equilibrium the electron capture and emission for the centre must be equal, so from (2.8), (2.9) and (2.12)

\[
e_r = c_r \exp[\frac{E_T - E_F}{k_B T}] \hspace{1cm} (2.13)
\]

where \( c_r = C_r n \). So where the trap energy coincides with the Fermi energy, \( e_r = c_r \). Substituting for \( c_r \) given that the electron concentration is

\[
n = N_0 \exp\left[\frac{E_0 - E_F}{k_B T}\right] \hspace{1cm} (2.14)
\]

where

\[
N_0 = 2 \sqrt{\frac{2m_e k_B T}{\hbar^2}}^{3/2} \hspace{1cm} (2.15)
\]
we get the familiar expression:

$$e_n = \frac{\sigma_n<\nu_n>N_C}{g} \exp \left[-\frac{E_C-E_T}{k_B T}\right]$$  \hspace{1cm} (2.16)

where $g$ is the degeneracy factor to allow for the degeneracy of the level (Landberg (1957)). A similar expression holds for holes.

The net change in electron occupancy will be given by the rate at which electrons are captured from the conduction band (electron capture less emission) minus the rate at which holes are captured from the valence band (hole capture less emission). So the rate equation governing the concentration of defects occupied by electrons, $n_T$, for a deep level concentration $N_T$, assuming no illumination, will be

$$\frac{dn_T(t)}{dt} = (c_n + e_n) (N_T-n_T(t)) - (c_p + e_p) n_T(t) \quad (2.17)$$

In the steady state condition when $dn_T(t)/dt = 0$

$$n_T(\infty) = \left[\frac{c_n + e_n}{c_p + e_n + c_n + e_p}\right] N_T \quad (2.18)$$

which gives the steady state probability of electron occupancy. The time dependence of the level occupation
is important as it can be used to determine the trap parameters. Solutions of the rate equation 2.17, give the following expressions:

\[ n_r(t) = n_r(\infty) + \left[ \frac{c_p + e_n}{c_p + e_n + c_n + e_m} \right] N_r \exp\left(-\frac{(c_p + e_n + c_n + e_m)t}{c_p + e_n + c_n + e_m}\right) \] (2.19)

for traps initially occupied with electrons, and

\[ n_r(t) = n_r(\infty) \left[ 1 - \exp\left(-\frac{(c_p + e_n + c_n + e_m)t}{c_p + e_n + c_n + e_m}\right) \right] \] (2.20)

for traps initially empty of electrons. It is interesting to note that the time dependence of the level occupation in the simple case is always exponential with a time constant equal to the reciprocal of the sum of all the carrier capture and emission rate constants. Usually one of these processes dominates and use of this is made to extract these parameters from measurements made on semiconductor junctions and will be described in §3.

The energy released during the capture process can be emitted in the form of light in the case of radiative transitions; can be transferred to another electron or hole in an Auger process, or can be transferred to phonon modes. The first is simply photoluminescence, the second is not very common in non-radiative centres, except in heavily doped material. Non-radiative capture by phonon emission has been explained in terms of two processes:
cascade capture, relevant to shallow levels, where the center has closely spaced levels near the band edge; and multiphonon capture which occurs because of the existence of local phonon modes with strong electron-phonon coupling, which is not restricted to defects with large lattice relaxation (see §2.5.7). The analysis so far assumes that the capture cross-section, $\sigma_n$, is temperature independent and while some levels exhibit a very weak or non-existent temperature dependence of the capture cross-section (Majerfeld et al (1978)), in many cases this is not so and, over a limited range of temperature, $\sigma$ can show an exponential behaviour which can be represented by (Henry and Lang (1977)):

$$\sigma_n(T) = \sigma_{n\infty} \exp \left(-\frac{E_g}{k_B T}\right)$$

where $\sigma_{n\infty}$ is temperature independent. The exponential term then becomes $(E_C - E_T + E_m)/k_B T$, where $E_m$ is the barrier to capture.

Now, returning to the description of a deep level as a trap or a recombination centre, it is possible to define these in terms of capture and emission rates. So the former is a deep level where one of the capture rates exceeds the other (i.e. for an electron trap $c_m \gg c_p$) and the latter as one where the two rates are comparable and, for example, the center can capture an electron from the conduction band and transfer it to the valence band by
capturing a hole, resulting in the anihilation of a free electron-hole pair. Bearing in mind the dependence of the capture rates on carrier concentration, it becomes apparent that a deep level with a particular electron and hole capture cross-section can act either as a recombination centre or a trap depending on the doping and temperature. Similarly, a deep level can act as a generation centre if its electron and emission rates are comparable and electrons and holes are emitted alternately, transferring valence electrons to the conduction band creating electron-hole pairs.

One of the consequences of lattice relaxation in the vicinity of a deep level has already been mentioned. It is important to note that this also affects the emission of carriers and this is described in the following section.

2.5.7 THE EFFECTS OF LATTICE RELAXATION

The strength of defect-lattice coupling depends critically on the localisation of the electron or hole wavefunction at the defect. If during any transition this localisation changes substantially the lattice around the defect usually undergoes strong rearrangement. This is called lattice relaxation. The observable effect of lattice relaxation, caused by the different equilibrium positions of the lattice for initial and final charge states, is the difference in the optical and thermal
activation energy. There are two main types of lattice relaxation: one preserves the symmetry of the deep level (breathing mode) and the other produces symmetry-breaking distortions, changing the overall symmetry.

The effects of lattice relaxation are best visualised using a configuration coordinate diagram. The total energy of the system, $E$ (electronic plus elastic) is plotted against the local lattice displacement represented by the so-called lattice coordinate $Q$. In reality $Q$ can rarely be ascribed to a real displacement and is usually a fictitious parameter characterising vibronic interactions in the system (Toyozawa (1976)). A typical configuration-coordinate diagram for a system showing lattice relaxation is shown in figure 2.6. There are three types of energy "depths": (1) the optical depth, $E_{\text{opt}}$, corresponding to transitions at constant lattice coordinate (e.g. from photocapacitance measurements), (2) the thermal equilibrium depth, $E_{\text{eq}}$, corresponding to the activation energy of the equilibrium carrier concentration where the center is the dominant donor (e.g. Hall measurements) and (3) the thermal activation energy, $E_a$, corresponding to the energy needed to surmount the barrier between the bound and free state (e.g. from transient capacitance measurements (see §3)).
Fig. 2.6 Configuration coordinate diagram showing the energy of lattice relaxation or Frank-Condon shift, $\Delta \omega$. 
In addition to these, there is the activation barrier to the thermal capture of a free electron, $E_a$. From the diagram it can be seen that the thermal activation energy derived from transient capacitance differs from that obtained from Hall measurements by an amount equal to $E_m$ and is given by:

$$E_a = E_{tr} + E_m$$  \hspace{1cm} (2.21)$$

The energy of lattice relaxation (or the Frank-Condon shift) is given by:

$$E_r = S\hbar\omega$$  \hspace{1cm} (2.22)$$

where $S$ is the Huang-Rhys parameter which characterises the strength of the vibronic coupling (Huang and Rhys (1950)) and $\hbar\omega$ is the phonon energy. $E_r$ is related to the other energies as follows:

$$E_{opt} = E_{tr} + E_r$$  \hspace{1cm} (2.23)$$

We need to distinguish between these depths to make use of results obtained by different methods.
2.6 QUANTUM WELL STRUCTURES

2.6.1 INTRODUCTION

When two different semiconductors are joined to form a heterojunction their conduction and valence band edges do not necessarily match across the interface. The resulting discontinuities in the conduction and valence band edges, $\Delta E_c$ and $\Delta E_v$ are of fundamental importance to all device applications. We know that in a properly lattice-matched system the symmetry of the crystal remains the same and the transition between the band structure on either side of the interface is relatively smooth (Lassnig (1985)).

2.6.2 ENERGY BAND-GAP DISCONTINUITIES

In figure 2.7 three typical examples for the relationship of band-edge energies at heterojunctions and their respective superlattices or multiquantumwells are shown together with corresponding band-bending and carrier confinement at the interface. For the purpose of interpreting the results of the study of quantum well structures reported in chapter 7 it is necessary to consider one type, that denominated type I, in which the sum of the band gap discontinuities is equal to the difference of the band gaps. A "sandwich" of a semiconductor material between layers of a material with a larger band gap leads to the formation of a potential well in the low band gap material with quantised subbands.
Fig. 2.7 The relationship of band-edge energies at a heterojunction for (a) GaAs-AlGaAs, (b) InGaAs-GaSbAs and (c) InAs-GaSb showing carrier confinement.
whose energies are determined by the well width and depth. The determination of the ratio of the bandgap offsets $\Delta E_G: \Delta E_v$ has been studied in several material systems and, in GaAs/AlGaAs, has been the subject of much controversy. Early work carried out by Dingle et al (1974) deduced a ratio of 85:15 from infrared absorption on GaAs/AlGaAs material of one composition. Since then a lot of theoretical and experimental work has been carried out and it would seem that the accepted value is at present around 60:40 (see Duggan (1985) for a review). Another system of interest is InGaAs/InP where results reported oscillate around a ratio of 40:60. Forrest (1982) and Lang et al (1987) obtained values of 39:61 and 42:58 respectively from electrical measurements and Skolnick et al (1986) a value of 38:62 from optical spectroscopy.

2.6.3 CAPTURE AND EMISSION PROCESSES AT A QUANTUM WELL

Experimental and theoretical studies of carrier collection in single quantum wells have shown that the collection mechanism depends sensitively on the band structure (Tang et al (1982)). Studies have been performed to determine how the emission rate of electrons and holes at interfaces or from quantum wells differs from the behaviour of bulk crystals. The idea of treating a quantum well as a giant trap has been suggested (e.g. Martin et al (1983) and Hamilton et al (1985)).
Invariably capture into a well has been shown to become increasingly more difficult as a build up of the potential around the well increases as more electrons are captured and it is concluded that capture into a well is not comparable to point defects. Results on the investigation of the capture and emission at GaAs/AlGaAs single wells in order to distinguish between well and bulk emission will be reported in chapter 7 where electron emission from a well in the space-charge region of a reverse-biased Schottky barrier is used to estimate the conduction band offset in the GaAs/AlGaAs system. Preliminary measurements on InP-InGaAs superlattices are also presented.
CHAPTER 3

ELECTRICAL CHARACTERISATION OF IMPURITY LEVELS

3.1 INTRODUCTION:

A large number of experimental techniques for studying shallow and deep levels have been developed in the last decade. Detection methods can be divided into two main categories, bulk and space charge measurement techniques. Bulk techniques include Hall effect and resistivity measurements, photoconductivity, luminescence and optical absorption. These methods enable studies to be made in regions of the semiconductor where there is no significant electric field. The purely optical methods such as luminescence and absorption have been used successfully to study shallow levels but are seldom used for the characterisation of deep states, mainly due to the fact that the deeper levels of interest are generally non-radiative and detectors operating in the infra-red are not usually as sensitive as in the visible part of the spectrum. A review of optical spectroscopy and electron spin resonance of deep levels in III-V semiconductors is given by Schneider and Kaufmann (1981).
Space charge methods can be used successfully in the study of deep levels although great care has to be exercised in the analysis of experimental results as the space charge field necessary may modify the trap properties. The use of space-charge techniques has been reviewed by Sah (1976), Sah et al (1970), Lang (1979) and Miroeau et al (1980) for example. Miller et al (1977) discuss capacitance transient methods and Milnes (1973) extensively treats the older deep level methods, including thermally stimulated current techniques. Within the space charge techniques we can distinguish between transient methods in which the deep level occupancy is altered dramatically and "steady-state" methods in which the level occupancy is only perturbed slightly.

The work carried out in this thesis has mainly involved Hall and resistivity measurements, capacitance transient spectroscopy and frequency resolved capacitance spectroscopy. The properties measured using these methods and their significance are outlined in the following sections and details of the experimental techniques are given in chapter 4. Details of other methods used for comparative purposes are briefly discussed in §3.6.

3.2 HALL AND RESISTIVITY MEASUREMENTS:

The majority carrier concentrations as well as the mobility as a function of temperature (and pressure) are generally derived from Hall experiments (Putley (1960))
using the van der Pauw technique (van der Pauw (1958, 1959), described in §4.3). It is useful to consider the statistics of a partially-compensated p-type semiconductor in order to analyse the results obtained on the Mn acceptor level in the quaternary alloy GaInAsP lattice-matched to InP, presented in chapter 5. The temperature dependence of the free hole concentration, \( p_0 \), in a partially-compensated semiconductor can be described by the expression (Blakemore (1962)):

\[
\frac{p_0(p_0+N_0)}{N_a-N_0-p_0} = \frac{N_a}{g} \exp\left(-\frac{E_{tr}}{kT}\right)
\]

where \( E_{tr} \) is the thermal activation energy of the level, \( N_a \) and \( N_0 \) are the acceptor and donor concentrations and \( g \) is the degeneracy factor for the acceptor level. The valence band density-of-states, \( N_v \), is given by:

\[
N_v = 2 \left( \frac{2\pi m_0 k_b T}{\hbar^2} \right)^{3/2}
\]

where \( m_0 \) is the combined density-of-states effective mass. This takes into account the fact that \( p_0 \) is made up of carriers from both the light and heavy hole bands which are degenerate at the valence band maximum. It is calculated using the expression:
\[ m_d = \left[ (m_1)^{3/2} + (m_i)^{3/2} \right]^{2/3} \]  

(3.3)

where \( m_1 \) and \( m_i \) are the light and heavy hole effective masses, respectively. Provided the Fermi level is several \( k_B T \) from the valence band edge, then in the low-temperature regime, where \( k_B T < E_{\text{tr}} \), provided \( p_0 \ll N_0 \), equation 3.1 tends to become

\[
p_0 = \left[ \frac{N_A - N_D}{N_D} \right] N_D \exp\left(-E_{\text{tr}}/k_B T\right) \tag{3.4}
\]

The activation energy can be deduced from the low-temperature portion of an experimental \( \ln(p_0 T^{-3/2}) \) versus \( 1/T \) curve. An approximate value of \( N_A/N_D \) can be obtained from the intercept. These values can then be used as starting estimates in a computer fit to the full expression (3.1) using \( E_{\text{tr}} \), \( N_A \) and \( N_D \) as adjustable parameters.
3.3 SPACE CHARGE (CAPACITANCE) METHODS:

3.3.1 INTRODUCTION:

In conjunction with other well known electrical characterisation techniques, capacitance measurements, have been used extensively in the study of carrier capture and emission phenomena. They have provided information on energy levels in insulators and semi-insulating materials. Due to their relatively high conductivity, some semiconductors do not lend themselves readily to these methods. The use of Schottky diodes and asymmetric p-n junctions make measurements in a region of the semiconductor material virtually devoid of mobile carriers possible. The basic concept is to alter the population of states in the depletion region and either detect the current produced in the external circuit by released carriers or monitor the change in space charge by observing the depletion capacitance. The latter method is discussed in the following sections.

3.3.2 THE CAPACITANCE OF A SCHOTTKY BARRIER:

The formation of a p-n junction results in a space charge or depletion region with a built-in voltage potential. The depletion layer of a metal-semiconductor contact is similar to that of a one side of an abrupt asymmetrical p-n junction (eg a Schottky on n-type material and a p+n junction). In the simplest case, for a uniformly doped, non-degenerate semiconductor, the width
of the depletion region (in the lightly doped side of the junction), \( W \), is given by:

\[
W = \left( \frac{2\varepsilon}{qN_d} \cdot \frac{(V_o + V_R - k_BT)}{q} \right)^{1/2}
\]  (3.5)

where \( \varepsilon \) is the permittivity, \( q \) the electronic charge, \( N_d \) the donor doping concentration, \( V_o \) the diffusion potential, which represents the built-in potential difference in the absence of a current, and \( V_R \) is the applied reverse bias voltage. The term \( k_BT/q \) arises from the contribution of the majority-carrier distribution tail.

The diffusion potential is given by the difference between the work functions of the p and n-type materials and can be expressed by:

\[
V_o = \frac{k_BT}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right)
\]  (3.6)

where \( n_i \) is the intrinsic carrier concentration and \( N_A \) is the acceptor doping concentration. For a Schottky barrier, however, \( V_o \) is largely determined by the existence of surface energy states at the metal-semiconductor interface and not by the difference in work functions. The distribution of surface states is characterised by a neutral level \( \phi_o \) (see figure 3.1).
Figure 3.1: Energy-band bending at a reverse biased (a) p±n junction and (b) Schottky diode on n-type material.
which usually occurs about one third of the band-gap energy as measured from the valence band (Mead (1966)). In general the barrier height is determined by both the metal work function and the surface states. If the density of states is very high then $\phi_0 = E_{F_m}$ (metal Fermi level) and the barrier height $\phi_0$ is said to be 'pinned' by the high density of states. The barrier height will then be determined by the doping and properties of the semiconductor surface.

Assuming that the depletion region consists only of ionized donors and acceptors and that there is no mobile charge at the edge of this region, then for a asymmetric junction with an arbitrary impurity distribution, $N_D(x)$, from Poissons equation in one dimension,

$$\frac{dE}{dx} = \frac{-\rho(x)}{\epsilon}$$

(3.7)

where $\rho$ is the net charge density and $E$ is the electric field we may write for the change in reverse bias, $\Delta V_R$, and the incremental change in charge per unit area at the edge of the depletion region, $\Delta Q$, associated with it

$$\Delta V_R \propto \frac{q N_D(x) \Delta x}{\epsilon}$$

(3.8)

$$\Delta Q = qN_D(x) \Delta x$$

(3.9)
where $\Delta x$ is the corresponding change in depletion width $x$. The differential capacitance per unit area, $C^*$, is defined as:

$$C^* = \frac{\Delta Q}{\Delta V_r} \quad (3.10)$$

and when combined with equations 3.8 and 3.9 gives for the capacitance

$$C = \frac{\varepsilon A}{x} \quad (3.11)$$

i.e. the depletion region behaves as a parallel plate capacitor with plates separated by a distance $x$ (dependent on the bias voltage). The depletion capacitance of a reverse biased p$n$ junction or Schottky diode on n-type material is therefore given by:

$$C = A \left( \frac{\varepsilon qN_o}{2(V_o+V_r-k_BT/q)} \right)^{1/2} \quad (3.12)$$

where $A$ is the junction area. For a uniformly doped semiconductor a graph of $1/C^2$ as a function of reverse voltage $V_r$ should be a straight line with a slope $2/q\varepsilon N_o$ and negative intercept on the voltage axis $k_BT/q - V_o$. Thus $N_o$ and $V_o$ can be found.

The presence of an interfacial oxide layer between the metal and semiconductor can modify the dependence of
the depletion region charge on the applied voltage as part of it is dropped across the layer. The effect of an interfacial layer on the capacitance has been analysed in detail by Cowley (1966) and Crowell and Roberts (1969). For layers sufficiently thin an almost ideal Schottky barrier can be obtained. The interface states are emptied or filled by the tunnelling of electrons from the metal and make no direct contribution to the capacitance but they affect the capacitance indirectly because they may modify the way in which the charge due to the uncompensated donors depends on the bias voltage. The current-voltage characteristics of a nearly ideal diode are described in terms of the ideality factor, \( n \):

\[
\frac{1}{n} = \left[ 1 - \frac{\delta \phi_m}{q \delta V} \right] \quad (3.13)
\]

where \( \delta \phi_m / \delta V \) is the change in barrier height with applied voltage due to the layer. If the states at the oxide-semiconductor interface are evenly distributed in energy, \( n \) will not be very voltage dependent. The depletion region charge, \( Q_d \), is given by:

\[
Q_d = \left[ 2q \varepsilon N_0 (V_d + V_R - k_B T/q) \right]^{1/2} \quad (3.14)
\]

By substituting for \( qV_d = (\phi_m - \phi_n) \) into this equation and differentiating with respect to voltage we get the following expression for the depletion capacitance:
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\[ C = qA \frac{e N_0}{2(\delta_0 - \delta_n - kTqV_f)} j^{\frac{1}{2}} \left(1 - \frac{\delta_0}{\delta V}\right) \]  

which in terms of the ideality factor \( n \) (from 3.13) is:

\[ C = qA \frac{e N_0}{n 2(\delta_0 - \delta_n - kTqV_f)} j^{\frac{1}{2}} \]  

The slope and intercept of a \( 1/C^2 \) versus \( V_f \) plot are scaled up by the effect of the interfacial layer. For a nearly ideal diode the value of \( N_D \) (although underestimated) is not changed very much, but the barrier height deduced from the intercept will be significantly larger than that obtained from I-V measurements.

3.3.3 THE EFFECT OF DEEP TRAPS:

In the depletion region of a Schottky barrier where the bands are bent, the energy level of a deep trap varies with respect to the Fermi level and the occupation of the level (and hence its charge state) will also vary. The degree of band bending depends on the bias voltage applied. The charge state of the trap will depend on this voltage and as a result the capacitance will change.

The effect of a deep trap on the depletion region of a one-sided p'n junction or n-type Schottky barrier is shown in figure 3.2, assuming a uniform distribution of shallow \( (N_D) \) and deep \( (N_T) \) levels. The principal feature is the presence of a transition region, \( \lambda \), between the
space charge and neutral regions in which generation-
recombination processes are both active in determining
the equilibrium trap occupancy. Integration of Poisson's
equation over the region \( x, <x<V \) will give the value of \( \lambda \)
for a level at energy \( E_T \), which for a deep acceptor, is
given by:

\[
\lambda = \left[ \frac{2\varepsilon (E_r - E_T)}{q^2 (N_d - N_T)} \right]^{1/2}
\]

Deep levels lying more than several \( k_BT \) below \( E_r \)
will tend to fill, while those above will tend to empty,
according to the Fermi-Dirac law. The emission and
capture processes which determine the steady state
probability of occupancy within the depletion region,
described in §2.5.6, will thus affect the steady-state
frequency response and transient time response of the
diode. The leading edge of the depletion region is marked
by the spillover of electrons from the neutral region,
truncated with the characteristic Debye screening length,
\( l_D \), which is the natural limitation to spatial resolution
in capacitance measurements and is given by:

\[
l_D = \left[ \frac{\varepsilon k_BT}{q^2 N_d} \right]^{1/2}
\]

The junction capacitance is measured, in most cases, by
superimposing a small oscillating voltage on the applied
bias and measuring the current induced by it. As shown in
figure 3.2, the depletion width \( W \) remains approximately
Figure 3.2: Electronic structure of reverse biased junction with one deep trap. (a) Deep donor and (b) deep acceptor.
unchanged, while the oscillating voltage uncovers charge
both at $x_i$ and $V$ where free carriers are swept away and
emitted from traps to the conduction band, respectively.
In the case that the deep level is an acceptor, for
example, if the test frequency is low compared with the
emission rate of electrons from the trap $E_r$, e.g.,
(equation 2.16) then the measured capacitance will depend
primarily on $N_0$, as the deep levels at $x_i$ can follow the
voltage variation by capture and emission processes and
both charge at $x_i$ and $V$ will contribute. If, however, the
test frequency is high enough, only the untrapped charge
at $W$ will be able to respond and the capacitance will
depend primarily on $N_0 - N_r$. In both cases the limiting
process is the emission rate because it is slower than
capture when the Fermi level is above the trap level.

The influence of deep levels on the junction
properties has an effect on the capacitance measurement
and this is the basis for determining the deep level
parameters such as activation energy and capture cross-
section. The various capacitance methods can be classed
as being of either a steady-state or transient type. The
study of deep levels by observing steps in capacitance-
frequency behaviour (Sah et al (1964)), peaks in
admittance-frequency characteristics (Losee (1972)) or
more recently by Frequency Resolved Capacitance
Spectroscopy (Homewood and Benyon (1988)) can be classed
as steady-state techniques. Transient techniques are
those where junctions initially in equilibrium are perturbed and then allowed to relax back to the steady state equilibrium condition.

3.4 CAPACITANCE TRANSIENT SPECTROSCOPY:

3.4.1 INTRODUCTION:

In the space charge region, totally depleted of mobile carriers, the deep level occupation is controlled through emission processes. So under conditions where space charge processes dominate the junction response may be interpreted unambiguously in terms of emission rates. States within the space charge region have no possibility of being filled by capture processes so emission processes can only be observed following the forced introduction of carriers which are to be captured. Voltage pulses (or optical pulses), of sufficient duration to fill traps in this normally depleted region, are applied to the junction, and the transient capacitance response following the pulses (attributed to these emission processes) monitored. The variation of the characteristic emission rate with temperature can be used to deduce the thermal activation energy and capture cross-sections using equation 2.16.

Capacitance transient measurements generally (Grove (1967)) obey a relationship of the form:

\[ C_m - C_t = (C_m - C_o) \exp \left( -\frac{t}{\tau} \right) \]  \hspace{1cm} (3.19)
where

\[ C_m = \text{Diode capacitance at } t \rightarrow \infty \quad \text{(Traps empty)} \]
\[ C_0 = \text{Diode capacitance at } t=0^+ \quad \text{(Traps full)} \]
\[ C_t = \text{Diode capacitance at time } t \quad \text{(Traps emptying)} \]

Let \((C_m-C_t) = \Delta C(t) \) & \((C_m-C_0) = \Delta C(0)\). Rewriting (3.19):

\[ \Delta C(t) = \Delta C(0) \exp\left(-t/T\right) \tag{3.20} \]

where \(\Delta C(0)\) is the maximum change in capacitance at \(t=0^+\) which is determined by the trap density, and \(\Delta C(t)\) is the time varying capacitance transient due to emission from the traps. The value of the time constant for emission can be obtained from the slope of a plot of \(\ln(\Delta C(t))\) vs \(t\).

3.4.2 THEORY:

The four basic processes of electron/hole capture and emission by a deep trap have been described in §2.5.5. The time dependence of trap occupancy is exponential provided the total number of conduction band electrons and holes in the valence band is much greater than the trap concentration, \(N_T\).

The energy band diagrams of a Schottky barrier containing majority carrier traps, (i) electron traps in an n-type semiconductor and (ii) hole traps in p-type material are shown in figure 3.3, together with the biasing sequence and the capacitance response. Let us consider the former:
Figure (1)(a) shows the diode under large reverse bias $V_R$ with the traps positively charged in most of the depletion region. The resulting capacitance is denoted by $C_m$. Fig. (1)(b) shows the diode at a reduced bias $V_R$, where the depletion layer has been collapsed for sufficient time to allow the traps to fill, becoming neutral by capturing an electron from the conduction band. The capacitance decreases from $C_m$ to $C_0$. The reverse bias $V_R$ is re-established and the capacitance increases as the traps begin to empty as the captured electrons are emitted to the conduction band as shown in fig. (1)(c), eventually returning to the equilibrium value $C_m$ as $t \rightarrow \infty$ and all the traps are empty. The arguments remain parallel for the case of a majority trap in p-type material, as shown in figures (ii)(a-c). The explanation for majority carrier traps is also valid for asymmetric p-n junctions but differs in the case of minority carrier traps. In this case traps are filled with minority carriers, increasing the net space charge immediately after the pulse and hence the capacitance to a value $C_0$ from the steady-state value $C_m$, returning to this value as $t \rightarrow \infty$. The charge states of the defect level in a p$^+$n and n$^+$p junction are shown in figure 3.4. The biasing sequence is also shown, together with the resulting capacitance transient. In the case of a p$^+$n junction, driving the junction into forward bias results in hole injection, most of which will occur in the more lightly
Figure 3.3: Schottky barriers on (i) n-type and (ii) p-type semiconductors containing majority carrier traps showing (a) steady-state, (b) filling and (c) emptying of traps.
doped n-type region. For a Schottky barrier in forward bias, the minority carrier injection will be insignificant and an optical pulse is necessary with the diode under reverse bias.

3.4.3 DETERMINATION OF TRAP ACTIVATION ENERGY:

The thermal activation energy, $E_a$, and the capture cross-section, $\sigma_c$, can be obtained from capacitance transient measurements as a function of temperature. From the equation for the emission rate derived in §2.5.5, (eqn. 2.16) we get:

$$\ln(T^{2-1}) = \frac{E_a}{k_b} \frac{1}{T} + \ln \frac{g}{2} \frac{m_e}{3k_b} \frac{\hbar^2}{2\pi m_e k_b} \frac{\tau}{\sigma_c} \frac{1}{\varphi} \quad (3.21)$$

A plot of $\ln(T^{2-1}) v 1/T$ yields a slope proportional to $E_a$ and an intercept proportional to $\sigma_c$. The accuracy with which these can be obtained depends on the measurement of $\tau$ and $T$ and on the range over which each may be varied. More accurate values for the capture cross-section can be obtained from measurements of $\Delta C(0)$, the capacitance transient amplitude at $t=0^+$, as a function of pulse width, where the traps are not allowed to fill completely, resulting in a reduction of $\Delta C(0)$ which is related to the pulse width by:
in Schottky diode, minority carriers are generated by light pulse

Figure 3.4: p-n and n-p junctions containing minority carrier traps, showing: (a) steady-state, (b) carrier injection and (c) emission.
where $\Delta C(0)_m$ is the value of the amplitude as the pulse width, $t_0$, and $c$ is the capture constant which can be obtained from a plot of $t_0$ against $\ln[\Delta C(0)_m - \Delta C(0)]$. As $\sigma_n$ and the capture rate, $c$, are related by equation (2.8) it is possible to obtain $\sigma_n$ as a function of temperature by measuring the capture rate. A correction to the measured activation energy, $E_a$, then becomes necessary to obtain the trap energy. The value of the activation energy ($E_a - E_T$) in equation 2.16 is in fact a free energy whereas the thermodynamic quantity, $E_a$, derived from the Arrhenius of the thermal emission rate is actually an enthalpy. This can be seen if we note that the slope of the plot is given by

$$\frac{d}{d(1/T)} \frac{G}{T} = G + \frac{dG}{d(1/T)}$$  \hspace{1cm} (3.23)$$

where $G$ is a Gibbs free energy, which is appropriate for solids where the pressure is kept constant. Now, using

$$\frac{dG}{dT} = -S$$  \hspace{1cm} (3.24)$$
where $S$ is the entropy, we see that the right hand side of equation 3.24 becomes $G + TS$, which is the definition of enthalpy. It can be shown that at a given temperature $T$ the value of $G$ linearly extrapolated back to $T=0$ is identically equal to $H$ at the temperature $T$. Thus the activation energy obtained from the slope of an Arrhenius plot is equal to the free energy obtained by a linear extrapolation to $T=0$ of the temperature dependent free energy at the temperature of measurement.

3.5 FREQUENCY RESOLVED CAPACITANCE SPECTROSCOPY

3.5.1 INTRODUCTION

We have seen how the space charge region of a semiconductor junction can be used to controllably alter the deep level population by varying the applied bias. It was noted that by observing the emission rates of carriers as a function of temperature, the thermal activation energy characteristic of the center could be obtained. In contrast to capacitance transient spectroscopy, this is a frequency domain technique. In its basic form, the depletion bias is modulated with a small amplitude sinusoidal voltage. The sample response to the modulation is measured using quadrature lock-in detection. The schematic diagram of the basic FRCS spectrometer is shown in figure 3.5. The sample diode is mounted in one arm of a capacitance bridge which is driven by a signal generator. A lock-in amplifier is
connected across the bridge as shown. A reference signal is taken directly from the signal generator to the lock-in reference input. The signal from the purely capacitive side of the bridge is fed to one (A) of the differential lock-in inputs and is used as an absolute measure of the phase of the excitation and is used to set the lock-in to quadrature by nulling the output; the centre point of the side containing the diode and variable capacitor is fed to the other input (B). The differential input when taken across the bridge directly provides the FRS response at the applied frequency. The Deep Level spectrum is generated either by recording the quadrature signal as a function of frequency or observing the change in the signal as a function of temperature.

3.5.2 INTRODUCTION TO THEORY OF FRCS

The sample acts as one of four capacitances in a bridge (figure 3.5) and may be represented as a time-varying capacitance. Let us consider a Schottky diode on n-type material or p"n junction. From eqn.3.12, we can write for the capacitance per unit area of an ideal diode:

\[ C = \sqrt{\frac{q\epsilon_0 N_D}{V}} \frac{1}{V^{1/2}} \]  

(3.25)
Figure 3.5: Schematic diagram of the basic FRCS spectrometer
For small excursions in voltage we may write:

\[ \frac{dC}{dV} \propto -dV \]  

(3.26)

We know that deep levels result in a slow change of capacitance in response to a change in voltage with a characteristic time constant \( \tau \). For an applied voltage \( V(t) = V_o + V_m e^{i\omega t} \) with \( V_m \ll V_o \) we may write for the capacitance response of the sample:

\[ C = C_o + C' e^{i\omega t} + C'' e^{i(\omega t - \phi)} \]  

(3.27)

where \( \phi \) and \( C'' \) are frequency dependent and \( C', C'' \ll C_o \) for \( V \ll V_o \). The first term represents the depletion capacitance; the second term represents the small change in capacitance due to the modulation of the depletion edge, and the third represents the capacitance response from the deep levels, which lags the applied voltage. From equation 3.25 we may write for \( C_o, C' \) and \( C'' \):

\[ C_o = \sqrt{\frac{q\varepsilon_0 N_0}{2V_o}}^{1/2} \]  

(3.28)

and

\[ C' = \frac{dC}{dV} \bigg|_{V=V_o} = -\sqrt{\frac{q\varepsilon_0 N_0}{2}} \frac{V_m}{V_o^{3/2}} \]  

(3.29)
$C''$ and $\phi$ are obtained from the convolution of the sinusoidal voltage and the expected exponential response from the deep levels as follows. Using the known relation between the capacitance and applied voltage we may write:

$$C' = \frac{N_0}{V_m} \int dx$$

where $dx$ is the change in depletion width for $V_m$ and traps remain full. For traps remaining empty we may write:

$$C' = \frac{N_r + N_0}{V_m} \int dx$$

The difference between these quantities is $C''$ at low frequencies:

$$C''_{\omega=0} = \frac{N_r}{N_0} C'; \quad = -\frac{N_r}{N_0} C_0 \frac{V_m}{V_o}$$

The exponential decay gives for a frequency $\omega$,

$$C'' = C''_{\omega=0} \int_{-\infty}^{t} e^{-\frac{(t-t')}{\tau}} e^{i\omega t'} dt'$$

$$C'' = C''_{\omega=0} \frac{1}{1 + \frac{\omega\tau^2}{}}$$
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So the capacitance response due to the deep levels is given by:

\[
\frac{C''}{C_0} = - \frac{N_T}{N_D} \frac{V_m}{V_o} \frac{1}{\sqrt{1 + \omega^2 \tau^2}} \quad (3.30)
\]

We now have the complete expression to model the capacitance response of a diode with a uniform donor concentration and a deep level with a single exponential time constant. Returning to the circuit diagram of figure 3.5, we can determine the input voltage to the lock-in amplifier, \( V_{in}(t) \). The two points on the bridge, A and B, are taken to the differential inputs of the lock-in amplifier, thus \( V_{in}(t) = V_A(t) - V_B(t) \). So

\[
V_{in}(t) = \frac{1}{i\omega C_2} - \frac{1}{i\omega C_3} \quad \text{for} \quad V_{me} \quad 1 \omega t
\]

Substituting for \( C_a \) in terms of the capacitance response of the diode to the applied voltage (eqn. 3.27) we get:
\[ V_{in}(t) = \frac{C_1 - \frac{C_0 + C'e^{i\omega t} + C''e^{i(\omega t-\phi)}}{C_1 + C_2}}{C_3 + C_0 + C'e^{i\omega t} + C''e^{i(\omega t-\phi)}} \times V_{me} \]

Now, \( \frac{C'}{C_3 + C_0} \) and \( \frac{C''}{C_3 + C_0} \ll 1 \), so this reduces to \( V_{in}(t) \)

\[ V_{in}(t) = \frac{C_1 - \frac{C_0}{C_1 + C_2} \left( 1 + \frac{1 - e^{-i\omega t}}{e^{-i\omega t}} \right) + \frac{C''}{C_3 + C_0} \times V_{me} \]

To simplify we can set \( C_1 = C_2 = C_3 = C_0 \) and \( C', C'' \ll C_0 \) to obtain the final expression for the voltage at the lock-in inputs,

\[ V_{in}(t) = \frac{1}{4} \left[ \frac{C'}{C_0} + \frac{C''}{C_0} \right] e^{i\omega t} \times V_{me} \quad (3.31) \]

The quadrature lock-in output in is then given by

\[ V_{out} = \frac{\omega}{2\pi} \int_{0}^{2\pi/\omega} V_{in}(t')e^{i(\omega t'-\pi/2)} dt' \]
\[ V_{\text{out}} = \frac{\omega}{2\pi} \left( \frac{1}{4} \right) \int_0^{2\pi/\omega} \left( \frac{C'}{C_0} \cos \omega t' + \frac{C''}{C_0} \cos(\omega t' - \phi) \right) V_m \cos(\omega t' - \pi/2) \, dt' \]

\[ = \frac{\omega}{2\pi} \left( \frac{V_m}{4} \right) \int_0^{2\pi/\omega} \left( \frac{C'}{C_0} \cos \omega t' + \frac{C''}{C_0} \cos(\omega t' - \phi) \right) \cos \omega t' \, dt' \]

\[ = \frac{\omega}{2\pi} \left( \frac{V_m}{4} \right) \frac{C''}{C_0} \frac{1}{2\pi} \left( \frac{2\pi}{\omega} \right) \frac{2\pi}{\omega} \frac{\sin \phi}{\sin \phi} \]

\[ V_{\text{out}} = \frac{V_m C''}{8 \sqrt{C_0}} \sin \phi \quad (3.32) \]

Now, substituting for \( C''/C_0 \) from equation 3.30 we get the expression for the quadrature lock-in output voltage and its dependence on the driving frequency and the time constant of the expected exponential decay due to the deep levels:

\[ V_{\text{out}} = \frac{V_m}{8 N_0} \frac{V_m^2}{V_0} \frac{\omega}{1 + \omega^2 \tau^2} \quad (3.33) \]

This function is plotted against \( \log \omega \tau \) in figure 3.6. It is symmetric, peaking at \( \omega \tau = 1 \). Thus a logarithmic frequency sweep gives a spectrum of the emission lifetimes of the diode directly. From these measurements as a function of temperature, the activation energy may be obtained. Comparative measurements on the same sample
structure using FRCS, admittance spectroscopy and deep level transient spectroscopy (DLTS) are presented in chapter 7.

3.6 OTHER METHODS OF INVESTIGATING DEEP LEVELS

3.6.1 ADMITTANCE SPECTROSCOPY

This is a "steady-state" technique in which measurements of the complex admittance of semiconductor junctions as a function of temperature provide a spectroscopy of deep levels. In particular, thermal scans of capacitance $C(T)$ and conductance $G(T)$ are made. In general, $C$ changes from a low temperature value to a high temperature value and $G$ has a peak at the step in $C$. The peak in $G$ and the step in $C$ correspond to the thermal emission rate of trapped carriers being equal to the angular measurement frequency. The measurements are usually carried out with using an expensive digital LCR meter. For a discussion see Lossee (1975). Measurements which require the temperature to be ramped while at high pressure are not desirable as it is difficult to maintain the pressure constant for large changes in temperature. This will be discussed later.

3.6.2 DEEP LEVEL TRANSIENT SPECTROSCOPY (DLTS)

DLTS is based on the measurement of capacitance transients as described in §3.4.
Figure 3.6: Quadrature FRCS spectrum
The basis of the measurement lies in the electronic processing of the transient signals. The essential feature of DLTS is the ability to set an emission rate window such that the apparatus only responds when it detects a transient within this window. The window is defined by the rate at which the capacitance signal is sampled and this in turn is related to the repetition rate of the applied voltage. The output of the system is displayed as a spectrum as a function of temperature where each peak corresponds to a different trap; the height of the peak is a measure of the trap concentration and the polarity indicates the trap type as in Capacitance transient spectroscopy. The type of signal processing initially employed by Lang (1974) uses a double boxcar detector but other methods of detection are in current use. These include the use of a lock-in amplifier to average the transients by using a symmetrical square wave function described by Kimerling and a correlation method (Miller et al (1975)) which performs a real-time cross-correlation between the experimental transient signal and an internally generated reference exponential. There are many variations of the standard technique such as constant-capacitance DLTS (Johnson et al (1979)) and optical DLTS (Mitonneau et al (1977) for example.
CHAPTER 4

APPARATUS AND EXPERIMENTAL TECHNIQUES

4.1 INTRODUCTION:

During the study of impurity levels reported in this thesis, a variety of experimental techniques were employed. Hall effect and resistivity measurements as a function of temperature in the range 77 to 450K were carried out on epitaxial layers of both p and n-type materials. Transient capacitance measurements as a function of temperature and pressure were also carried out in order to study deep majority and minority carrier traps. Frequency Resolved Capacitance Spectroscopy (FRCS) was used in the study of majority carrier traps and was found to be particularly suited to measurements at high pressures. The apparatus and methods used in these experiments and the way in which the samples and contacts were prepared are described in this chapter.

4.2 SAMPLE PREPARATION:

For the Hall effect and resistivity measurements on epitaxial material 'clover leaf' shaped samples were
prepared using photolithography. For bulk material, due to their greater thickness, samples were prepared by ultrasonic cutting. Transient capacitance and FRCS measurements were, in some cases, made on Schottky barriers placed in the centre of the clover leaf shaped samples.

4.2.1 PHOTOLITHOGRAPHY:

Clover leaf shaped samples were obtained from epitaxial material by chemical etching. A small section of the slice (typically 5 x 10 mm) was cleaved or cut from the material supplied and thoroughly cleaned using standard cleaning procedures, boiling methanol, trichloroethylene and isopropyl alcohol, to remove grease and other contaminants from the surface. Three layers of positive photoresist were applied and the material was spun at 8000 rpm for 1 minute, producing a uniform 0.7μm layer of resist. The resist was hardened by prebaking the material at 80°C for 20 minutes. The resist was exposed to ultraviolet light through a mask defining a pair of clover leaves and was then developed using a 1% solution of NaOH. The unexposed resist was washed away. The sample was then baked at 120°C for 30 minutes to harden the resist further. The exposed material was etched away at 50°C using a 3:1:1 mixture of sulphuric acid, hydrogen peroxide and water at a rate of 2μm/min. The sample was thoroughly rinsed in deionised water and the resist
removed in acetone. The material was then cut to separate the two samples.

4.2.2 ULTRASONIC CUTTING:

This technique was only used for bulk material. The material was obtained in the form of slices of thickness 1-2 mm and approx 20 mm diameter. A piece of the material was polished down to a thickness =300-400 μm using 5μm diamond and then to the desired thickness using 1μm diamond, which were sprayed on to the polishing mat. The surface was then chemically polished using a 1% Bromine Methanol solution.

The sample was fixed, polished side down, onto a microscope slide using shellac wax. The sample was placed under the appropriate size bronze cutting tool attached to an ultrasonic vibrator. The abrasive agent consists of a suspension of tungsten carbide granules in water. It was found that if vibration continued after the cutting process had been completed damage to the sample could occur.

4.2.3 SURFACE PREPARATION:

All samples were given the standard cleaning treatment prior to further processing. In addition to the normal cleaning process, InP samples were left in concentrated nitric acid for 30 min, were rinsed in deionised water and left in buffered hydrofluoric acid
for 10 minutes to strip the grown oxide layer. In this way a clean surface was produced. These extra steps were not found necessary for GaAs.

4.2.4 OHMIC CONTACTS:

In general, epitaxial layers were contacted using evaporation of Au-Sn/Ni, Au-Ge/Ni or Au-Zn/Ni alloys onto regions defined by a mask, followed by annealing typically at 425°C for 5 minutes in a dry hydrogen/nitrogen atmosphere. Some InGaAsP layers, however, had dots of In/5%Sn or In/5%Zn alloyed in at 420°C for 2-5 minutes. In the case of compounds containing phosphorus, in order to minimise phosphorus loss, alloying took place in a covered crucible lined with InP. Contacts produced by evaporation were contacted with 1/1000 inch gold wire using a pulse tip bonder or with silver loaded epoxy which was cured at 120°C for 20 minutes. Ohmic contacts to n-GaAs and bulk InP were made with In dots alloyed in at 450-500°C for 5-10 minutes and gold wires soldered on to these. The I-V characteristics of all contacts were checked for linearity using a curve tracer.

4.2.5 SCHOTTKY BARRIERS:

Gold of high purity (99.9999%) was used to produce Schottky diodes by vacuum evaporation. After the cleaning procedures described previously had been carried out, the
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sample was covered by a mask and a gold layer a few hundred Å thick was deposited. Diode diameters were in the range 600-1000 μm. Good Schottky diodes on InP were produced by growing a thin oxide layer in a furnace prior to Au evaporation.

4.3 HALL COEFFICIENT AND RESISTIVITY MEASUREMENTS:

Temperature dependent measurements of the Hall voltage and resistivity of the semiconductor samples under investigation were made using the van der Pauw technique on clover leaf samples prepared as described previously. Measurements were made in an Oxford Instruments DN704 liquid nitrogen reservoir cryostat using helium as the exchange gas. The van der Pauw technique requires only four contacts to the perimeter of a sample of uniform thickness. It requires four measurement configurations to obtain the Hall coefficient and resistivity. In order to correct for sample geometry and the effect of thermally generated voltages, measurements of all configurations with current and field reversal were made by measuring the configurations as illustrated in figure 4.1. A constant current source was used and the current Iᵢ and voltage difference Vᵢ recorded for i=1 to 4 to calculate the resistivity and for i=5 to 6 with a magnetic field of ~0.2 Tesla to measure the Hall coefficient. In all, twenty measurements are made to
obtain optimum averaging. The resistivity, $\rho$, in ohms-cm is calculated using:

$$
\rho = \frac{n t}{\ln 2} \cdot \frac{(R_1 + R_2)}{2} \cdot f(R_1/R_2)
$$

where $t$ is the sample thickness in cm, $R_1$ and $R_2$ are the resistances as defined in figure 4.1 and $f$ is a dimensionless quantity dependent on the ratio of the resistances $R_1$ and $R_2$ and is given by van der Pauw (1958) as:

$$
f(R_1/R_2) = \frac{1}{\ln 2} - \frac{R_1 - R_2}{R_1 + R_2} \cdot \frac{\ln 2}{R_1 + R_2} - \frac{(\ln 2)^2}{R_1 + R_2} - \frac{(\ln 2)^3}{4} - \frac{(\ln 2)^4}{12}
$$

provided $R_1$ and $R_2$ are almost equal. The Hall coefficient, $R_{H}$, in cm$^2$C$^{-1}$ is given by:

$$
R_{H} = 10^{19} \cdot \frac{\Delta R_{H}}{B}
$$

where $\Delta R_{H}$ is the change in resistance $R_{H}$ when a magnetic field of $B$ Gauss is applied perpendicular to the sample. The Hall electron concentration in cm$^{-3}$ is given by:

$$
n_{H} = \frac{1}{eR_{H}}
$$

and the Hall mobility in cm$^2$V$^{-1}$s$^{-1}$ by:

$$
\mu_{H} = \frac{R_{H}}{\rho}
$$
Figure 4.1: Sample connections for taking resistivity and Hall voltage measurements.

Figure 4.2: Schematic of guarded van der Pauw system
4.3.1 HIGH RESISTIVITY MATERIALS:

The presence of deep levels in some of the p-type InP layers measured gave rise to material of resistivity of the order of 10 Ωcm at room temperature for a free hole concentration of $10^{16}$ cm$^{-3}$ with a resistance of the order of 1 MΩ between the contacts on a layer ≈1-2μm thick. As the temperature of the sample is lowered the resistivity may increase by about three orders of magnitude over the range studied here, requiring the use of high input impedance devices to reduce sample loading. A system based on a method adopted by Hemenger (1973) and used by Shantharama (1986) to measure samples with a resistance up to $10^{9}$ Ω was therefore employed. The circuit consists of four high input impedance unity gain amplifiers, one on each probe to the sample and ordinary laboratory voltmeters. A guarded system, where the unity gain output is fed to the shield for a particular line and helps to reduce leakage currents and removes stray capacitances, hence reducing the time constant of the system. Errors produced by small offset voltages in the amplifiers are eliminated by the magnetic field reversal. The schematic diagram of the guarded van der Pauw system is illustrated in figure 4.2. The different configurations required are obtained by a multiple position rotary switch which allows for the by-passing of the amplifiers during current injection using relays. The leads on the high impedance side are kept as short as
possible and the entire matching unit is housed in a
small diecast box which fits on the end of the sample
holder. All switching is carried out on the low impedance
lines from the amplifier outputs and the current flowing
through the sample was measured using a Keithley 617
electrometer.

4.4 PRELIMINARY MEASUREMENTS:

Before studying a sample some initial checks were
carried out in order to assess the quality of the
contacts and the devices to be used. These consisted of
current-voltage and capacitance-voltage measurements.

4.4.1 CURRENT-VOLTAGE MEASUREMENTS:

Ohmic contacts on clover leaf samples and samples
intended for capacitance measurements were simply checked
for linearity using a Tektronics curve tracer.

When measuring the I-V characteristics of Schottky
barriers, the sample under investigation was placed in
the cryostat and a point by point measurement of forward
and reverse current using a Keithly electrometer with a
programmable voltage source was made at a given
temperature.

The parameters obtained from these measurements
were: the reverse saturation current \( I_r \), the ideality
factor \( n \), the barrier height \( \phi_m \), and the reverse
breakdown voltage \( V_r \). The ideal diode equation modified
for non-ideal behaviour, valid for $V$ greater than a few $k_B/T$ is:

$$I = I_s \left\{ \exp\left(\frac{eV}{nk_B T}\right) \right\}$$  \hspace{1cm} (4.6)

where the saturation current $I_s$ is given by:

$$I_s = A R^* T^2 \exp\left(-\frac{e\phi}{k_B T}\right)$$  \hspace{1cm} (4.7)

$A$ is the diode area and $R^*$ is the effective Richardson constant. The ideality factor and saturation current were obtained from plots of $\ln(I)$ versus forward voltage $V$ where the gradient is proportional to $1/n$ and the intercept gives $I_s$. A typical $I$-$V$ characteristic and $\ln(I)$-$V$ plot for a sample of bulk InP with contacts fabricated as described in section 4.2 are illustrated in figure 4.3(a) and 4.3(b) respectively.

4.4.2 CAPACITANCE-VOLTAGE MEASUREMENTS:

Point by point capacitance-voltage measurements were carried out at 1MHz using a Boonton 72BD Capacitance meter and a programmable voltage source which could provide voltage steps of 0.05 V. In the cases where the junctions were found to be abrupt and uniformly doped the doping concentration and diffusion potential were obtained from a plot of $1/C^2$ versus reverse voltage.
Fig 4.3(a): Typical I-V characteristics for an InP sample.

Fig 4.3(b): Logarithm of forward current against V for same sample.
Figure 4.4: $1/C^2 - V$ for bulk InP sample (as4.3(a), (b))
These measurements were made in the dark with the sample in the cryostat at a fixed temperature. A $1/C^2$ vs $V$ plot for the same sample as the current-voltage graphs in the previous figures is shown in figure 4.4.

4.5 CAPACITANCE TRANSIENT MEASUREMENTS:

A block diagram of the Transient capacitance data acquisition system is shown in figure 4.5. The sample was placed in an Oxford Instruments DN704 liquid nitrogen reservoir cryostat, mounted on a sample holder in good thermal contact with a calibrated Rhodium-Iron resistance thermometer. Miniature stainless steel coaxial cable was used between the sample and vacuum sealed connectors on the top of the holder. The sample space was evacuated to remove any moisture and filled with helium exchange gas to a pressure of $\approx 1$ bar. The Rh-Fe sensor was operated independently from the temperature control sensor. Details of the cryostat and temperature sensor can be found in appendix 4. The sample temperature could be varied between 77K and 500K and maintained stable to within $\pm 0.1K$.

A Boonton 72BD 1MHz capacitance meter was used to measure the capacitance transient following the excitation pulse. The sample leads were connected to the TEST input of the capacitance meter, which was used in differential mode. A variable capacitance box (4-2000 pF)
Figure 4.5: Block diagram of Transient Capacitance Apparatus
was connected to the DIFF terminals to offset stray capacitances and make use of a more sensitive range. Bias to the sample was provided by a Wavetek pulse generator with adjustable DC bias, via the biasing network of the capacitance meter. This was found to be satisfactory for pulses longer than ≈2 ms since the meter has a response time of about 1 ms. The meter response can be improved (Chappel et al. 1984) by removing the internal filter capacitors but with the penalty of a factor of three increase in the noise. Use of the internal bias circuitry was found satisfactory for most applications. If shorter pulses are required, for capture measurements for example, biasing can be provided externally without making use of the internal biasing circuitry. The capacitance meter provides an analogue output in the range 0-2 V proportional to the capacitance signal. The analogue signal was fed to an amplifier powered by an external supply. The amplifier output was either fed to a Y-T chart recorder or sampled by a CUBAN-12B 12-bit successive approximation analogue-to-digital converter connected to a BBC microcomputer via its 1MHz bus. The former was used for single-shot long time constant signals, while the latter enabled faster sampling rates and time averaging together with visual inspection and time constant calculation. Triggering of the pulse generator, ADC sampling rate and data acquisition were software generated using machine code routines making use
of the BBC's programmable interrupt timer. The plotting program was written in BBC Basic. The cryostat and all screens were connected to one common earth point. The computer program extended the range of time constants that could be recorded, enabling a more accurate value for the trap activation energy to be obtained.

The required temperature was set on the temperature controller and the sample temperature was monitored until the necessary stability was reached. The reverse bias across the diode and the filling pulse amplitude were set with the aid of an oscilloscope and the voltage (field) dependence of the emission time constant was investigated for reverse voltages ranging from a few tenths of a volt to near the breakdown voltage maintaining the same filling pulse peak voltage. A reverse bias voltage was chosen as low as possible while maintaining a good capacitance transient amplitude. The pulse width was increased from 1 ms until no further increase in capacitance transient amplitude could be observed. The sample temperature was monitored throughout the experiment by recording the resistance of Rh-Fe sensor on another chart recorder. By repeating the measurements as a function of temperature and plotting the results on an Arrhenius graph, the trap's thermal activation energy could be obtained.
4.6 FREQUENCY RESOLVED CAPACITANCE SPECTROSCOPY:

As was pointed out in chapter 3, in contrast to capacitance transient spectroscopy, FRCS is a frequency domain technique. In its basic form, the depletion bias is modulated with a small amplitude sinusoidal voltage and the sample response to the modulation is measured using quadrature lock-in detection. The schematic diagram of the basic FRCS spectrometer was shown in figure 3.5. The deep level spectrum is generated in one of two ways:

4.6.1 ISOTHERMAL FREQUENCY SCAN:

The sample was mounted in the cryostat as for the TCAP experiments described in section 4.5 and temperature stability monitored in the same way. Bridge balance was obtained by maximising the signal at A using the phase-shifter and then switching the lock-in inputs to measure A-B and adjusting the variable capacitor until a minimum in-phase voltage was detected. This procedure had to be repeated several times if the bridge was far from balance. With the bridge now balanced and the lock-in differential input connected across the bridge, the phase was shifted by 90° and the quadrature FRS response at the applied frequency noted. This procedure was repeated at several frequencies (typically 15-20 points were taken) and a typical result is shown in figure 4.7. The emission time constant for a given temperature was calculated from the peak in the quadrature response as described in
The in-phase component of the FRS signal is simply the signal at A in a balanced bridge. The trap thermal activation energy was obtained by repeating these measurements as a function of temperature.

4.6.2 FIXED FREQUENCY TEMPERATURE SCAN:

The Deep Level spectrum may also be generated by keeping the applied frequency constant and ramping the temperature. The sample was mounted in the cryostat in the usual manner and the temperature ramped at a rate of about 0.2 K/s. The quadrature FRS signal was fed to the Y-input of an X-Y recorder and the analogue output of the digital multimeter measuring the Rh-Fe sensor resistance to the X-input. The position of a peak in the signal was used to determine the temperature range in which isothermal frequency scans were to be carried out. Towards the end of the project a program was written to read the lock-in output voltage and the resistance of the temperature sensor from the instruments via the IEEE bus and store it on personal computer which controlled the data acquisition. Typical scans showing emission from two levels, obtained using this program, are shown in figure 4.8. The position of the peaks shift to higher temperature as the applied frequency is increased in a way analogous to changing the rate window in DLTS.
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Figure 4.7: Typical quadrature FRCS signal

Figure 4.8: Fixed frequency temperature scan.
4.7 HIGH PRESSURE SYSTEMS AND MEASUREMENTS:

4.7.1 INTRODUCTION:

Transient capacitance, Frequency Resolved Capacitance Spectroscopy and resistivity measurements were made as a function of pressure using either a piston and cylinder system up to 15kbar at room temperature, a capillary-fed miniature BeCu cell up to 8kbar between ±160-400K or a Bridgmann anvil system to ±50 kbar.

4.7.2 PISTON AND CYLINDER APPARATUS:

The system consists of a cylinder, a moving piston and a fixed piston. Pressure is generated by a hydraulic ram operated by either a handpump or an electric pump. The hydraulic ram moves the thrust piston into the cylinder, compressing the liquid pressure transmitting medium. The cylinders of the systems used in the investigations were double-walled. They consist of an outer cylinder (jacket) which is designed to apply a compressive stress to the inner cylinder (liner) thereby reducing the stress at the inner surface of the latter when at high pressure. The liner is designed to have an interference fit with the inner surface of the jacket. The cylinders can be joined by heating the jacket to a high temperature so that its bore expands enough to slide over the liner, or alternatively, as in the case of the
15kbar system at Surrey, the surfaces can be tapered and forced together.

4.7.2a 15 KBAR SYSTEM:

A diagram of the double-wall cylinder used is shown in figure 4.9. The cylinder is made of hot-worked die steel and the pistons of suitably hardened tool steel and ground to fit the cylinder. The cylinder was honed to an inner diameter of ≈29 mm. Details of the piston with sample leads are shown in figure 4.10. Six leads, (including three coaxial cables) are passed through a hole in the centre of the piston to hardened steel electrical feedthroughs in the top of the piston.

Castor oil is viscous, easy to seal and is regularly used up to 8 kbar as a pressure medium. At about 10 kbar it freezes at room temperature, producing non-hydrostatic stresses on the sample, so for measurements up to 15 kbar a 1:1 mixture of castor oil and amyl alcohol was routinely used. Sealing between the pistons and cylinder is achieved by means of a phosphor-bronze or nylon bevelled ring together with a neoprene 0 ring. Sealing is at first carried out by the 0 ring and eventually by the slightly deformed bevelled ring. Sealing of the electrical feedthroughs is by ceramic sleeves which are suitable for these viscous fluids.

A pressure gauge consisting of a coil of manganin wire of resistance ≈130Ω is mounted on the bottom piston,
Figure 4.9: diagram of 15 kbar compound cylinder
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Figure 4.10: Details of 15 kbar piston with seals and feedthroughs.
which is fixed. Prior to use the coil is temperature and pressure cycled to eliminate stresses. The resistance of manganin increases with a pressure coefficient of $2.3 \times 10^{-3}$ kbar$^{-1}$ (Peggs (1983)). The pressure in the cylinder is determined from measurements of the resistance of the coil at atmospheric pressure, $R(0)$, and at a pressure $P$, $R(P)$, using the expression:

$$P = \frac{1}{\lambda_m} \ln \frac{R(P)}{R(0)}$$  \hspace{1cm} (4.8)

where $\lambda_m$ is the pressure coefficient of manganin.

4.7.2b 8 KBAR PORTABLE INTENSIFIER:

This system, designed by Lambkin et al (1987), is based on an Enerpac 14 ton double-acting hydraulic ram acting on a 15 mm piston and cylinder and is illustrated in figure 4.11. The assembly is mounted vertically, as shown, with the fixed piston at the bottom and the blank top piston clamped to the arm of the hydraulic ram. Sealing between the piston and cylinder is by a bevelled nylon ring and an O ring. Electrical leads were passed through a Harwood three way coupler and a short length of capillary feed (Harwood 0.125 inch O/D 0.025 inch bore) through the fixed piston to a manganin pressure gauge wrapped in PTFE tape which rested on the piston head. The capillary was sealed to the piston and coupler using
Figure 4.11: Portable 8kbar intensifier with pressure gauge.
Fig 4.12: Details of Electrical seals and Harwood coupler.
standard Harwood metal-metal cone seals. Details of the coupler and electrical lead seals are given in fig. 4.12. The pressure transmitting medium used was a 1:1 mixture of n-pentane and isopentane. Pressure was transmitted through ~2 metres of capillary to a miniature pressure cell suitable for use in a cryostat.

4.7.3 LOW TEMPERATURE CELL:

The small (19mm outer diameter) high pressure cell developed by Lambkin et al (1987) for high pressure measurements up to 8 kbar at low temperature is shown in figure 4.13. The cell fits easily into the Oxford Instruments cryostat used for Deep Level studies and was used successfully in the range 150 to 390K.

The cell is of double-wall construction made of grade 250 Cu:Be machined half-hard and heat treated to a final hardness of Rockwell 35C. The inner bore of the liner was reamed to 5mm after assembly of the cylinder. Each end of the cylinder is sealed with a fixed piston and a nylon and rubber O ring. The bottom piston is blank and is backed by a threaded plug. The top piston is fixed, using a Harwood seal, to a length of capillary, also used to hold the cell in place in the cryostat. Enamelled copper wires, of diameter 0.07 mm, sealed in a stub using a nylon cylinder and epoxy resin (see fig. 4.12) were fed to the brass sample holder on the top
Figure 4.13: The low temperature cell.
piston via a three way coupler outside the cryostat and the supporting capillary. The pressure fluid from the intensifier enters the system via the horizontal port on the three way coupler, along the same route as the electrical leads.

As a safety precaution the high pressure capillary is covered by a reinforced rubber sleeve to help contain a jet of high pressure fluid and restrain the fractured capillary in the event of capillary failure, and steel plates are placed round the cryostat.

4.7.4 BRIDGMAN OPPOSED ANVIL SYSTEM:

A high pressure Bridgman opposed anvil system suitable for high pressure electrical and optical measurements, based on a system at STC Technology Ltd., was developed at Surrey and was used extensively by Shantharama (1986) for Hall effect measurements. A schematic diagram of the system is shown in figure 4.14(a), showing the fibre bundle in the lower anvil.

Transient capacitance and resistivity measurements at room temperature were made using the original system, without optical access up to ~50 kbar. Pressure in the blind anvil system was determined from the load v pressure calibration of Shantharama (1986). When the modified system was used, photoconductivity measurements were performed. A sample mounted in a MgO loaded epoxy gasket is shown in figure 4.14(b).
Figure 4.14: (a) Bridgman opposed anvil system.
(b) Sample in MgO loaded epoxy gasket.
CHAPTER 5

PAIRING OF Mn-ACCEPTORS AND Te-DONORS
IN InP AND Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$

5.1 INTRODUCTION

Before discussing Mn+Te doped InP AND Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$ it is useful to outline the reasons which have led to the use of Mn as a dopant in some III-V semiconductor materials and the subsequent study of these concurrently doped with Mn and Ge. A variety of dopants are used as acceptor impurities in the growth of InP and the quaternary alloy Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$ lattice matched to InP by liquid-phase epitaxy (LPE). These impurities suffer from several disadvantages. For example Zn and Cd have high vapour pressures and tend to contaminate the growth system and reduce the controllability of carrier concentrations and dopants such as Be are particularly toxic. The advantages of manganese include a low diffusivity in III-V solids, low toxicity and vapour pressure and low reactivity with oxygen. Thus, considerable interest has been shown in the use of Mn as a dopant for LPE material. The electrical properties of
Mn have been studied in InP (Mahory et al (1983)), in the quaternary alloy with $y=0.55$ (Fujita et al (1982)) and in Ga$_{0.47}$In$_{0.53}$As lattice matched to InP (Whitney et al (1985)) and lattice matched to GaAs (Phatak et al (1980)) for example. Mn doped materials have been used successfully in improved devices. For example, Takanohashi et al (1988) have shown that the use of a Mn doped InP layer in the current blocking region of a GaInAsP/InP Buried Heterostructure laser improves its small signal response.

There is also considerable interest in the pairing of transition metal impurities with shallow donors in III-V semiconductors. Ennen et al (1981) studied the photoluminescence spectra at 4.2K from GaAs and GaP crystals grown with a variety of donor dopants and subsequently doped with nickel by diffusion, and deduced that Ni has a strong tendency to form nearest neighbour pairs with at least five donors (S, Se, Te, Si and Sn) in GaAs. Masterov et al (1984) studied Mn+Te pairing in GaAs. In addition to this, the electrical characteristics of Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ layers grown on InP and concurrently doped with Mn and Ge have been investigated by Shantharama et al (1985). They found that when the concentration of Ge in the sample exceeded that of Mn, n-type material with low mobility was produced. However, p-type material with the concentration of Mn higher than that of Ge showed unexpectedly high hole mobilities. The
temperature dependence of the mobility suggested that there was very little ionized impurity scattering and this was ascribed to the formation of neutral donor-acceptor pairs. This result had important implications: it would seem that in order to produce layers with a high hole mobility it was not necessary to place fastidious attention to purity, as material with a high overall impurity content could, in cases where the activation energy of Mn is high, produce material with a hole mobility almost as high as the expected phonon limited mobility in pure material. It would be interesting to know whether this was a peculiar interaction between Mn and Ge or whether its interaction with other donors would produce similar effects. In order to ascertain this, we studied layers of the quaternary alloy Ga$_{1-x}$In$_x$As$_y$P$_{1-y}$ concurrently doped with Mn and Te. By studying materials across the alloy range we could then see if the new donor, this time from group VI, would interact with Mn to produce similar results in material where the activation energy of Mn differs.

Hall and resistivity measurements as a function of temperature will give the mobility and free hole carrier concentration from which the activation energy of Mn and information on the dominant scattering mechanisms can be deduced. The results obtained can be readily divided into two groups: one, in material where the activation energy of manganese is high (low y) and where we would expect to
see the a similar effect if the pairing of Mn is not limited to Ge or group IV donors, and two, in material where its activation energy is low (high \( y \)) and we expect no donor-acceptor pairing. The results obtained are presented in this fashion, with those for InP in the next section and those for material of high \( y \) in \S 5.3. In all, three compositions, \( y=0, 0.8 \) and 1 were investigated. The conclusions are drawn together in \S 5.4. In all cases, the single layers were grown at the SERC central growth facility in Sheffield.

5.2 ELECTRICAL CHARACTERISTICS OF Mn+Te DOPED InP

5.2.1 GROWTH

The single layers were grown on semi-insulating Fe-doped InP (100) substrates. Growth was initiated at 659°C and the temperature was ramped down throughout the growth period at a constant rate. The melts had a supersaturation of 10°C at the commencement of growth and contained a fixed concentration of Mn. The concentration of Te in the melts was increased on successive runs until n-type material was produced.

The concentration of contaminants (such as sulphur) present in the Mn used have been reduced in the past by pre-baking the In-Mn melt prior to growth (Greene (1985)). However, no observable difference could be detected between InP layers grown with or without a pre-bake, suggesting a high Mn purity. The thickness of the
epitaxial layers was 10-15 \mu m for p-type layers and 2 \mu m for the n-type layer. In-Zn dots or Au-Ge/Ni ohmic contacts were prepared on van der Pauw clover-leaf shaped samples.

5.2.2 DOPING DEPENDENCE OF MOBILITY

Table 5.1 presents the electrical characteristics of the InP layers, in which the phonon controlled mobilities of holes and electrons are normally expected to be about 140 (Wiley (1975), Nahory (1983)) and about 6000 cm²V⁻¹s⁻¹ (Boud (1988)) cm²V⁻¹s⁻¹ respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Te Doping Level (cm⁻³)</th>
<th>Carrier type</th>
<th>Carrier concentration (cm⁻³)</th>
<th>Mobility (290K) (cm²V⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS360</td>
<td>—</td>
<td>p</td>
<td>7.4 x 10¹⁵</td>
<td>115</td>
</tr>
<tr>
<td>AS361</td>
<td>10¹⁷</td>
<td>p</td>
<td>4.8 x 10¹⁵</td>
<td>129</td>
</tr>
<tr>
<td>AS362</td>
<td>5 x 10¹⁷</td>
<td>p</td>
<td>3.7 x 10¹⁵</td>
<td>129</td>
</tr>
<tr>
<td>AS363</td>
<td>10¹⁷</td>
<td>p</td>
<td>3.4 x 10¹⁵</td>
<td>135</td>
</tr>
<tr>
<td>AS364</td>
<td>10¹⁸</td>
<td>n</td>
<td>1.5 x 10¹⁵</td>
<td>780</td>
</tr>
</tbody>
</table>

Table 5.1: Electrical characteristics of InP layers grown from a melt doped to 5 x 10¹⁸ cm⁻³ with manganese.
These were grown from a melt doped with manganese to $5 \times 10^{18} \text{ cm}^{-3}$ and Te as shown. The low electron mobility in the last layer is consistent with a high ionized impurity content of about $2 \times 10^{19} \text{ cm}^{-3}$ (Anderson et al. (1985)) suggesting that the sample is heavily compensated and the mobility is dominated by ionized impurity scattering. On the other hand, the preceding layers have a hole mobility almost as high as that for high purity, phonon controlled, p-type layers although the number of ionized Mn and Te atoms is $\approx 2 \times 10^{18} \text{ cm}^{-3}$. The measured hole mobility actually increases slightly as the Te content increases through the series and the density of holes decreases. This would imply that all the Te atoms are paired off and the holes come from single ionized Mn atoms whose numbers are reduced by increasing amounts of Te.

5.2.3 Temperature Dependence of Mobility and Carrier Concentration

Measurements of the mobility as a function of temperature were carried out in order to confirm the presence of ionized impurity scattering in n-type material and its insignificance in p-type material concurrently doped with Mn and Te. The temperature dependence of the mobilities of majority carriers in these InP samples is presented in figure 5.1. The measurements were made using the apparatus described in §4.3. The resistivity of the p-type samples was of the
Figure 5.1: Temperature dependence of mobility in InP doped with Mn and Te. Solid symbols are p-type Mn+Te doped layers and squares are n-type sample.
order of 10 Ωcm at room temperature, increasing exponentially with decreasing temperature by 3 orders of magnitude in the temperature range investigated. Measurements were made at room temperature and at decreasing temperatures until the resistance of the sample approached the limit imposed by the input impedance of the buffer amplifiers (>10''Ω). It can be seen that the temperature coefficient of the mobility, \(\frac{d\mu}{dT}\), has opposite signs in the two types of material. The positive value of \(\frac{d\mu}{dT}\) for n-type material (open circles) suggests that ionized impurity scattering dominates the mobility (appendix-1) whereas that in p-type samples (solid circles and triangles) is characteristic of phonon scattering dominated mobility, suggesting that the effect of ionized impurity scattering is almost negligible.

The temperature dependence of the measured free hole concentration for the three p-type samples is shown in figure 5.2. The full curves show computed fits to the expression for the temperature dependence of the free hole carrier concentration in a partially compensated semiconductor (§3.2 eqn. 3.1):

\[
\frac{p_p(p_p + N_d)}{N_A - N_d - p_p} = \frac{N_D}{g} \exp\left(-\frac{E_A}{k_B T}\right)
\] (5.1)
Figure 5.2 Temperature dependence of measured free hole concentration for three p-type InP layers.
using the acceptor and donor concentrations $N_a$ and $N_D$ and the thermal activation energy $E_a$ as adjustable parameters with a value of $g=4$ assuming that each acceptor impurity can accept one hole of either spin and the impurity level is doubly degenerate as a result of the two degenerate valence bands at $k=0$. The density of states of the valence band was derived from the combined density of states effective mass described in §3.2. The computed value for the thermal activation energy of the acceptor level in InP is $233\pm5$ meV and is in good agreement with that obtained by Smith et al (1983) using PL. This indicates that the Frank-Condon shift is negligible.

We have seen that concurrent doping of InP, where the activation energy of Mn is large, with Mn and Te does produce material with high hole mobilities, as for InP doped with Mn and Ge. We now consider the other end of the alloy range, Ga$_{0.47}$In$_{0.53}$As and quaternary material of approximate composition $y=0.8$ similarly doped, where the activation energy of Mn is low.

### 5.3 Mn and Te DOPED Ga$_{0.47}$In$_{0.53}$As and Ga$_{x}$In$_{1-x}$As$_y$P$_{1-y}$

#### 5.3.1 GROWTH

The ternary layers were grown lattice matched to Fe doped InP by LPE at $569^\circ$C from melts with $21^\circ$C of supersaturation and doped to $1 \times 10^{18}$ with Mn and increasing amounts of Te. The quaternary layers were produced in the same way as the InP layers described previously.
5.3.2 DOPING DEPENDENCE OF MOBILITY:

The hole mobility in LPE GaInAs lattice matched to InP has been studied by Chand et al. (1981), Silberg et al. (1983) and Whitney and Fonstad (1985) as a function of Mn doping. Their findings are consistent with a decrease in the hole mobility from around 180 to ~90 cm$^2$V$^{-1}$s$^{-1}$ as the hole concentration increased from $10^{17}$ to $3 \times 10^{18}$ cm$^{-3}$ for growth temperatures in the range 550 to 650°C.

The electrical characteristics of the ternary single layers concurrently doped with Mn and Te are shown in Table 5.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Te Doping level (cm$^{-2}$)</th>
<th>Carrier type</th>
<th>Carrier concentration (cm$^{-3}$)</th>
<th>Mobility (290K) (cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS402</td>
<td>-</td>
<td>p</td>
<td>$1.0 \times 10^{18}$</td>
<td>109</td>
</tr>
<tr>
<td>AS380</td>
<td>$10^{16}$</td>
<td>p</td>
<td>$1.4 \times 10^{18}$</td>
<td>114</td>
</tr>
<tr>
<td>AS388</td>
<td>$10^{17}$</td>
<td>p</td>
<td>$1.3 \times 10^{18}$</td>
<td>100</td>
</tr>
<tr>
<td>AS414</td>
<td>$10^{18}$</td>
<td>p</td>
<td>$3.4 \times 10^{17}$</td>
<td>78</td>
</tr>
<tr>
<td>AS424</td>
<td>$5.5 \times 10^{18}$</td>
<td>n</td>
<td>$4.0 \times 10^{16}$</td>
<td>2510</td>
</tr>
</tbody>
</table>

Table 5.2: Electrical characteristics of Ga$_{0.47}$In$_{0.53}$As doped with $1 \times 10^{18}$ cm$^{-3}$ with Mn and Te as shown.
The table shows a decrease in the room temperature hole mobility and a drop in free hole carrier concentration as the Te doping is increased. The mobility of sample AS402 agrees well with the observations Whitney and Fonstad et al., but sample AS414 with a mobility of 78 and free hole concentration of $3.4 \times 10^{17}$ cm$^{-3}$ is highly compensated. The electrical characteristics of these samples are conspicuously different from those of the Mn and Te doped InP layers shown in §5.2, as are those of the quaternary layers of approximate composition $y=0.8$ shown in table 5.3. They were also grown on Fe-doped InP substrates by LPE and were doped to $10^{18}$ cm$^{-3}$ with Mn and Te as indicated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>y</th>
<th>Te Level (cm$^{-3}$)</th>
<th>p/n</th>
<th>Carrier Conc. (cm$^{-3}$)</th>
<th>Mobility (290K) (cm$^{2}$/V/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS510</td>
<td>0.34</td>
<td>0.78</td>
<td>-</td>
<td>p</td>
<td>$1.4 \times 10^{16}$</td>
<td>72</td>
</tr>
<tr>
<td>AS515</td>
<td>0.34</td>
<td>0.81</td>
<td>$3.5 \times 10^{18}$</td>
<td>p</td>
<td>$1.0 \times 10^{18}$</td>
<td>48</td>
</tr>
<tr>
<td>AS518</td>
<td>0.32</td>
<td>0.75</td>
<td>$1.6 \times 10^{18}$</td>
<td>p</td>
<td>$4.3 \times 10^{17}$</td>
<td>52</td>
</tr>
<tr>
<td>AS521</td>
<td>0.34</td>
<td>0.80</td>
<td>$2.0 \times 10^{18}$</td>
<td>n</td>
<td>$3.8 \times 10^{18}$</td>
<td>2330</td>
</tr>
</tbody>
</table>

Table 5.3 Electrical characteristics of the quaternary layers of composition $y \approx 0.8$. 
Figure 5.3: Temperature dependence of mobility for p-type layers of Ga$_{0.47}$In$_{0.53}$As/InP.
5.3.3 TEMPERATURE DEPENDENCE OF MOBILITY AND CARRIER CONCENTRATION

The temperature dependence of the hole mobility in the ternary layers is presented in figure 5.3. On cooling from room temperature the mobility increases but the rate of change declines and eventually reverses sign in the case of the most highly Te doped sample still displaying p-type characteristics. In this sample the mobility at low temperatures decreases rapidly with decreasing temperature.

The temperature dependence of the free hole concentration is shown in figure 5.4. The solid curves represent fits to equation 5.1 using a value of $m_e/m = 0.573$ (Alavi et al (1979)) in $N_0$. These provided a value for the activation energy of Mn in Ga$_{0.47}$In$_{0.53}$As of 57±3 meV, in good agreement with the value of 52.3±1.8 meV of Whitney et al (1984).

The temperature dependence of the hole mobility for the three quaternary p-type layers is shown in figure 5.5. As with the GaInAs layers, where the activation energy of Mn is low, the mobility is reduced by the presence of ionized impurities. In addition to this, alloy scattering is also more likely to play a more significant role than in the ternary material.
Figure 5.4 Temperature dependence of free hole carrier concentration in the p-Ga$_{0.47}$In$_{0.53}$As layers.
Figure 5.5 Temperature dependence of mobility for p-type quaternary layers doped with Mn and Te.
5.4 DISCUSSION

It is concluded that Mn forms electrically neutral pairs with Te-donors in p-InP in a similar manner to the previously reported pairing with Ge-donors, even though Te occupies P sites whereas Ge occupies In sites. However, such pairing is not apparent in p-Ga$_{0.47}$In$_{0.53}$As or in a quaternary layer with high As content. The difference is ascribed to the relative ease with which Mn can diffuse in the various semiconductors by adopting an interstitial site rather than a substitutional one on the In sublattice. The behaviour of Mn is explicable in terms of three forms related by the equation

\[ \text{Mn}_{\text{in}}^{2+} + \text{h}^+ \rightarrow \text{Mn}_{\text{i}} \rightarrow \text{Mn}_{\text{i}} + \square \text{h}^+ \]  

(3)

where the square represents a vacancy. In all n-type materials and in p-type materials where Mn forms a shallow acceptor the equilibrium is well to the left side of the equation. However, in p-InP Mn exists as a deeper acceptor and significant concentrations of Mn$_{\text{in}}$ and hence Mn$_{\text{i}}$ exist in the crystal. The electrostatic interaction between the ionized donor D$^+$ and Mn$_{\text{in}}^{2+}$ renders the Mn$_{\text{in}}^{2+}$D$^+$ pair more stable than Mn$_{\text{in}}^{2+}$ elsewhere in the lattice, so that most donors will be paired if the unpaired Mn atoms spend sufficient time in the mobile interstitial state as happens in p-InP.
6.1 INTRODUCTION

The use of Capacitance Transient Spectroscopy on Schottky barriers and p^+n junctions to characterise deep levels has been described in chapter 3. The work presented in this chapter can be divided into two parts: the first, §6.2, deals with the preliminary experiments carried out during the setting up of the CTS system described in chapter 4, namely the measurement of the temperature dependence of the emission rate of carriers from the well known deep gold acceptor and donor centres in Silicon and some other centres detected in bulk and epitaxial n-GaAs and InP to demonstrate the range of activation energies measured. The second part, §6.3, deals with the use of the system to characterise the extensively reported, but not too well understood, mid-gap donor level EL2 in VPE GaAs. The pressure dependence of the emission rate was investigated in order to establish its relation to the band structure.
6.2 Part I: PRELIMINARY MEASUREMENTS

6.2.1 THE GOLD RELATED DEEP CENTRES IN SILICON:

Gold is one of the impurities that have been studied most in silicon and has been well documented. A deep acceptor level at $E_C - E_F = 0.553 \text{ eV}$ and a deep donor level at $E_F - E_V = 0.350 \text{ eV}$ have been reported by many authors (e.g. Sah et al 1969). We know that the capture cross-section of the acceptor level is temperature (and pressure) independent (Samara et al 1987) which makes this an ideal centre for our first measurements to test the transient capacitance apparatus described in §4.5.

Measurements were carried out on a $p^+n$ diode supplied by the department of electrical engineering and electronics of U.M.I.S.T. Typical transients at several temperatures are shown in figure 6.1 for the electron and hole traps. The plots of $\ln(\Delta C(t))$ against time were found to be linear over several decades. Graphs of $\ln(T_\gamma^2\gamma)$ vs $1/T$ for measurements of emission rate taken in the range 180-220K for the acceptor, and 110-140K for the donor are shown in figure 6.2. They show an electron trap at a depth of $0.55 \pm 0.01 \text{ eV}$ below the conduction band, and a hole trap $0.35 \pm 0.01 \text{ eV}$ above the valence band edge. The capture cross-sections, as determined from the intercept, are $\sigma_n = 9.5 \times 10^{-15} \text{ cm}^2$ and $\sigma_p = 6.6 \times 10^{-14} \text{ cm}^2$. The results obtained are in good agreement with the dark current and capacitance transient data of Sah et al (1969).
Figure 6.1: Majority (---) and minority (____) carrier capacitance transients for gold-doped silicon p' n junction.
Figure 6.2: Arrhenius plots of $T^{-2} \tau$ vs $1/T$ for electron and hole traps in Si:Au.
6.2.2 BULK GaAs

The capacitance transients recorded from this sample were non-exponential. However, the transients could be separated easily as demonstrated in figure 7.3 in the following chapter. The logarithm of the emission time constants, corrected for $T^2$, are plotted against $1/T$ in figure 6.3. As can be seen the temperature dependence is clearly exponential. The activation energies obtained from the slopes and the capture cross-sections deduced from the intercepts are tabulated below:

<table>
<thead>
<tr>
<th>$E_a$ (eV.)</th>
<th>$\nu_n$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.72</td>
<td>$7.7 \times 10^{-18}$</td>
</tr>
<tr>
<td>0.15</td>
<td>$4.0 \times 10^{-24}$</td>
</tr>
</tbody>
</table>

The first level is suitable for high pressure studies using the 15 kbar piston and cylinder apparatus described in chapter 4 as the emission time constant at room temperature is such that at 15 kbar it would not be so long that the pressure and temperature could not be held constant during the recording of the transient. However, high pressure measurements up to 8 kbar could be made on either of these levels using the low temperature cell.
Figure 6.3: $\ln(\tau_n T^2) \propto 1/T$ for two levels in bulk GaAs.
A level similar to the 0.72 eV level has been observed by Samuelson et al (1981) in MOVPE GaAs.

6.2.3 EPITAXIAL GaAs:Cr

It is known (see chapter 1) that the transition metal Chromium gives rise to an acceptor level in GaAs. An n-type sample on a conducting substrate has been measured. Due to the absence of minority carriers in a Schottky barrier these are generated using an optical pulse with the diode under reverse bias. The minority carriers, holes in this case, are trapped by the level, while the majority carriers are swept away by the reverse field and the capacitance transient is recorded when the illumination is removed. The results obtained for the level at $E_t - E_F = 0.81$ eV with a capture cross-section of $2.5 \times 10^{-16}$ cm$^2$ are shown in figure 6.4. In order to measure the pressure dependence of this level optical access into the high pressure cell, via an optical fibre or a sapphire window, would have to be provided.

6.2.4 EPITAXIAL InP:

The plot of $\ln(\tau T^2)$ v 1/T for an electron level in VPE-InP is shown in figure 6.5. An activation energy of 0.63 eV and a capture cross-section of $3.4 \times 10^{-16}$ cm$^2$. A similar level has been reported in bulk/VPE-InP by Chowdhury et al (1979) and Bremond et al (1981).
Figure 6.4: Arrhenius plot for hole emission from n-GaAs:Cr
Figure 6.5: Arrhenius plot for electron level in VPE-InP.
6.2.5 SUMMARY

From the diverse results presented in the previous section it has been shown that the system described in §4.7 has been used successfully to detect deep levels with thermal activation energies in the range 0.15 to 0.72 eV in Si, GaAs and InP. The next move was to study a technologically important level and make use of the changes in the band structure that can be induced by hydrostatic pressure in order to provide further information which may shed some light on the possible nature of the level. This study is reported in the next sections.
6.3 THE MID-GAP DONOR LEVEL EL2 IN GaAs

6.3.1 INTRODUCTION

Considerable interest in this level in the last decade has stemmed from the marked influence it has been shown to have on the properties of semi-insulating materials which are important in their use as substrates in GaAs integrated circuit technology. Several hypotheses have been forwarded to explain its origin but, to the author's knowledge this has not been resolved satisfactorily yet. This level is commonly referred to as EL2 after Martin et al (1977). In the past EL2 has been associated with oxygen in GaAs, mainly based on the results of Hall effect measurements. Experiments on the intentional oxygen doping of GaAs carried out on Bridgman crystals showed that this process was quite inefficient (Emori et al (1982)). Very low concentrations of oxygen, down to $\approx 2 \times 10^{15}$ cm$^{-3}$, measured by SIMS showed that the concentration of oxygen was distinctly lower than that of EL2 of around $1.5 \times 10^{16}$ cm$^{-3}$ and this was taken as direct proof that EL2 was not related to oxygen at all (Huber et al (1979)). Although EL2 is not found in thick layers of GaAs grown by liquid phase epitaxy (LPE) (Lang and Logan (1975)) or molecular beam epitaxy (MBE) (Neave et al (1980)), which was confirmed by the author in attempts to find samples containing EL2, its presence in layers grown by vapor phase epitaxy (VPE) is widespread. Several authors (e.g. Wolfe et al (1977)) have shown that
the introduction of oxygen during VPE growth produces a decrease in the free carrier concentration but does not produce a shallow level. The electron mobility in such layers was lower than expected and the presence of oxygen related acceptors was postulated (Palm et al (1979)), although it was also suggested that the low mobility may be due, at least in part, to local inhomogeneities of the resistivity of the layers as has been suggested for bulk materials (Martin et al (1980)). Recent hypotheses based on electron paramagnetic resonance (EPR) include possibilities that EL2 is an antisite defect but conclusive experiments are still necessary before this can be confirmed. Here we present results obtained on the native defect observed in VPE n-GaAs which support the idea that electron emission from this level is to the L conduction band minima and that it moves away from the valence band maximum as hydrostatic pressure is applied to the sample, remaining almost fixed with respect to the vacuum level.

6.3.2 MATERIAL

The single layers studied came from a sequence of n-type samples grown by VPE on semi-insulating substrates at STL. The electrical characteristics of the samples measured are tabulated below.
6.3.3 THERMAL ACTIVATION ENERGY:

Typical majority carrier transients obtained from one of the nominally undoped VPE-GaAs samples are shown in figure 6.6. The increase in the time constant, $r_n$, with decreasing temperature is clearly shown. It should also be noted that the maximum value of the capacitance at $t=0^+$, $\Delta C(0)$, remains constant as a function of temperature since the same reverse bias and forward bias amplitude and duration were maintained. The exponential nature of the transients can be seen from the plots of $\ln(\Delta C(t))$ against time, shown in figure 6.7 for transients taken at different temperatures. A plot of $\ln(r_n T^2)$ as a function of $1/T$ yields a straight line. An activation energy of $0.833 \pm 0.005$ eV below the conduction band and a capture cross-section of $5 \times 10^{-15}$ cm$^2$ for this electron level were deduced from the graph. Results for three different VPE samples in which this level, referred to as 'EL2' in the literature, was detected are shown in figure 6.8. It has been shown that an electric field dependence of the emission time constant may lead to spurious values of activation energy (Pons (1979)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>epi.thick. ($\mu$m)</th>
<th>$N_D - N_A$ ($\text{cm}^{-3}$)</th>
<th>Mobility (290K) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S163A</td>
<td>12.5</td>
<td>$1.83 \times 10^{15}$</td>
<td>7220</td>
</tr>
<tr>
<td>S173A</td>
<td>12.0</td>
<td>$1.40 \times 10^{15}$</td>
<td>7230</td>
</tr>
<tr>
<td>S177D</td>
<td>8.3</td>
<td>$2.1 \times 10^{14}$</td>
<td>6530</td>
</tr>
</tbody>
</table>
Figure 6.6: Typical capacitance transients from VPE GaAs sample.
Figure 6.7: $\ln(\Delta C(t))$ v time for S163A.
Figure 6.8: $\ln(\tau_n T^2)$ vs $10^9/T$ for three VPE n-GaAs samples.
However, no variation of $\tau_m$ was found with fields of up to $1.5 \times 10^{16} \text{ Vcm}^{-1}$. The results obtained at three temperatures are shown in figure 6.9.

Assuming a uniform spatial trap distribution in the sample and keeping the other parameters constant, the amplitude of the capacitance transient $\Delta C(0)$ is proportional to $V_R^{3/2}$ as shown in figure 6.10(a). The sampling of a larger number of traps in the depletion region as it is increased with reverse bias produces a larger capacitance change. The signal from the traps can be maximised by careful choice of the reverse bias voltage and capacitance range on the measuring bridge. Figure 6.10(b) shows the results of a complementary experiment in which the change in $\Delta C(0)$ is monitored as the filling pulse amplitude is reduced for a fixed bias voltage and pulse width. It will be shown in chapter 7 that the latter experiment is useful when trying to distinguish between emission from a bulk trap and emission from a quantum well.
Figure 6.9: Field dependence of emission time constant for S163A
Figure 6.10: Variation of $\Delta C(0)$ with (a) reverse bias and (b) pulse forward voltage.
6.3.4 THE HYDROSTATIC PRESSURE DEPENDENCE OF EL2:

A study of the pressure dependence of the emission rate of electrons from the level can tell us the direction of the change in energy with respect to the band edge and the pressure coefficient of its energy. We know that the conduction band edge in GaAs moves away from the valence band at 10.7 meV/kbar as determined by Wolford et al (1986). Therefore, the pressure coefficient of the energy of 'EL2' may establish the binding of 'EL2' to a particular band minimum and/or its relation to the vacuum level. Measurements were made up to 15 kbar using the piston and cylinder apparatus described in §4.7.2. Some of the transients obtained are shown in figure 6.11. The plots of \(\ln(AC(t))\) vs time at different pressures show an increase in time constant with pressure and, therefore, an increase in the separation between 'EL2' and the band edge with pressure. The exponential nature of the transients can be seen clearly. The variation of \(\tau_0\) with pressure up to 15 kbar for two different samples is shown in figure 6.12. The pressure dependence of the emission rate, \([\delta \ln n_0/\delta P]^+\), is supralinear up to \(\approx 15\) kbar, the limit of the piston and cylinder apparatus. At this limit the emission time constant was about 17 minutes. The value of \(dE_0/dP\) obtained from a straight line throughout data up to 8 kbar is 3.5 ± 0.3 meV/kbar at room temperature, which is in excellent agreement with
Figure 6.11: \( \ln(\Delta C) \) against time, at high pressure.
Figure 6.12: Variation of $\tau_n$ with pressure for 'EL2'.

VPE-GaAs
n-type
T=290 K

$\tau_n$ (sec.)

P(kbar)

S 163 A
S 173 A
the value of $3.8 \pm 0.3$ meV/kbar obtained by Zylberstein et al. (1978), who measured the pressure dependence of the emission rate up to 5 kbar.

6.3.5 DISCUSSION:

Transient capacitance measurements on the electron trap EL2 commonly observed in VPE GaAs were made as a function of temperature and hydrostatic pressure. The temperature measurements yield an emission thermal activation energy of 0.833 eV and a capture cross-section of $5 \times 10^{-16}$ cm$^2$ derived from the intercept.

The expression for the emission rate of electrons from the level (equation 2.16) is:

$$
\nu_n = \frac{\nu_n <\nu_n> N_c}{\varepsilon_0} \exp \left(-\frac{E_a}{k_b T}\right)
$$

(6.1)

Now, taking the logarithmic partial derivative of $\nu_n$ with respect to pressure at a constant temperature we get:

$$
\left[ \frac{\delta \ln \nu_n}{\delta P} \right]_T = \left[ \frac{\delta \ln \nu_n}{\delta P} \right]_T + \left[ \frac{\delta \ln <\nu_n>}{\delta P} \right]_T + \left[ \frac{\delta \ln N_c}{\delta P} \right]_T - \frac{1}{k_b T} \left[ \frac{\delta \ln E_{tr}}{\delta P} \right]_T
$$

(6.2)

where $E_{tr} = E_C - E_T$. Further, if the capture cross-section is not temperature independent (see eqn. 2.21), as has
been shown for BL2 by Zylberstejn (1978), then this must also be taken into account. Thus,

\[
\frac{\delta \ln n_{\text{e}}}{\delta P} = \frac{\delta \ln \langle v \rangle}{\delta P} + \frac{\delta \ln N_{\text{c}}}{\delta P} + \frac{1}{k_{\text{B}} T} \frac{\delta \ln \mathcal{V}_{\text{e}}}{\delta P} + \frac{1}{k_{\text{B}} T} \frac{\delta \mathcal{E}_{\text{e}}}{\delta P}
\]

(6.3)

The average thermal velocity \( \langle v \rangle \) is proportional to the inverse square root of the effective mass (eqn. 2.11), so we may write:

\[
\frac{\delta \ln \langle v \rangle}{\delta P} = -\frac{1}{2} \frac{\delta \ln m_{\text{e}}}{\delta P}
\]

(6.4)

The effective density of states in the conduction band, \( N_{\text{c}} \) is proportional to \( m_{\text{e}}^{3/2} \) (eqn. 2.15), so we may write:

\[
\frac{\delta \ln N_{\text{c}}}{\delta P} = \frac{3}{2} \frac{\delta \ln m_{\text{e}}}{\delta P}
\]

(6.5)

The pressure dependencies of \( N_{\text{c}} \) and \( \langle v \rangle \) partially cancel each other out and the sum of the pressure derivatives of these equals \( \frac{\delta \ln m_{\text{e}}}{\delta P} \). The pressure dependence of the electron effective mass in GaAs has been measured (Shantharama (1986)), thus
Since we have not measured the pressure dependence of the electron capture cross-section directly it is necessary to estimate the pressure dependence of the energy barrier to capture before we can deduce the pressure coefficient of the depth of EL2. The energy $E_e$ may be written in terms of the thermal equilibrium depth $E_{tr}$ and the Frank-Condon shift, $\Delta_{FC}$ using the relation (Henry et al (1977))

$$E_e = \frac{(E_{tr} - \Delta_{FC})^2}{4\Delta_{FC}}$$

(6.7)

Also, the Frank-Condon shift is given (Lax (1957)) by

$$\Delta_{FC} = \frac{F^2}{2M\omega^2}$$

(6.8)

where $F$ is a term describing the electron-phonon coupling interaction, $M$ is the reduced mass and $\omega$ is the phonon frequency (usually an average of the LO and TO phonon frequencies). If we assume that $F$ is pressure independent (Barnes and Samara (1983)) then the pressure dependence of the Frank-Condon shift can be written as
Chapter 6

\[
\frac{\text{d} \ln \Delta_{FC}}{\text{d} P} = -2 \frac{\text{d} \ln \omega}{\text{d} P} \tag{6.9}
\]

which shows that the Frank-Condon shift is expected to decrease with pressure. From equations 6.7 and 6.9 we may write for the pressure dependence of \(E_a\):

\[
\frac{\text{d} E_a}{\text{d} P} = \frac{E_{th} - \Delta_{FC}}{2 \Delta_{FC}} \left[ \frac{\text{d} E_{th}}{\text{d} P} + (E_{th} + \Delta_{FC}) \frac{\text{d} \ln \omega}{\text{d} P} \right] \tag{6.10}
\]

Now, from equations 6.3, 6.6 and 6.9 we get

\[
\left[ \frac{\delta E_{th}}{\delta P} \right]_T = k_BT \left[ \frac{\delta \ln \omega}{\delta P} - \left[ \frac{\delta \ln \eta}{\delta P} \right]_T \right] + \frac{\text{d} E_a}{\text{d} P} \tag{6.11}
\]

which after substituting for \(\text{d} E_a/\text{d} P\) from eqn. 6.10 and rearranging gives

\[
\frac{\text{d} E_{th}}{\text{d} P} = \frac{2}{E_{th}} \frac{\delta \ln \omega}{\delta P} + \frac{\delta \ln \eta}{\delta P} \left[ \frac{\delta \ln \eta}{\delta P} \right]_T = \frac{2}{E_{th}} \frac{\delta \ln \omega}{\text{d} P} - (E_{th} + \Delta_{FC}) \frac{\text{d} \ln \omega}{\text{d} P} \tag{6.12}
\]

Now, using \(\Delta_{FC} = 0.14 \pm 0.01\) eV (Lang et al (1986)), \(E_{th} = 0.76\) eV (from \(E_a - E_b\)) and a value of \(\text{d} \ln \omega/\text{d} P\) calculated from the average of the values of the LO and TO phonon frequencies and their pressure dependence we obtain
The effect of pressure on the energy barrier to capture is to increase it, while the Frank-Condon shift decreases and the level moves away from the conduction band minimum to which it is emitting at about 1.8 meV/kbar.

White et al (1977) measured the EL2 to L minimum and valence band to EL2 transitions as a function of pressure using a photocapacitance technique. From their results and using a value for the increase of the indirect band gap at the L point taken from an average of 5.5 meV/kbar (Aspnes (1976)) and 3.8 meV/kbar (Gell et al (1987) with respect to the top of the valence band, the position of EL2 relative to the valence band maximum varies at the rate of 2.2±0.9 meV/kbar. If we assume that emission from EL2 is to the Γ minimum in our capacitance transient spectroscopy experiments, then the value for the variation of the separation of EL2 from the valence band maximum deduced from our results would be around 9 meV/kbar, assuming that \( \frac{dE_{r}}{dP} = 10.7 \text{ meV/kbar} \). If, however, emission from EL2 was to the L minimum, we would deduce a value of around 2.9±1.5 meV/kbar which would agree with the results of White et al within experimental error. Recently, Samuelson and Nilsson (1988) have reported that the valence band edge shifts by about -1.1±0.2 meV/kbar by using the transition metal impurity
Mn as a marker. Thus, it would seem that the shift of EL2 with respect to the vacuum level is around 1.8±1.7 meV/kbar, consistent, within experimental error, with the idea that its position may be fixed with respect to the vacuum level.

So far we have assumed that \[\frac{\Delta \ln \sigma_{\text{c},n}}{\Delta P} = 0\]. If we assume that the capture cross-section decreases slightly with pressure then the supralinearity of the pressure dependence of \(\tau_n\) can be accounted for. Figure 6.13 shows the variation of the activation energy \((\mathcal{E}_{\text{tr}} + \mathcal{E}_e)\) with pressure. The dashed line corresponds to the averaged results of the variation of \(\tau_n\) with pressure for the two samples measured assuming \[\frac{\Delta \ln \sigma_{\text{c},n}}{\Delta P} = 0\] (solid line in fig.6.12). If it is assumed that the capture cross-section decreases with pressure at the rate of 0.05x10^{-14} cm^2/kbar then the continuous straight line shown in figure 6.13 is obtained, giving an increase in energy \((\mathcal{E}_{\text{tr}} + \mathcal{E}_e)\) of 3.5 meV/kbar.

The deduced negative pressure coefficient of the capture cross-section is not totally unexpected. Matsumoto and Bhattacharya (1982) have shown that the capture cross-section of the 0.83 eV level decreases with composition in GaAlAs alloys, and since the effect of hydrostatic pressure on GaAs is similar to that of increasing the alloy composition in Ga_{1-x}Al_xAs it is also expected that the capture cross-section will decrease with pressure, as found for EL2.
Figure 6.13: Variation of activation energy with pressure at room temperature. Solid line assumes $\frac{d\sigma}{dP} = -0.05 \times 10^{-14}$ cm$^2$/kbar.
Figure 6.14: Position of 'EL2' in GaAs relative to valence band maximum as a function of pressure assuming emission to the L minimum and the value of $\frac{dE_L}{dP}$ shown.
The energy separation between the $\Gamma$ and $L$ minima, $\Delta E_{\Gamma-L}$, is 0.29 eV at room temperature (Sugeta et al. (1977) and Aspnes (1977)), giving an energy for 'EL2' below the $\Gamma$ minimum of $\approx 0.54$ eV. This is in good agreement with the results of Bhattacharya et al. (1979) who obtained a value of $\approx 0.55$ eV from capacitance-voltage measurements, and provides further support to the idea that emission from EL2 is to the $L$ minima.
CHAPTER 7

CAPACITANCE TRANSIENT SPECTROSCOPY:
RESULTS ON GaAs/Ga$_{1-x}$Al$_x$As QUANTUM WELLS

7.1 INTRODUCTION:

Capacitance Transient Spectroscopy has been applied to single GaAs/AlGaAs quantum well structures. Electron emission from bulk traps in the AlGaAs barriers and from a 100Å quantum well in Al$_{1-x}$Ga$_x$As of aluminium composition close to 30% has been studied as a function of temperature and pressure. The dependence of the capacitance transients on reverse bias in the two cases is remarkably different as is the pressure dependence of the emission rate. These factors, together with the observed difference in capture behaviour have been used to distinguish between emission from the bulk traps and emission from the quantum wells. A value for the conduction band offset for the system is deduced from the temperature dependence of the emission rate at atmospheric pressure. The structures studied are described in §7.2 and the investigation is divided into two areas: (a) emission from bulk traps in the AlGaAs
barrier and (b) emission from the GaAs quantum well, reported in §7.3 and §7.4, respectively.

Finally, in section 7.5 we present the preliminary results of a comparative study of InP-InGaAs superlattices using three different techniques.

7.2 MATERIAL:

The GaAs single quantum wells were grown by MBE at U.M.I.S.T. PL measurements on these samples give the bandgap of the GaAlAs as 1.756 eV, which corresponds to an aluminium composition of 28%, calculated using the known band structure of the alloy (Saxena 1980b). Samples containing wells of 100Å and 25Å were studied. The structure of the samples is shown in figure 7.1. The first GaAlAs layer (with aluminium composition = 30%) was preceded by a GaAs buffer layer. The silicon doping level and the depth of the well below the last grown surface had been chosen such that the depletion edge of a Schottky barrier could be controllably swept through the well. Electrochemical C-V profile plots, carried out at U.M.I.S.T., for the two samples studied are shown in figures 7.2 and 7.3, and the values of well depth and electron density in the well, \( n_w \), obtained from these are summarised in table 7.1.
GaAs/GaAlAs quantum well structure. (Sample № QW495).
Figure 7.2: Profile plots for QW495. (Courtesy of UMIST).
Figure 7.3: Profile plots for QW496. (Courtesy of UMIST).
Table 7.1: Characteristics of QW samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Well width A</th>
<th>Well depth microns</th>
<th>nω (peak value) cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>QW495</td>
<td>100</td>
<td>0.36</td>
<td>2x10¹⁷</td>
</tr>
<tr>
<td>QW496</td>
<td>25</td>
<td>0.27</td>
<td>8x10¹⁵</td>
</tr>
</tbody>
</table>

7.3 BULK TRAPS IN AlGaAs BARRIERS

7.3.1 TEMPERATURE DEPENDENCE OF EMISSION RATE

Transient capacitance measurements were made as a function of temperature using filling pulse widths of ≈ 10 ms. Some of the transients obtained around room temperature are shown in figure 7.4. The measurements were made at a bias such that the well was not depleted. The transients are non-exponential but may be characterised in terms of two exponentials with time constants τ_L and τ_S as shown in figure 7.5. The longer time constant, τ_L, is deduced from the slope of the plot of log(ΔC) versus time at large values of t and τ_S is obtained by subtracting the first from the whole transient. Extracting the time constants in this way two electron levels with activation energies of 0.84 and 0.73 eV were observed in both samples measured, although the
Figure 7.4: Transients from bulk traps in QW495.
Figure 7.5: Room temperature transient from QW496 showing separation of time constants.
capture cross-sections deduced from the intercepts differed in both cases as shown. Figures 7.6 and 7.7 show the Arrhenius plots for both samples and the results are summarised below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E_a$ (eV)</th>
<th>$\sigma_n$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QW495</td>
<td>0.84</td>
<td>$6.5 \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>0.73</td>
<td>$7.1 \times 10^{-15}$</td>
</tr>
<tr>
<td>QW496</td>
<td>0.84</td>
<td>$1.1 \times 10^{-15}$</td>
</tr>
<tr>
<td></td>
<td>0.73</td>
<td>$7.1 \times 10^{-15}$</td>
</tr>
</tbody>
</table>

7.3.2 VOLTAGE AND PULSE WIDTH DEPENDENCE OF $\Delta C$

The results of the variation of $\Delta C$ with reverse bias for a given forward voltage and pulse width for the trap observed at room temperature in QW495 are shown in figure 7.8(a). Figure 7.8(b) shows the dependence of $\Delta C$ on filling pulse height for a fixed bias and pulse width. As expected, $\Delta C$ increases with applied reverse bias voltage as a larger portion of the depletion layer is sampled. It has been shown that for bulk related traps, such as EL2 in GaAs (§6.3.3), $\Delta C$ increases with reverse bias voltage as a larger number of traps are sampled with the increasing depletion width. The 0.84 eV and 0.73 eV levels also follow this pattern, demonstrating that they are bulk traps. Electron levels with about the same activation energy and capture cross-sections in GaAlAs layers have been reported by Matsumoto and Bhattacharya (1982) and Wangner et al (1980), providing support to the idea that they are in the GaAlAs layer.
Figure 7.6: Electron traps with $E_a = 0.84$ eV.
Figure 7.7: Electron traps with \( E_A = 0.73 \text{ eV} \).
Figure 7.8: Dependence of ΔC from bulk traps on (a) reverse bias, and (b) pulse height.
7.3.3 PRESSURE DEPENDENCE OF EMISSION RATE

The variation with pressure of the emission time constant at room temperature for the 0.84 eV level was measured up to 15kbar using the piston and cylinder apparatus. The variation of ln(ΔC) versus time taken at different pressures is shown in figure 7.9. The time constant increases at a linear rate of 0.55 seconds/kbar (figure 7.10) up to about 7 kbar where the rate is found to decrease. This may be interpreted immediately as an increase in the activation energy of 13.8±0.8 meV/kbar with respect to the conduction band edge up to 7 kbar. It was shown in chapter 6 that the bulk level EL2 in GaAs approximately followed the top of the valence band. Its apparent activation energy and pressure coefficient were 0.83 eV and 3.5 meV/kbar, respectively, and although the activation energies are similar we are clearly looking at different levels. If the capture cross-section of the 0.84 level were not thermally activated then assuming that the pressure coefficients of the Γ, X and L minima with respect to the top of the valence band (from table 2.1) are 10.7, -1.4 and 3.9 meV/kbar, respectively, the pressure coefficient of the level with respect to the top of the valence band, assuming emission to the Γ, X and L minima would be about -3.1, +15.2 and -9.9 meV/kbar, respectively. Figure 10.6 shows the case for emission to the Γ minimum. The net effect is for the activation energy to decrease with respect to the valence band, that
Figure 7.9: ln(ΔC) v time for 0.84 eV level in QW495.
Figure 7.10: Pressure dependence of 0.84 level in QW495.
Figure 7.10b The position of the 0.84 eV level in AlGaAs shown with respect to the valence band maximum.
is to say that, if there is no barrier to capture, the level position \( E_r \) would move towards the top of the valence band at \( 3.1 \pm 0.8 \text{ meV/kbar} \). This rate is closest to the variation of the \( X \) minima which moves towards the top of the valence band at \( 1.4 \text{ meV/kbar} \), suggesting that the level, although emitting to the \( \Gamma \) minimum, may be coupled to the \( X \) minimum. Support for this may be found in the fact that as the pressure is increased the \( X \) minima energy decreases and hence \( \tau \) is expected to decrease (eqn. 2.16) which is what we observe above \( 7 \text{ kbar} \). However, centres in AlGaAs showing large lattice relaxation are commonly reported (e.g. Li et al (1987)) with pressure coefficients of the barrier to capture, \( \frac{dE_i}{dP} \), of typically \( +2.5 \text{ meV/kbar} \). Therefore, the position of this level could easily be constant with respect to the valence band maximum if the its barrier to capture increased at \( \approx 3 \text{ meV/kbar} \). Thus, in the absence of capture data, the coupling of this level to a particular minimum cannot be confirmed.

7.4 QUANTUM WELL EMISSION

In all the experiments reported so far filling pulse widths in the range 0.1 to 1 ms have sufficed to completely fill the traps. However, when pulses of similar width were used to initiate the transients due to
emission from the well, the data did not fall on a straight line on an Arrhenius plot and were indeed irreproducible. This led to a study of the change in $\Delta C$ as a function of pulse width, $t_0$. The results obtained are shown in figure 7.11(a) and 7.11(b) for the 100Å and 25Å wells taken at different temperatures. From these it will be noted that in order to obtain an increased signal it is preferable to use longer pulse widths and take measurements at the lower temperatures. Pulses of the order of 5 seconds were found sufficient to obtain a large enough signal that values of the time constant could be obtained reproducibly.

7.4.1 LOCATION OF QUANTUM WELL

An investigation of the dependence of $\Delta C$ on reverse bias for different pulse widths yielded a curve with an initial increase in $\Delta C$ with reverse bias with a gradual change in slope and eventual decrease in $\Delta C$ as the reverse bias is increased (see figure 7.12(a)-(b)). These results are markedly different from those of the bulk traps reported previously and are a characteristic of emission from a quantum well.
Fig. 7.11(a) $\Delta C$ vs $\ln(t_D(s))$ for 100Å well

Fig. 7.11(b) $\Delta C$ vs $\ln(t_D(s))$ for 25Å well
Fig. 7.12(a) $\Delta C$ versus bias for QW emission from QW495

Fig. 7.12(b) $\Delta C$ versus bias for QW emission from QW496
The position of the peak in $\Delta C$ in the previous figures occurs at a position where the depletion layer boundary is at the quantum well. From the slope of the $1/C^2$ versus $V_r$ plot (eqn. 3.12) for the 100Å quantum well sample a value for $N_0$ of $6.83 \times 10^{18}$ cm$^{-3}$ is deduced. This gives a value of the depletion width, $W$, equal to 0.31 μm (from eqn. 3.5) for a voltage of 3.73V. Similarly, for the 25Å well, we obtain a value of 0.26 μm. These compare well with the values of 0.37 and 0.273μm obtained from the electrochemical C-V plots and show that the peak position in the $\Delta C$ versus $V$ plot occurs at the voltage where the depletion layer boundary meets the quantum well. The occurrence of a peak may be explained as follows: $\Delta C$ increases with reverse bias for a large trap density and decreases with bias for a low trap density so for voltages lower than the peak voltage, where the edge of the depletion layer has not swept through the well, a bulk trap with a high density is observed and hence $\Delta C$ increases with bias; for voltages larger than the peak voltage the boundary sweeps the well (where the trapped electron density is lower) and $\Delta C$ drops (see appendix-4).

7.4.2 TEMPERATURE DEPENDENCE OF THE EMISSION RATE: DETERMINATION OF THE CONDUCTION BAND OFFSET

Figure 7.13 shows the logarithm of the capacitance transients versus time for the 100Å well.
Figure 7.13 Ln(ΔC) v time for QW495 - 100Å well
Using pulse widths of the order of seconds, reproducible values of the emission time constant were obtained. Figure 7.14 shows an Arrhenius plot of the data obtained on QW495 using a 5 second forward filling pulse pulse. The activation energy deduced from the slope is 0.20 eV and the capture cross-section deduced from the intercept is 3.3x10^-15 m^2. The longer filling pulse widths required suggest that capture is rather more difficult than for bulk traps, as expected. One reason for this may be the build up of a Coulombic repulsive field by the electrons captured initially, inhibiting further electron capture. Capture rates at quantum wells have been studied by Hamilton et al (1985), who have shown that for a 25 Å well, the increase in well electron concentration, \( \frac{dn_w}{dt} \), is proportional to \( \exp(-nw^2) \). Martin et al (1983) have made transient capacitance measurements on large quantum well heterostructures and found that due to the long capture times involved, the system may not reach equilibrium during the short bias pulses of a DLTS experiment. Their observation is in agreement with our findings.

Figure 7.15 shows the band structure of the GaAs/Gao.73Al0.28As quantum well drawn relative to the vacuum level. The ionisation potential in GaAs has been taken as -5.48 eV and for \( x=0.28 \) a linear interpolation between GaAs and AlAs was used. The ionisation potential
Figure 7.14 Arrhenius plot for emission from 100 Å well.
Figure 7.15: Band structure of GaAs/Ga$_{0.72}$Al$_{0.28}$As Quantum well.
in AlAs was assumed equal to that in GaP (-5.91 eV) as no data was available for AlAs (Ledebo and Ridley (1982)). From this simple model the values of the conduction and valence band offsets are 0.218 and 0.120 eV, respectively ($\Delta E_c: \Delta E_v = 66:34$).

In a capacitance transient spectroscopy experiment we assume that emission is from the first confined state to the bottom of the barrier conduction band. Thus the confinement energy has to be added to the observed activation energy in order to obtain the conduction band offset. The confinement energy was calculated taking into account the effects of conduction-band non-parabolicity (Hiroshima and Lang (1986)). The parameters used in the calculation were derived from the values given in Table 2.1, for all energies at 0K and assuming a $\Delta E_c = 0.65 \Delta E_n$. The calculated value for the first confined state in the 100Å well is 27.3 meV. The calculated value is not in fact very dependent on the value of the band-offset ratio chosen. For a variation from $\Delta E_c / \Delta E_n = 0.85$ to 0.5 the calculated values can be described by $E_i = 27 \pm 2$ meV. The conduction band-offset (at 0K) works out as $(200 \pm 10) + (27 \pm 5) = 227 \pm 15$ meV, which corresponds to 65\% of the total discontinuity.

7.4.3 THE EFFECT OF PRESSURE ON QUANTUM WELL EMISSION

If $L$ is the width of the quantum well, then considering the well as a square potential energy well,
Fig. 7.16 Conduction band edges of GaAs and AlGaAs (x=0.28) versus pressure, all referenced to top of AlGaAs valence band.
the ground state \((n=1)\) quantised energy level is given by the well known relation:

\[ E_n = \frac{n^2 \hbar^2}{2m_0 L^2} \]  

(7.2)

The quantum well will only approximate a square potential well for an undoped or low-doped structure where there is little band bending. The structures studied by the author were low-doped so this approximation has been considered. The conduction band offset is expected to be relatively insensitive to pressure in this alloy system due to the very small difference in the pressure coefficients of the band gaps of GaAs and AlGaAs and the assumption that their ionization potentials vary similarly with pressure. The band structure of a GaAs/GaAlAs\(x=0.28\) quantum well as a function of hydrostatic pressure shown relative to the top of the AlGaAs valence band is shown in figure 7.16, using the energy pressure coefficients given in table 2.1. The value of \(dE_r/dP(x=0.28)\) for the well is taken as 9.8 meV/kbar (Venkateswaran et al (1986)) in order to estimate an upper limit for the expected pressure variation. This gives a value for \(d(\Delta E_V + \Delta E_C)/dP = 0.6 \text{ meV/kbar}\), which assuming that 65% of the change is taken by \(\Delta E_C\) gives \(d(\Delta E_C)/dP \approx 0.6 \text{ meV/kbar}\). From eqn. 7.2 we may write:

\[ \frac{dE_r}{dP} = -\frac{1}{m_r} \frac{dm_r}{dP} E_r \]  

(7.3)
we know that $1/m_*(dE_0/dP) = 0.77 \times 10^{-2} \text{kbar}^{-1}$ so we estimate the change due to the increase of effective mass as $\approx -0.2 \text{meV/kbar}$. $E_1$ also depends on the well width but the change in $L$ due to the reduction in lattice constant is minute. The net change in activation energy expected from this simple treatment is an increase of around $0.4 \text{meV/kbar}$, which is much smaller than our experimental error. It must be noted that this is not the case for all the material systems. In InGaAs/InP the pressure dependence of the conduction band offset has been deduced to be $2.3 \pm 0.6 \text{meV/kbar}$ (Lambkin et al (1988)).

The conduction band discontinuity is formed between the $\Gamma$ bands of GaAs and GaAlAs up to the band crossover pressure. For higher pressures the discontinuity is between the $X$ minimum of GaAlAs and the $\Gamma$ minimum of GaAs and (see fig. 7.16). Thus, little or no change, in the activation energy is expected with pressure up to the critical pressure for cross-over (about 12 kbar) where the $X$ minima in GaAlAs becomes equal in energy to the $\Gamma$ minimum. The pressure coefficient of the conduction band offset is expected to be about $-7.9 \text{meV/kbar}$ (for $dE_r/dP = 9.8 \text{meV/kbar}$) or around $-12.2 \text{meV/kbar}$ ($dE_r/dP = 10.7$). This means that the time constant for emission at a given temperature (determined from figure 7.14) should be pressure independent up to the critical pressure if the prefactor in the expression for capture does not vary with
pressure. The results for such an experiment made on the 100Å well at 160.3 K in the Be/Cu cell are shown in figure 7.17. The transients, and hence $\tau_n$, remain almost unchanged up to $\approx 4.2$ kbar, where the experiment was terminated due to leaks via the electrical feedthrough. The solid and dashed lined include the total change in the transient between 0 and 4.21 kbar. The limit of the Be/Cu cell is $\approx 8$ kbar. If measurements at higher pressure could be made, one would expect to see $\tau_n$ change appreciably after the cross-over pressure. The fact that almost no change in activation energy with pressure was observed further confirms that we were observing emission from the well.
Fig. 7.17 $\ln(\Delta C)$ vs temperature for QW emission 0-4.2 kbar
7.5 A COMPARATIVE STUDY OF InP/InGaAs SUPERLATTICES

7.5.1 INTRODUCTION

A number of space-charge capacitance techniques have been used to observe emission from InP/InGaAs superlattices in order to demonstrate the validity of FRCS. The experiments were carried out on the same device keeping the experimental conditions as similar as possible. The samples consisted of a 1.0 µm buffer layer of n-InP (6x10\(^{17}\) cm\(^{-3}\)) on an n\(^+\) InP substrate followed by a 2.0 µm layer of n-type GaInAs and a 10-period n-type superlattice grown with alternating layers of 300Å of GaInAs and 500Å of InP. The devices supplied were mesa diodes of diameter 325 µm formed by photolithography. The measurement techniques used were Frequency Resolved Capacitance Spectroscopy, Admittance Spectroscopy and Deep Level Transient Spectroscopy.

7.5.2 FREQUENCY RESOLVED CAPACITANCE SPECTROSCOPY

These measurements were carried out using the system described in §4, using a modulation of 50 mV p-p across the bridge with no applied DC bias. The isothermal FRCS taken at 126.07K are shown in figure 7.18. Two clearly resolved peaks can be seen. For the purpose of a comparative study we will not expand on their significance. The spectra of a temperature ramp for a
Figure 7.18. Isothermal FRCS scan at 126.07 K.

Figure 7.19: FRCS temperature ramp at 40Hz.
fixed frequency of 40 Hz are shown in figure 7.19. These experiments were repeated at different temperatures and at different frequencies, respectively, and the combined results are shown in an Arrhenius plot in figure 7.20. The activation energies deduced from the slopes, corrected for $T^2$, are 0.207 and 0.172 eV respectively.

7.5.3 ADMITTANCE SPECTROSCOPY

The admittance spectroscopy measurements were made using an HP 4275A digital LCR meter at frequencies in the range 10 kHz to 1 MHz with an amplitude of 3 mV. The conductance $G$ was monitored as a function of temperature. A typical plot of $G/\omega$ against $T$ is shown in figure 7.21. Again, two peaks were observed. The results are shown on an Arrhenius plot in figure 7.22. The activation energies obtained are 0.209 and 0.168 eV respectively, in excellent agreement with the FRCS results.

7.5.4 DEEP LEVEL TRANSIENT SPECTROSCOPY

DLTS measurements were made by two visiting Czech scientists on these devices. The DLTS system was taken to its limit by keeping the reverse bias on the sample down to 20 mV and using an excitation pulse of 40 mV. A typical spectrum is shown in figure 6. The Arrhenius plot is shown in figure 7. The activation energies deduced from the slopes are 0.204 and 0.193 eV respectively. The activation energy deduced from the main peak is in
Figure 7.20: FRCS combined results.
Fig. 7.21: Admittance spectroscopy, spectra at 10kHz
Fig. 7.22: Arrhenius plot of Admittance spectroscopy data.
Figure 7.23. Typical DLTS spectrum
Figure 7.24: Arrhenius plot of DLTS data

- $E_A = 0.193$ eV
- $E_A = 0.204$ eV

$10^{-3}$

$10^{-4}$

$10^{-5}$

$10^3/T$ (K$^{-1}$)

$E_A = 0.193$

$E_A = 0.204$ eV
excellent agreement with that obtained from the previous methods.

7.5.5 SUMMARY

It has been shown that the three techniques used provide reproducible measurements of the activation energy for emission from the GaInAs wells. If the energy of the first confined state is added to the activation energy of electron emission from the wells, the conduction band offset can be determined as for the GaAs-AlGaAs system reported previously.
CHAPTER 8

THE EFFECT OF PRESSURE ON DEEP LEVELS IN InP:V

8.1 INTRODUCTION

Developments in III-V semiconductor electronic and optoelectronic devices during the last fifteen years have led to a search for good semi-insulating substrates and the consequent search for the ideal dopant that gives a deep acceptor near mid-gap and is thermally stable. This has lead to a study of different transition metal impurities in several III-V compounds. A number of transition metal impurities have been successfully used to produce semi-insulating substrates (e.g. Fe in InP or Cr in GaAs) and more recently vanadium doped GaAs which has been shown to be thermally stable (Kütt et al 1984, 1985). Ledebo and Ridley (1982) proposed that in cases where the impurity is very localised, deep levels are largely tied to the vacuum level and independent of the host lattice, based on results on Fe, Cr, CuA and CuM in three hosts (InP, GaAs and GaP) where their absolute energy positions remain remarkably constant. It can be shown that according to this hypothesis the vanadium
acceptor level should be above the conduction band minimum. Hydrostatic pressure has been used to bring a deep level into the gap in InP:V. These results, would confirm, for the first time, that the Vanadium level in InP is indeed above the conduction band minimum at atmospheric pressure. First, however, direct confirmation that the level is due to Vanadium is needed.

We have also studied the pressure dependence of another level in this material which is of interest as it can be inadvertently introduced during normal device processing at moderate temperatures.

8.2 THE VANADIUM LEVEL IN InP

The optical properties associated with vanadium (i.e. the luminescence and absorption spectra) are very similar for InP, GaAs and GaP and studies of InP:V using Zeeman and piezospectroscopy techniques have been made by Nash et al (1984) and Kane et al (1984) respectively who have explained their observations in terms of $V^{3+}$. It is interesting to look at the various levels attributed to vanadium that have been detected in various III-V compounds. These are shown in figure 8.1 plotted relative to the vacuum level together with some other transition metal impurity levels observed in GaAs InP and GaP. It can be seen that there is reasonable agreement for the hole trap at $E_T - E_C = 0.58$ eV in GaAs (Terao et al (1982)) and that in GaP at $E_T - E_C = 0.55$ eV (Abagyan et al (1974)).
Figure 8.1 Some deep levels attributed to transition metal impurities, including Vanadium, in GaAs, InP and GaP shown relative to the vacuum level.
However, the level observed using DLTS by Bremond et al (1985) in p-type material co-doped with zinc does not agree. No other vanadium levels have been reported within the band gap in InP:V (Lambert et al 1983). An electron trap has been observed in GaAs by several authors. Litty et al (1983) performed DLTS and DLOS on n-type GaAs:V and attributed two levels to vanadium: one at $E_C - E_T = 0.14$ eV and another at $E_C - E_T = 0.23$ eV, but could not detect a hole trap. Recently Brandt et al (1985) obtained a value of $E_C - 0.15$ eV from DLTS. Now if we accept the value of around 0.15 eV in GaAs, then from the hypothesis of Ledebo and Ridley we would expect the vanadium acceptor level to lie around 0.16 eV above the conduction band minimum and hence be undetectable by normal electrical techniques. However, we can use hydrostatic pressure to vary the band structure of the host and if the transition metal impurity levels are tied to the vacuum level they must have the same pressure coefficients. We know that the Cr level in GaAs moves away from the valence band at 2.1 meV/kbar (White et al (1977)) and that the conduction band moves away from the valence band at about 8.5 meV/kbar in InP so we might expect any level in InP pinned to the vacuum level to move at about 6.4 meV/kbar relative to the conduction band edge. Using this assumption we would then expect the vanadium level to appear within the gap at around 25 kbar, above which we should be able to observe carrier trapping by the V
level. Details of the material investigated and the new results obtained from the experiments we carried out are given in the next sections.

8.3 MATERIAL

The material used was a liquid encapsulated Czochralski (LEC) single-crystal of InP doped to $2 \times 10^{16} \text{ cm}^{-3}$ with vanadium during growth (Cockayne et al (1981)) and its electrical characteristics have been given by Skolnick et al (1983).

8.4 PRESSURE RESULTS ON THE VANADIUM LEVEL IN InP

The room temperature resistance of a bar sample was measured as a function of pressure up to 50 kbar using the Bridgman system described in §4.7.4. The results are shown in figure 8.2. The dashed curve is the estimated electron concentration for the measured resistance values (Saxena (1988)) assuming that the observed sudden increase in resistivity is due to the loss of mobile electrons into trapping states moving below the $\Gamma$ conduction minimum with pressure. This is justified because although the mobility is expected to drop due to the increase in effective mass as the pressure is increased, and also change (it is not clear unless we know the charge state of V whether the mobility will increase or decrease) as electrons trap out due to the variation in ionized impurity density and the change
Figure 8.2 Variation of resistance with pressure for InP:V, showing the V level moving into the gap between 20 and 30 kbar.
in screening, in any case, these effects are negligible with respect to the large (orders of magnitude) change. We see a clear trap-out of electrons in the region 20-30 kbar as expected. While this type of experiment does not in itself lead to a detailed identification of the position and type of level detected, the knowledge of the sample characteristics as grown does give us a good idea of which is the predominant level. This is the first experiment of its kind to show that the V level in InP does in fact lie above the conduction band edge at atmospheric pressure. In this experiment, pressure was determined from a load-pressure calibration curve (Shantharama (1986)). A more accurate method of measuring the pressure is to obtain the photoconductive response from the sample as a function of wavelength at each pressure, from which the pressure can be calculated if the pressure coefficient of the band edge is known. Also, Hall measurements give much more information about electron transport than simple resistance measurements. Such an experiment was performed using a Bridgman system with optical access via a fibre bundle sealed using MgO loaded epoxy in a hole passing through the centre of one of the anvils. The photoconductive response at atmospheric pressure is shown in figure 8.3(a). The position of the peak at 906 nm (1.37 eV) was followed as a function of load (fig 8.3(b)) and the pressure calculated assuming a change of 8.5 meV/kbar.
Figure 8.3(a) Photoconductive response at 0 kbar and 
(b) variation of peak position with load.
Figure 8.4 Pressure dependence of normalised resistivity and carrier concentration.
The other peak is due to a level at around $E_c - E_r = 27$ meV at 0 kbar which moves at around 7.8 meV/kbar. The variation of normalised resistivity and carrier concentration as a function of pressure is shown in figure 8.4. The observed increase in resistivity is consistent with the change in resistance observed in the run performed in the apparatus without optical access using the load calibration of Shantharama (1986) which provides a degree of confidence in the pressure scale. The observed opposite variation of resistivity and carrier concentration with pressure leads to only a very small increase in the mobility with pressure which in a simple approximation enables us to treat the increase in resistance as a decrease in carrier concentration with increasing pressure. At higher pressures we lost the photoconductive signal in several attempts to repeat these measurements due to the problems with the fibre bundle slipping, something which is not usually a problem, but was probably caused by incomplete filling with epoxy of the gaps between the fibres. However, in each case we did not observe a dramatic change in $\mu, n$ and $\rho$ as expected. While the need for further results together with deep level measurements on the sample as a function of temperature once the level has been brought into the gap is apparent, it may be concluded from our preliminary results that there exists a level above the conduction band minimum in InP which under the
assumptions made previously is about $E_c + 0.16\pm0.04$ eV at atmospheric pressure, in good agreement, within experimental error, with that expected for the vanadium level in InP from the hypothesis of Ledebo and Ridley.

8.5 TEMPERATURE AND PRESSURE STUDIES OF A DEEP LEVEL IN InP:V BY FREQUENCY RESOLVED CAPACITANCE SPECTROSCOPY.

8.5.1 INTRODUCTION

In order to establish that there was no electron trap attributed to Vanadium in the InP gap at atmospheric pressure, before the measurements reported in the previous section were carried out, a study of the sample by frequency resolved capacitance spectroscopy was made. The measurements were to provide interesting results.

8.5.2 RESULTS

Ohmic contacts and Schottky barriers were prepared as described in §4.2 and the sample was mounted on a header in close contact with a Rh-Fe calibrated resistance thermometer in the liquid nitrogen cryostat. An FRCS fixed-frequency temperature scan showed a single peak and the isothermal quadrature frequency response was studied at several temperatures. Figure 8.5(a) shows the spectra obtained. The solid curves are the theoretical fits assuming emission from a single centre. The position of the peaks in the spectra at different temperatures...
corrected for $T^2$ are shown below on an Arrhenius plot in figure 8.5(b). The solid line corresponds to an activation energy of 0.49 eV. The FRCS spectra at room temperature as a function of pressure in the range 0 to 8 kbar for the same level obtained using the piston and cylinder system are shown in figure 8.6(a). The logarithm of the emission time constant is plotted against hydrostatic pressure in figure 8.6(b). This indicates an accurately exponential shift in emission rate with pressure and enables us to obtain a pressure coefficient of 0.16 decades/kbar. Figure 8.7 shows an Arrhenius plot of the normalised emission rates of the FRCS spectra taken at several pressures with variable temperature. The activation energy of 0.490 eV fits the data at all pressures up to 8 kbar.

8.5.3 DISCUSSION

The temperature dependence of the emission rate at ambient pressure gives a straight line on the $T^2$ Arrhenius plot and may be interpreted immediately as the apparent activation energy of the centre and identified as its depth at zero temperature from the band to which it is emitting (provided the barrier to capture is negligible). Following previous authors, the pressure dependence of the emission rate would naturally be interpreted in terms of the pressure coefficient of the
Figure 8.5(a) FRCS spectra at different temperatures measured at atmospheric pressure.

Figure 8.5(b) Arrhenius plot of peak positions of (a).
The line is a fit to an activation energy of 0.490 eV.
Figure 8.6(a) Capacitance spectra measured at different pressures at 294 K.

Figure 8.6(b) Peak positions of (a) at different pressures showing its accurately exponential behaviour.
Figure 8.7 Pressure dependence of activation energy as a function of pressure. Data normalised to unity at 300 K. The solid line corresponds to an activation energy of 0.490 eV.
depth of the centre and would give a value of 9.4 meV/kbar. This is close to the value expected for emission to the conduction band Γ-point from a level stationary with respect to the average of the bands. However, this interpretation is ruled out by the measurements of activation energy at high pressure which shows that it is the prefactor, or capture rate, which changes with pressure and not the depth of the centre. This is a very interesting result. The theory of deep levels (e.g. Ridley (1978)) is not explicit on the relationship between the capture rate and the lattice constant; it appears however that terms which are exponential in phonon frequency will yield an exponential dependence of a multi-phonon capture rate with pressure. Further work, including direct measurements of the capture cross-section with pressure are needed. The lack of any significant change in activation energy with pressure is at first sight harder to explain. While particular minima in the Brillouin zone may move rapidly in either direction with pressure, the overall effect of pressure on the conduction and valence bands is to broaden them. Consequently, a deep level whose wavefunction is made up of contributions from all the bands is expected to move slowly, if at all, with pressure. Of the band extrema, the conduction band Γ-minimum is anomalous with its large shift (8.5 meV/kbar in InP and 10.7 meV/kbar in GaAs). This is primarily due
to its $\sigma$-like character. It would be very surprising if a deep level state was made up only of $\Gamma$-point conduction band states, and yet this is the only way in which a pressure coefficient of essentially zero with respect to the conduction band could be obtained.
9.1 CONCLUSIONS

In this thesis the use of several electrical characterisation techniques for the study of deep levels in semiconductors have been discussed. The Hall effect and capacitance techniques as a function of temperature have been used to characterise a number of III-V materials. The pressure dependence of the energy levels associated with defects in these materials can reveal valuable additional information about these centres. We have described a new method of measuring deep levels which is particularly suited to measurements at high pressure, where, except for gas pressure cells, it is difficult to vary the temperature over a large range while maintaining the pressure constant. Using the techniques of capacitance transient spectroscopy and frequency resolved capacitance spectroscopy we have studied the pressure dependence of deep levels in GaAs, InP and $\text{Al}_{x}\text{Ga}_{1-x}\text{As}$. All but one of the levels was shown to be sensitive to pressure. In addition, emission
from a single GaAs-GaAlAs quantum well and its temperature and pressure dependence have been investigated.

It has been shown that the pairing of the transition metal impurity, Mn, with donors in InP and GaInAsP of low $y$ is not limited to Ge but is also possible with Te, a donor from group VI. We have also shown that in material of high $y$, where the activation energy of Mn is low, no pairing of Mn acceptors and Te donors occurs and no reduction in ionised impurity scattering is apparent.

The temperature and pressure dependence of the time constant for emission from the mid-gap donor EL2 has been measured using Capacitance Transient Spectroscopy. The results indicate an increase of the activation energy of $3.5\pm0.3$ meV/kbar. The pressure dependence of the barrier to capture was estimated from the pressure dependence of the average LO and TO phonon frequencies. Using this information, we deduce that EL2 moves away from the conduction band edge to which it is emitting at a rate of $1.8\pm0.6$ meV/kbar. If it is assumed that emission occurs to the L minimum, then we deduce that EL2 moves away from the top of the valence band at about $3.7$ meV/kbar.

A study of GaAs-ALGaAs quantum well structures using capacitance transient spectroscopy revealed two levels in the ALGaAs buffer layers. One of these showed a
strong pressure dependence in contrast to the emission observed from the quantum well. Measurements of emission from the quantum well yielded a value of the conduction band offset of $65\pm5\%$ of the total gap discontinuity.

Three electrical characterisation techniques, frequency resolved capacitance spectroscopy, admittance spectroscopy and deep level transient spectroscopy, were used to measure the activation energy for emission of carriers from InP-InGaAs superlattices. The results obtained using the three techniques were found to be in excellent agreement.

Hydrostatic pressure was used to bring a deep level into the forbidden gap in InP:V at about 25 kbar. This was consistent with the Vanadium related level expected from the hypothesis of Ledebo and Ridley based on its position in GaAs and the band-offsets between the two materials.

In conclusion, the experimental techniques necessary to measure the pressure coefficient of deep levels due to transition metal impurities required in order to confirm, or establish the accuracy, of the hypothesis of Ledebo and Ridley have been developed. These have been used successfully to measure the pressure coefficients of a number of levels in different materials and have been used to measure band-offsets and their pressure dependence. Also it has been established that the interaction of the transition metal impurity Mn with
a donor is not limited to Ge or indeed to donors from group IV. As pointed out by Shantharama (1986), the elimination of ionised impurity scattering in heavily doped highly compensated materials is of considerable importance for device fabrication. If the dipole model is correct and electrons suffer from little ionized impurity scattering then optical devices, such as p-i-n diodes, with the intrinsic region produced by Mn-donor compensation might be expected to have characteristics similar to those produced in high quality epitaxial material.

9.2 RECOMMENDATIONS FOR FUTURE WORK

In order to test the model of Ledebo and Ridley using purely electrical techniques with Schottky barriers without the need for optical excitation to perturb the deep level population it would be desirable to have a series of p-type single crystals of say GaAs and InP each doped with a different transition metal impurity, in which the the impurities would form majority carrier traps. Alternatively, p-n junctions could be grown in which the minority carrier traps can be detected using forward bias filling pulses. Then the pressure coefficients of the energy levels associated with more than one transition metal could be measured in each III-V compound.
If it was concluded that the transition metal impurity levels are fixed with respect to the vacuum level this would justify a systematic study of using transition metals as markers to measure the absolute energy position of the band edges and the magnitude of the band-offsets at heterojunctions.

The pressure dependence of the conduction band-offset in the GaAs-AlGaAs system, though established to be small from the isothermal measurement of well emission, could be measured at different temperatures to confirm that the small change in time constant observed is not due to a change in the intercept (related to capture). Also, at pressures higher than the crossover of the \( \Gamma \) minimum in the GaAs and the \( X \) minimum in the AlGaAs, we would expect to see the activation energy changing rapidly with pressure.

Recently Lambkin et al (1988) deduced indirectly the pressure dependence of the conduction band offset in the InP-InGaAs system from photoluminescence measurements. They found it to decrease by 2.3\( \pm \)0.6 meV/kbar, approximately the difference in the pressure coefficients of the direct band-gaps of InP and InGaAs. It would be interesting if the measurements carried out at atmospheric pressure on the InP-InGaAs superlattices (reported in chapter 7) were repeated at high pressure to confirm this observation directly. With the reproducibility of the different techniques shown in
Chapter 7 it should be possible to confirm this using the small Cu:Be low temperature cell.

Further work is required on the Vanadium level in InP. Hall measurements in the Bridgman system should yield the carrier concentration directly, with the obvious advantages associated with four terminal measurements. The use of the optical fibre access to the sample space would allow the band edge obtained from photoconductivity measurements to be followed as the pressure was increased and hence give the pressure more reliably. If the pressure of the sample could be maintained constant at say 30kbar then the activation energy, at that pressure, could be obtained using the computerised FRCS or admittance spectroscopy programs suitably adapted to take measurements at several frequencies as the sample was slowly heated. The temperature could be read from a calibrated thermocouple which can be mounted close to the sample, passing through the MgO gasket in the same way as the electrical leads. This result would provide a further test of the hypothesis of Ledebo and Ridley.
APPENDIX-1: ELECTRON AND HOLE SCATTERING MECHANISMS

PART I: ELECTRON MOBILITY

A1.1 Polar optical phonon scattering

\[ \mu_{\text{opt}} = 0.199 \left( \frac{T}{300} \right)^{3/2} \left( \frac{e^*}{e_0} \right)^2 \frac{\hbar}{\gamma_0} \left( 10^{32} \eta \right) \left( 10^{32} \eta_\omega \right) \left( 10^{32} \eta_\xi \right) \left( 10^{32} \eta_\zeta \right) (e^* - 1) G(z) \]

where the effective charge, \( e^* \), is given by

\[ e^* = \frac{K \omega_1 \omega_2^2 V_0}{4 \pi} \left[ \frac{1}{e_0} - \frac{1}{e_0} \right] \]

and \( z = \hbar \omega/2kT \), \( G(z) \) is given graphically (Ehrenreiche (1959)).

The volume of the unit cell in cm\(^3\), \( V_0 \), is \( a^3/4 \). The reduced mass \( K \) is in g and \( T \) in \( \text{°K} \). NB: \( \mu_{\text{opt}} \) decreases with temperature, \( d\mu_{\text{opt}}/dT < 0 \).

A1.2 Acoustic phonon scattering

\[ \mu_{\text{ac}} = 3.1727 \times 10^{-15} \frac{p^1 u_1^2}{(m_e/m_0)^{3/2}} \frac{T^{-3/2}}{E_{\text{ac}}} \]

A1.3 Nonpolar optical phonon scattering

\[ \mu_{\text{nop}} = 6.345 \times 10^{-15} \frac{p^1 u_1^2}{(m_e/m_0)^{3/2}} \frac{S'(\theta/T)}{E_{\text{nop}}} \theta T^{1/2} \]

where \( u_1 \) is the longitudinal sound wave velocity, \( \theta \) is the polar phonon temperature and \( S'(\theta/T) \) is given by Wiley (1975). \( E_{\text{ac}} \) and \( E_{\text{nop}} \) are the phenomenological acoustic and nonpolar optical deformation potentials respectively. Note: \( d\mu_{\text{ac}},_{\text{nop}}/dT \leq 0 \).

A1.4 Ionised impurity scattering

\[ \mu_{\text{imp}} = \frac{3.264 \times 10^{15} \epsilon_c e}{(m_e/m_0)^{3/2}} \frac{2^{3/2}}{N_i} \left[ \ln(1+b) - \frac{b}{1+b} \right] \]

\[ m_e T^2 \epsilon_c \]

where \( b = 1.294 \times 10^{-4} \), \( N_i \) is the number of ionised impurities per cm\(^3\) and \( n^o = n + (N_B - N_A - n)(n+n_A)/N_0 \), \( N_i = N + 2N_A \). NB: \( d\mu_{\text{imp}}/dT > 0 \).

A1.5 Alloy scattering

\[ \mu_{\text{al}} = \frac{8 \times 10^4 \nu_2^2 \hbar^2}{3 \omega^0 e} \frac{m_e^{-3/2} T^{-1/2}}{S(\alpha)} \Omega (\Delta U_e)^2 \]

where \( S(\alpha) \) refers to the degree of randomness of the atoms, \( \Delta U_e \) is the alloy scattering potential for electrons and \( \Omega \) = scattering volume.
PART II: HOLE MOBILITY

A1.6 Polar optic phonon scattering

\[ \mu_{po} = 2 K' \mu_{n, po} \]

The factor 2 arises from the p-like symmetry of the hole wave functions (Wiley (1975)). \( \mu_{n, po} \) is calculated from \( \mu_{n, po} \) by replacing \( m_0 \) by \( m_{cr} \). \( K' \) is a correction factor of order unity which accounts for the contribution from the light holes (Kranzer (1973)).

A1.7 Acoustic phonon and nonpolar optical phonon scattering

The combined acoustic phonon and nonpolar optical phonon mobility for holes is given by

\[ \mu_{ac, po} = 3.1727 \times 10^{-5} \frac{r^{2/2}(1+r^{1/2})}{(1+r^{3/2})^2} S(\theta, \gamma, T) \left( \frac{\nu_{ac}}{\nu_{po}} \right)^{2/2} T^{-3/2} \]

where \( r = m_{cr}/m_0 \), \( \gamma = (E_{po}/E_{ac})^{2/2} \); \( S \) is given graphically (Wiley (1975)) and \( \nu \) is the average sound velocity (Wiley (1975)).

A1.8 Ionised impurity scattering

\[ \mu_{ii} = V \frac{r^{3/2} + r^{3/2}}{1 + r^{3/2}} \mu_{n, ii} \]

where \( V \) is a factor of order unity \( (1 < VK < 2) \) which accounts for the p-like symmetry of the hole wave functions, \( \mu_{ii} \) is calculated from \( \mu_{n, ii} \) by replacing \( m_0 \) by \( m_{cr} \), \( n^* \) by \( p^* \) and \( N_1 \) by \( P_1 \). \( P_1 = p + 2 \mathcal{N}_0 \) and \( p^* = p + (m - m_0 - p)(p + \mathcal{N}_0)/\mathcal{N}_0 \).

A1.9 Alloy scattering

\[ \mu_{a1} = \frac{r^{2/2}(1+r^{1/2})}{(1+r^{3/2})^2} \mu_{n, a1} \]

where \( \mu_{n, a1} \) is calculated from \( \mu_{n, a1} \) by replacing \( m_0 \) by \( m_{cr} \), and \( \Delta U_p \) by \( \Delta U_p \), where \( \Delta U_p \) is the alloy scattering potential for holes (Hayes et al (1982)).
APPENDIX-2: CAPACITANCE MEASUREMENT (BOONTON 72BD)

The Boonton capacitance meter model 72BD provides three terminal and differential capacitance measurements from 0.02 to 2000 pF in four ranges. The analogue output from the meter provides a voltage proportional to the capacitance at the input which is 2.0 V at full scale on each range. The 1MHz test signal of 15 mV r.m.s. is suitable for measurement of the depletion capacitance of semiconductor junctions. There is provision for the application of a D.C. bias to either or both terminals of the sample under test.

A simplified schematic diagram of the instrument is shown in figure A1. The output of the 1MHz oscillator appears across the secondary of the transformer whose centre tap is at R.F. ground. The 'DIFF' terminals can be used to balance out stray capacitance or to remove a constant capacitance component and use a more sensitive range. When a sample is connected between the HI and LO 'TEST' terminals a current directly proportional to its susceptance flows through the low impedance series-resonant LC circuit to ground. The series resonant circuits for each range are selected by range switching circuits.
Figure A1: Schematic of the Boonton 72 BD
Voltage Bias Circuits

(a) D.C. Bias

For normal reverse bias C-V measurements on semiconductor junctions the HI side of the 'TEST' terminals is connected to the ohmic contact and the LO side to the other contact (for metal/n-type Schottky barriers or p"n junctions). A variable D.C. bias is applied to the instrument bias circuits as shown in figure 2.

(b) Pulsed bias

The internal bias circuits of the Boonton capacitance meter need adequate by-passing for the 1MHz test signal and are unsuitable for the application of short bias pulses. Provided, however, the rise and fall times of pulses are not less than about 200µs then pulses may be applied via these circuits for the purpose of capacitance transient spectroscopy. Figure 3 shows how a pulse generator is used in conjunction with a variable D.C. voltage supply.

Where there is a need for short pulses (say pulse widths < 1 ms) then these must be applied via external circuitry such as is shown in figure 4.
Figure 2: Internal bias circuit

Figure 3: Normal bias pulse circuit

Figure 4: Short bias pulse circuit
If the impedance of the pulse transformer secondary is small relative to $R_1$ then the test diode is effectively in series with a resistance of $\frac{R_1R_2}{(R_1+R_2)}$. Provided this value is small compared with the reactance of the test diode at 1MHz then the series resistance will be ignored by the phase sensitive detector. The ratio of the two resistors and their absolute values will depend on the pulse transformer and its load matching requirements as well as the nature and magnitude of the pulse needed for bias.

Response time

The specified rise time of about 1ms for the capacitance meter can be reduced to less than 0.2ms by either reducing or changing the output capacitor as shown in figure 1 (Chappell et al 1984). The cost of this is an increase in the noise by a factor of about 3.
APPENDIX-3

TEMPERATURE MEASUREMENT USING RHODIUM-IRON RESISTANCE SENSOR

From the expression for the emission rate of electrons from a deep level (eqn 2.16) we may write:

$$\frac{d\sigma}{\sigma} = \frac{(E_c-E_F)}{k_B T} \frac{dT}{T}$$

For instance $E_c-E_F = 0.5$ eV, $T= 290$ K and $dT = 0.1$ K $\sigma$ will be about 1%. Therefore the temperature stabilisation is important for precise measurement. Similarly the temperature has to be known to better than this. For this, a calibrated Rhodium-Iron resistance sensor was purchased. The sensor has a nominal resistance of 27Ω at 273K. A 1mA current was passed through the sensor giving a sensitivity of 1μV per 0.01K above 77K.

Calibration

The Rhodium-Iron Reference Scale 0.5 to 800K (1985) is defined in terms of a $Z_{R}$ function defined as:

$$Z_{R} = \frac{R(T)-R(4.2221)}{R(273.15)-R(4.2221)}$$

where $R(T)$ is the resistance at a temperature $T$ (Kelvin). A thirty-three point calibration (see table A3.1)
<table>
<thead>
<tr>
<th>TEMPERATURE (KELVIN)</th>
<th>RESISTANCE (OHMS)</th>
<th>$\Delta Z \times 10^6$</th>
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</thead>
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<tr>
<td>1.485</td>
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<tr>
<td>2.001</td>
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<td>273.233</td>
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<tr>
<td>300.598</td>
<td>29.78351</td>
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</tr>
</tbody>
</table>
was performed by Cryogenic Calibrations Ltd. They provided a function \( Z \) for this particular sensor as follows:

\[
Z = \frac{R(T)-1.82497}{24.64231} \quad \text{below 27K}
\]

and

\[
Z = \frac{R(T)-1.79065}{25.22305} \quad \text{Above 27K}
\]

The calibration consists of the resistance and the deviation of the calibration function from the reference scale, \( \Delta Z \), at each temperature.

**Calculating the temperature from the resistance**

The resistance of the sensor was monitored using a Keithley 196 digital multimeter with an IEEE interface. The resistance was read and the temperature computed from the calibration table as follows:

1. The value of \( Z \) was calculated from the equations above.
2. The value of \( \Delta Z \) was found by interpolating between the values provided.
3. \( Z_{\text{cal}} = Z + \Delta Z \) was calculated and the temperature found from a Chebyshev polynomial fit to the reference scale. Details of the coefficients are given in table A3.2.
Table A3.2: Chebyshev Coefficients

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>0.5 to 32K</th>
<th>32K to 300K</th>
<th>300K to 800K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable Xc</td>
<td>Z_R</td>
<td>ln Z_R</td>
<td>Z_R</td>
</tr>
<tr>
<td></td>
<td>20.960455Z_R</td>
<td>0.6900838ln Z_R</td>
<td>0.8364331Z_R</td>
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<tr>
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<td>-0.5027729</td>
<td>+0.9015349</td>
<td>-1.760407</td>
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<tr>
<td>Order</td>
<td>Chebyshev Coefficients</td>
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<td></td>
</tr>
<tr>
<td>0</td>
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<td>1066.12878</td>
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<tr>
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<tr>
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<tr>
<td>3</td>
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<tr>
<td>4</td>
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<td>1.94117</td>
<td>1.99563</td>
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<tr>
<td>5</td>
<td>0.16528</td>
<td>-1.9553</td>
<td>-0.096488</td>
</tr>
<tr>
<td>6</td>
<td>-0.04750</td>
<td>-0.05827</td>
<td>0.01630</td>
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<td>7</td>
<td>0.00864</td>
<td>-0.00431</td>
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<tr>
<td>8</td>
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<td>0.01861</td>
<td>0.00854</td>
</tr>
<tr>
<td>9</td>
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<td>-0.00465</td>
<td>-0.00053</td>
</tr>
<tr>
<td>10</td>
<td>0.00063</td>
<td>0.00350</td>
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</tr>
<tr>
<td>11</td>
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<td>-0.00088</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-0.00070</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Range of Fit

- 0.5 to 35K
- 30 to 311K
- 250 to 800K

Root mean Square of Fit

- 0.8mK
- 0.8mK
- 2.4mK

Number of calibration points

- 38 (+6 extrapolated points between 1.4 & 0.5K)
- 44
- 62

To evaluate the Chebyshev series set c(n+2)=c(n+1)=0,
For j=n, n-1...0, calculate c(j)= 2·c(j+1)-c(j+2) + a(j)
and the temperature is given by 0.5(c(0)-c(2)).
Using this method it is estimated that the overall accuracy of the measurement should be of ±0.02K above 27K.

The resistor was about 3mm diameter by 20mm length and was inserted in a copper block (see figure A3.1) with the sample mounted on a header which fitted onto the same block about 0.5mm from the sensor.
Figure A3.1: Details of sample holder showing position of sensor.
THEORETICAL EVIDENCE FOR LOCATION OF QUANTUM WELL

A4.1 Low trap density: With the diode in reverse bias, let

\[ \text{C} = \text{diode capacitance} \]
\[ N_{\text{D}}^{\text{tr}} = \text{shallow ionized donor density} \]
\[ N_{\text{T}}^{\text{tr}} = \text{Density of deep donors} \]

then \[ C = \left[ B \left( N_{\text{D}}^{\text{tr}} + N_{\text{T}}^{\text{tr}} \right) \right]^{1/2} \]

where \( B \) is a constant. Since only \( N_{\text{T}}^{\text{tr}} \) changes with bias

\[ \frac{\delta C}{C} = \frac{B^{1/2}}{2} \left( N_{\text{D}}^{\text{tr}} + N_{\text{T}}^{\text{tr}} \right)^{-1/2} \]

\[ \frac{\delta C}{C} = \frac{1}{2} \left[ \frac{\delta N_{\text{T}}^{\text{tr}}}{\text{C}} \right] \]

and

\[ \delta C = \frac{1}{2} \left[ \frac{N_{\text{T}}^{\text{tr}}}{\text{C}} \right] \left[ \frac{A \varepsilon_{0}}{\text{W}} \right] \]

Hence, for low trap density, i.e. \( N_{\text{T}}^{\text{tr}} < N_{\text{D}}^{\text{tr}} \)

\[ \delta C \propto \frac{1}{\text{W}} \]

\( \delta C/C \) is limited by the resolution of the capacitance meter, which in our case is \( 10^{-5} \), hence from eqn. A4.3, if \( (N_{\text{D}}^{\text{tr}} + N_{\text{T}}^{\text{tr}}) \approx 10^{15} \text{ cm}^{-3} \), then \( \delta N_{\text{T}}^{\text{tr}} \approx 2 \times 10^{13} \text{ cm}^{-3} \).
A4.2 **High trap density:**

Let \( w \) = total depletion width

\( \lambda \) = part of depletion width where deep traps are charged

\( L \) = part of depletion layer where traps are neutral

The total charge of the depletion layer will be

\[
Q = q[\lambda (N_{D}^{+} + N_{T}^{+}) + LN_{D}^{+}]
\]

\[
= qN_{w}
\]

therefore \( \Delta C \propto w \)

Because with bias additional charge is contributed by the traps, \( Q \) must increase with \( w \) and hence \( \Delta C \) must also increase with reverse bias, unlike in low trap density case.

A4.3 **General Case:**

If \( V_{e} \) is the excess voltage associated with the traps, then Poisson's equation gives:

\[
\frac{dV_{e}}{dx} = \frac{qN_{T}}{\varepsilon_{n}} \lambda
\]

Integrating,

\[
V_{e} = \frac{qN_{T}}{\varepsilon_{n}} \frac{\lambda^{2}}{2}
\]

A4.5

Similarly,

\[
V_{n} = \frac{qN_{D}}{\varepsilon_{n}} \frac{L^{2}}{2}
\]

A4.6
Solving A4.5+6, we get
\[ V = \frac{1}{2} q H r [W - L] \]
so
\[ V = A (\varepsilon, q N r / 2)^{1/2} (1 / C_m - 1 / C_L) \]
where \( C_m = C_w \)
since
\[ \frac{1}{C^2} = \frac{2V}{qe Aw} \]

\[ \left[ \frac{1}{C_m^2} - 1 / C_w^2 \right] = 2V / (qe Aw^2) \]
\[ = \frac{N_T}{N_a} (1 / C_m - 1 / C_L)^2 \]
therefore,
\[ \frac{N_T}{N_a} = \frac{(1 / C_m^2 - 1 / C_w^2)}{(1 / C_m - 1 / C_L)} = \frac{\Delta C C_w}{C_w^2} \]
\[ \frac{N_T}{N_a} C_w = \frac{N_T}{N_a} C_w \left( \frac{W}{A \varepsilon} \right) \]
and
\[ \Delta C = \frac{N_T}{N_a} \frac{C_w^2}{C_w} = \frac{N_T}{N_a} \frac{C_w^2}{A \varepsilon} \]

so
\[ \Delta C \propto V \]
which is the result obtained for the high density case. From A4.7,
\[ \frac{N_T}{N_a} = [(C_m / C_w)^2 - 1] \]
and
\[ \frac{C_w}{C_m} (1 + \frac{N_T}{N_a}) = 1 - \frac{N_T}{2N_a} \] for \( N_T < N_a \)
\[ N_T / 2N_a = 1 - C_m / C = \Delta C / C_m \]
so
\[ \Delta C = (N_T / 2N_a) C_m = (N_T / 2N_a) A\varepsilon / W \]
so
\[ \Delta C \propto 1 / W \]
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