D. J. Titley

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ELECTRICAL MEASUREMENTS ON ION IMPLANTED GALLIUM PHOSPHIDE

by

D. J. Titley

A thesis submitted for the degree of Doctor of Philosophy to the
Faculty of Engineering, Department of Electronic and Electrical Engineering,
University of Surrey.

September 1976
The purpose of this study was to determine some of the properties, such as the energy level value, capture cross-section etc., of the defect centres introduced into gallium phosphide by ion bombardment. The majority of the work concentrated on the effects of proton irradiation, as protons have been used to create semi-insulating regions in GaP and other III-V compounds. A few experiments were carried out on sulphur implanted specimens for comparison.

It has been shown that several centres, of large capture cross-section, are introduced into semi-insulating GaP. These produce levels at $E_c - 0.19$, $E_c - 0.61$ and $E_v + 0.75$ eV in the semiconductor band gap. For proton doses of greater than $5 \times 10^{13}/\text{cm}^2$ a further level at $E_v + 0.4\text{eV}$ becomes evident. Measurements of the concentrations of these defects as a function of dose and energy indicated that a maximum concentration was reached by a dose of $10^{14}/\text{cm}^2$ and that with decreasing energy $< 300\text{keV}$, the number of centres introduced is greater than would be expected from calculations of the number of atomic displacements.

All defect centres, except those responsible for the $E_v + 0.4\text{ eV}$ level, anneal out by $650^\circ\text{C}$.

Thermally stimulated current and various capacitance techniques were used for the deep level measurements.
ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the help and encouragement given by my supervisor, Dr. G. Brown, throughout the course of this work. I would also like to thank Prof. D. R. Chick for the use of the facilities of his department and to Dr. K. G. Stephens for discussions on the preparation of this thesis.

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Finally, many thanks to Mrs. J. FitzGerald and Miss L. Loveday for their excellent typing of this thesis.
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Chapter 1

INTRODUCTION

1.1 Introduction

The effects of radiation upon the operation of semiconductors has become of increasing interest in recent years. This has been brought about by several factors, namely, the need to operate electronic equipment in radiation environments and the use of ion implantation\(^1\) (an established technique) for device manufacture. In the former case the effects of radiation (\(\gamma\) - rays, neutrons) usually result in a degradation in device performance but in the latter case the damaging of the semiconductor by ion bombardment can sometimes be used to advantage. Radiation damage has been studied most extensively in silicon and germanium\(^1\), there being comparatively little work reported in this connection, on the III-V compounds. This has been partly due to the fact that the manufacturing processes have introduced high concentrations of unintentional impurities and/or defects. These technological difficulties now seem to have been overcome, and two compounds, gallium arsenide (GaAs) and gallium phosphide (GaP) are being used extensively; gallium arsenide in microwave devices, and gallium phosphide in light emitting diode (LED) applications. It is with the damage produced by the ion bombardment of GaP with which this thesis is concerned.

1.2 Radiation damage in semiconductors

1.2.1 Type of radiation

The type of radiation determines the sort of damage produced. Electrons and \(\gamma\) - rays create vacancy-interstitial pairs (Frenkel defects) almost exclusively, whilst light ions such as protons and deuterons produce, in addition, more heavily damaged regions, containing divacancies, vacancy-impurity complexes (see
section (2.4.1.)) towards the end of their range\(^5\). These more complex defects also result from heavy ion or fast neutron bombardment. They are present in greater numbers, however, than in the case of the light ions. Blout\(^9\) compares the energy levels introduced into the bandgap of germanium by electrons and light ions. He conjectures that electrons produce little clustering, deuterons some clustering and neutrons extensive clustering of the defects.

A common application of ion bombardment is to introduce a dopant into the material. The electrical effects of the dopant, however, are difficult to separate from the electrical effects of the damage. In damage studies, therefore, it is necessary to implant ions which will not occupy substitutional sites such as H, He, Ar, Kr, and Xe.

1.2.2. Ion bombardment

Atomic displacements, both by primary and secondary impacts occur during the \(10^{-13}\) s an ion takes to come to rest after entering the solid crystal. A thermal spike surrounding the track dissipates in say \(10^{-12}\) s leaving a disordered region of broken bonds and displaced atoms. The bonds reform and atoms change their positions to form a relatively stable phase in a time greater than \(10^{-9}\) s. During this time, vacancies can escape by thermal diffusion from the disordered region surrounding the ion track\(^10\). The subsequent movement of the vacancies (and associated interstitials) through the lattice depends upon their charge state and the temperature at which the implantation is taking place. The distance over which they travel will depend upon the amount of damage present in the implanted region at that instant in time. Recombination or association with impurity atoms, or other defects, finally occurs.

The presence of structural defects in a crystal destroys the periodicity of
the lattice and makes it possible for electrons to take on energies which are forbidden in a perfect crystal. Each type of defect, therefore, will introduce an energy level into the semiconductor bandgap. Such additional levels do not extend throughout the material but are localised at the point of imperfection. Further these defects are non-radiative and act as carrier trapping or recombination centres. This means that the presence of many traps, and hence deep levels, in a material such as GaP will firstly, quench any photon emission and secondly, reduce the number of free carriers so increasing the resistivity.

These two effects caused by the implantation of ions into III-V compounds are the subject of sections (1.2.3, 1.2.4.).

1.2.3. Non-radiative centres in GaP

Gallium phosphide has a band gap of 2.3eV at room temperature which means that band to band photon emission is in the visible part (5600Å, green) of the spectrum. Certain impurities can increase the light output from p-n junctions made of the material section (2.3.4.). Several experiments have been carried out to try to improve GaP LED efficiency by using implantation to produce shallower junctions and higher doping concentrations than would normally be achievable with diffusion techniques. The non-radiative centres produced by the damage, however, have resulted in low efficiencies.

Merz et al implanted bismuth into GaP$^{14}$ and investigated the photoluminescence from the bismuth isoelectronic traps produced. The results proved to be discouraging as only ten per cent of the expected light intensity was observed under conditions of optimum dose and annealing. An investigation of nitrogen implantation, also Merz et al$^{15}$, showed that a large substitutional concentration could be achieved but the luminescence intensity was less than one per cent of that obtained using conventionally doped crystals having comparable nitrogen concentrations.
1.2.4. Deep levels in GaP

The introduction of deep levels into a semi-conductor bandgap, as a result of ion bombardment, causes the resistivity of the implanted layer to increase, section (1.2.2.). Spitzer and North\(^{11}\) have proton bombarded GaP, doped with various impurities, and have shown that regions of similar high resistivity are produced. Their results indicate that a series of levels, or a continuum of levels are created. No measurements were made, however, on the position of the energy levels in the bandgap or of the types of defect/impurities responsible. Deep level measurements have been made on bulk GaP, however, by B. L. Smith\(^{12}\) and E. Fabre\(^{13}\) (see table (6.3)). In both cases only the as-grown (unimplanted) material was examined.

Dyment et al have studied the effects of proton bombardment on GaAs and obtained similar results to those of Spitzer and North\(^{11}\) (i.e. an increase in resistivity). The large penetration depth of protons into III-V compounds (typically 1\(\mu\)/100keV) has meant that protons have been used extensively in the production of semi-insulating regions in these materials, and in GaAs in particular. Speight et al\(^{16}\) have proton isolated impatt diodes with a resulting improvement in efficiency whilst Foyt\(^{17}\) et al have isolated p-n junction devices on a GaAs substrate. Pruniaux\(^{18}\) et al have manufactured GaAs field-effect transistors by evaporating a gate electrode onto a semi-insulating layer produced on the substrate surface.

Because of the large number of possible applications of proton bombardment it was decided to concentrate on studying the damage created by this ion. A few specimens, however, bombarded with a heavier Z ion, sulphur, were also examined. Sulphur was chosen because it is a common dopant in GaP. A comparison of the trapping centres produced by light and medium Z ions could then be made.
1.3 Aims of the work

The general aim of the work was to try to determine some of the properties of the damage centres introduced into GaP by ion bombardment, and in particular by proton irradiation. Three categories of properties can be defined, namely, those which describe the trapping centres, those which are dependent upon the implantation conditions (ion energy; dose etc.), and those which are dependent upon the starting material. The first group includes the position(s) of the associated energy level(s) in the bandgap, the capture cross-section and the annealing behaviour. The trapping centre introduction rate (no. of centres/proton) is an example of a property which comes in the second group whilst the final category includes the dependence of the type of centre created upon the dopant and/or carrier concentration. The results of Spitzer and North[11] indicate that the resistivity changes were independent of the dopant whilst B. L. Smith[12], who examined undoped, Te and S- doped material, found that most of the energy levels were present in each kind of GaP. The dependence of the type of centre produced upon the dopant was not examined, therefore, but an investigation to show if the introduction rates of the different centres were related to the carrier concentration of the starting material was carried out.

Although Spitzer and North[11] have measured the resistivity of the implanted layer as a function of annealing temperature, the behaviour of the different traps may not follow the overall annealing curve. A further aim of the work, therefore, was to examine the annealing behaviour of each type of damage centre.

The aims of the work can be summarised as:-

1. to determine some of the properties of the damage centres introduced into GaP by ion bombardment, particularly as a result of proton irradiation.
2. to study the effects of the implantation conditions,
i.e. the ion energy and ion dose, upon the introduction rate of the
different centres.

3. to investigate the dependence of the type of centre produced upon
the carrier concentration of the starting material.

4. to determine the annealing behaviour of the centres.

1.4 Outline of Thesis

Chapter 2 discusses the manufacture of GaP, and then examines the
properties of the material which make it of such technological importance.
This is followed by short sections on the type of damage produced by ion
bombardment and the general preparation of specimens before measurements
can be made.

Chapter 3 first describes the accelerator facilities and the way in which
specimens were implanted and then goes on to outline the experimental tech-
niques which were used to evaluate some of the properties of the trapping centres
produced by the ion bombardment together with the corresponding pieces of appar-
atus. A thermally stimulated current apparatus was built for the work.

Chapter 4 discusses the analysis of the results. The basic theories are
examined and the thermally stimulated current theory is expanded to include
the case of non-discrete energy levels.

Chapter 5 presents the results which are in the following order:-

1. Some of the trapping centre properties of semi-insulating
GaP before and after proton implantation.

2. Some of the trapping centre properties of Te-doped medium
and low resistivity GaP, before and after proton implantation.

3. Trapping centre concentration measurements on proton bombarded
semi-insulating material as a function of proton dose, and proton energy.

4. Trapping centre concentration measurements on proton bombarded semi-insulating material as a function of anneal temperature.

5. Some of the trapping centre properties of sulphur implanted medium resistivity material.

Chapter 6 examines and draws conclusions from the results. Where possible, comparisons are made with other work reported in the literature.

Chapter 7 summarizes the conclusions and suggests, firstly, a few areas where further work would be profitable, and secondly, possible applications of the results.
Chapter 2

PROPERTIES OF GaP

2.1 Introduction

This chapter discusses the manufacture of GaP, and then examines the properties of the material which make it of such technological importance. This is followed by short sections on the type of damage produced by ion bombardment and the general preparation of specimens before measurements can be made.

2.2 Manufacture

The gallium phosphide used in the experiments described in this report was made by Mining and Chemical Products Electronics Ltd., (MCP), using a liquid encapsulation, crystal pulling technique. Crystal pulling is the only reported way of growing crystals from the melt so that they are relatively dislocation-free. This is due to the solid-liquid interface not being in contact with a crucible, and the radial temperature gradients being small through suitable design of the apparatus.

Further points to take into account are:

a) the temperature distribution in the melt should usually be such that the temperature at the solid-liquid interface is the lowest in the liquid, otherwise, there is a strong possibility of spurious nucleation.

b) The surface of the melt should be free of foreign particles and films.

c) The small piece of material used to start the pull (the seed) should have a low dislocation density, and have been etched to remove surface damage. The seed should also be pre-heated by lowering it very slowly to the melt surface so as not to introduce dislocations by thermal shock.
Pulling of Gallium Phosphide crystals
by liquid encapsulation
(from ref 24)

Preparation of Gallium Phosphide
(from ref 24)
The normal Czochralski techniques for pulling single crystals are useful only for materials of relatively low vapour pressures. The technique has to be modified in the case of gallium phosphide which melts at 1470°C and has a phosphorous vapour pressure of 35 atm.

This is done by heating the melt under pressure (to prevent boiling) using an inert gas such as argon, and by covering the melt with a suitable liquid to prevent evaporation (an added bonus is that this latter process also reduces contamination of the surface). This is known as the liquid encapsulation technique, the crystal being pulled through the liquid layer. A typical crystal pulling liquid encapsulation furnace is shown in figure (2.1). Boric oxide which has a low vapour pressure and high chemical stability is used as the encapsulant. Any film remaining on the gallium phosphide is easily removed with water. Pulling speeds are typically 2.5 cm/hr with a rotation of 10 r.p.m.

Suitable material for the melt is grown from gallium solution at a pressure of 8 - 10 atm and a temperature of 1450°C using a twin zone Bridgman apparatus. Figure (2.2) shows such an apparatus. A silica ampoule encloses the phosphorus with the gallium placed in a graphite tube. The phosphorus is heated to 500°C to produce the required pressure and a hot zone is created in the graphite by induction heating. At a transverse rate of 1 cm/hr solid, but very polycrystalline, gallium phosphide grows.

These growth processes result in oxygen, carbon, boron and silicon being introduced as dopants. Bass and Oliver found the following concentration levels in their material to be:

- Silicon 0.7 - 10 (ppm atomic)
- Boron 0.03 - 20
- Carbon 10 - 100
- Oxygen 10 - 100
Zinc-blende Structure

The structure consists of two interpenetrating face centred cubic sub-lattices.

Nearest neighbour distance $2.36 \text{Å}$
Tetrahedral radii of Ga $1.26 \text{Å}$, P $1.10 \text{Å}$ (ref (26))

Lattice constant $5.45 \text{Å}$

Fig(2.3)
Crystal Structure looking along a [110] axis

(111) surface

(111) surface

Ga

P

Fig (2,4)
2.3 Properties of the material

2.3.1 Structure

Gallium phosphide, in common with most of the III – V compounds, crystallizes in the zinc-blende structure, which consists of two interpenetrating face-centred cubic sub-lattices \(^{26,27}\). The origin of the first lattice, the group III element, is at \(0, 0, 0\) and the origin of the second, the group V element, at \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\). The two sub-lattices are orientated parallel to each other and are displaced by the vector \(\gamma = (a/4, a/4, a/4)\) where \(a\) is the edge length of the elementary cube of the face-centred lattice – \(\gamma\) is the distance between nearest neighbour atoms. Each atom on one sub-lattice is tetrahedrally surrounded by, and chemically bonded to, four nearest neighbours on the other sub-lattice figure (2.3). This structure, if monoatomic, would be the diamond lattice (e.g. Si), but because two different types of atom are involved, the symmetry of inversion about a point midway between any two atoms is missing. The absence of this centre of symmetry in III – V compounds gives rise to many of their unusual properties \(^{28}\).

The \{111\} planes in III – V compounds are of particular interest. Made up of alternate monolayers of gallium and phosphorus, each atom has three of its bonds directed downwards at \(70^\circ 32'\) to the normal and the fourth directed upwards. The three bonds-one bond configuration prohibits identical surfaces on the opposite \{111\} faces of zinc-blende structures, as it is more energetically favourable that the single bonds will be broken than will the triply-bonded layers. This results in \{111\} crystal faces being made up of atoms triple-bonded to the crystal, the (111) face being made up of gallium atoms, the (111) face of phosphorus atoms, figure (2.4).

The two types of surfaces, (111) and (111), exhibit different physical and chemical properties. The phosphorus surface atoms are very reactive chemically, since they are only triply-bonded to the surface, whereas their normal valence is five. On the other hand, surface gallium atoms, also triply-bonded to the lattice,
Energy-band structure in k space at 0K for GaP

The indirect bandgap of GaP as a function of temperature. ref (34).

Fig (25)

Fig (26)
have no free electrons, being trivalent, and so are relatively inactive. An example of this difference is preferential etching of the different \([111]\) surfaces\(^{29}\). The enhanced activity of the phosphorus atoms results in dislocation etch pits appearing on the (111) surface but not on the (\(\overline{1}11\)) surface of the GaP. This property can be used to identify the surfaces. Another example is diffusion. Zinc diffuses into the (111) Ga surface more readily than into the (111) P surface\(^{30}\).

2.3.2. Band structure

The band structure of GaP\(^{31}\) is shown in figure (2.5). The lowest minima in the conduction band lie in the \([100]\) directions in \(k\) space. Gershenzon, Thomas and Dietz\(^{32}\) have determined the indirect band gap at \(0^\circ\)K to be 2.325 eV, whilst Lorenz, Pettit and Taylor\(^{33}\) obtained a value of 2.338 eV. The direct gap (at \(0^\circ\)K) is 2.89 eV\(^{31}\).

The variation of indirect band gap (\(E_g\)) with temperature (\(0^\circ\)K) figure (2.6), was calculated from the formula of Panish and Casey\(^{34}\), who used the experimental data of reference (33).

\[
E_g = 2.338 - \frac{6.2 \times 10^{-4}}{(T + 469)} \cdot T^2 \text{ eV.}
\]

2.3.3. Energy levels in the band gap

Gallium phosphide is readily doped p-type by group II impurities (Zn, Cd, ...) which will occupy gallium sites or doped n-type by group VI impurities (S, Te ...) which will occupy phosphorus sites. Group IV impurities (Si ...) are amphoteric dopants.

When considering deep levels they may be associated not with a single impurity, but with an impurity complex or impurity-vacancy complex.

Some of the known levels in GaP are listed below in Table (2.1).
## Impurity Energy Levels in GaP

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Band gap position</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>$E_c - 0.065$</td>
<td>35</td>
</tr>
<tr>
<td>Te</td>
<td>$E_c - 0.089$</td>
<td>36</td>
</tr>
<tr>
<td>S</td>
<td>$E_c - 0.104$</td>
<td>36</td>
</tr>
<tr>
<td>O</td>
<td>$E_c - 0.896$</td>
<td>37</td>
</tr>
<tr>
<td>Cu</td>
<td>$E_v + 0.068$</td>
<td>38</td>
</tr>
<tr>
<td>Zn</td>
<td>$E_v + 0.062$</td>
<td>39</td>
</tr>
<tr>
<td>Cd</td>
<td>$E_v + 0.095$</td>
<td>39</td>
</tr>
<tr>
<td>C</td>
<td>$E_v + 0.048$</td>
<td>40</td>
</tr>
<tr>
<td>Mg</td>
<td>$E_v + 0.053$</td>
<td>41</td>
</tr>
<tr>
<td>Vp</td>
<td>$E_c - 0.07$</td>
<td>42</td>
</tr>
<tr>
<td>$V_{Ga}$</td>
<td>$E_v + 0.19$</td>
<td>42</td>
</tr>
<tr>
<td>Si amphoteric</td>
<td>$E_c - 0.08$</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>$E_v + 0.2$</td>
<td>36</td>
</tr>
<tr>
<td>$Z_{n}$ - 0 isoelectronic</td>
<td>$E_c - 0.24$</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>$E_v + 0.03$</td>
<td>43</td>
</tr>
<tr>
<td>Cd - 0</td>
<td>$E_c - 0.34$</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>$E_v + 0.035$</td>
<td>39</td>
</tr>
<tr>
<td>N</td>
<td>$E_c - 0.008$</td>
<td>45</td>
</tr>
</tbody>
</table>

Table (2.1.)
Intensity/wavelength relationship of a commercial GaP EL diode

Fig (2.7)
2.3.4. Electroluminescent properties

Because of gallium phosphide's broad band gap, radiative recombination of holes and electrons can occur in the visible part of the spectrum. The wavelength of the light emitted is inversely proportional to the energy \( \lambda = h c / E \). Table (2.2) shows the highest output efficiencies reported, for electroluminescent diodes with various dopants. The output efficiency, or external quantum efficiency, is defined as the number of photons emitted for each electron crossing the junction.

Some properties of GaP light-emitting diodes

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Photon Energy (eV)</th>
<th>Output Efficiency</th>
<th>Dopant(s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>699 (red)</td>
<td>1.77</td>
<td>7</td>
<td>Zn, 0</td>
<td>46</td>
</tr>
<tr>
<td>558 (green)</td>
<td>2.22</td>
<td>0.6</td>
<td>N</td>
<td>47</td>
</tr>
<tr>
<td>605 (yellow)</td>
<td>2.05 (at 77 K)</td>
<td>0.1 (at 77 K)</td>
<td>Mg, 0</td>
<td>41</td>
</tr>
</tbody>
</table>

Table (2.2)

Red, green and yellow EL diodes are available commercially as single devices or arrays. Variable colour displays are under development.

Figure (2.7) shows the spectrum of a red EL diode made commercially, the intensity wavelength distribution having been measured with an Optica CF4 spectrophotometer in the Chemical Physics Department of the University.

In an indirect gap semiconductor (like GaP), for an electron in the conduction band to recombine with a hole in the valence band, a momentum equal to \( k = k_c - k_v \) has to be accounted for, so that momentum is conserved. \( k_c \) and \( k_v \) are the electron and hole momenta at the conduction and valence bands respectively. Because
of this restriction on the crystal momentum, the intrinsic recombination probability of electrons and holes is low. However, the recombination of electrons and holes can be greatly enhanced by the addition of impurities which interact strongly with free carriers, enabling momentum to be conserved throughout the crystal due to impurity-carrier interactions. Some possible impurity induced transitions are:

a) recombination of an electron trapped by a donor, and a hole trapped by an acceptor
b) a trapped electron at a deep donor level recombining with a free hole.
c) recombination at an isoelectronic trap.

An isoelectronic trap is produced by replacing the host atom with an impurity atom which has the same valence as the host atom. This introduces a bound state for either an electron or a hole. Once one carrier is bound, the centre is charged and the carrier of opposite sign is readily trapped through Coulombic attraction to form a bound exciton. These isoelectronic traps may be either point defects or molecules; they provide the best impurity-induced luminescence efficiencies at room temperature in GaP. An example of a point defect isoelectronic trap is nitrogen. Lying 8 meV below the conduction band it traps an electron, which, on recombining with a hole, produces nearly full band gap radiation (green). The Zn-O complex is an example of a molecule acting as an isoelectronic centre. Oxygen donors are approximately 0.83 eV below the conduction band at 300°K, and generate emission in the infra-red region. The binding energy may be reduced, however, by introducing an acceptor onto a nearest neighbour gallium site. Zinc reduces the binding energy of the electron to 0.24 eV, whilst cadmium reduces it to 0.34 eV. Together with these radiative centres there can be present in the material centres which will
dissipate energy by non-radiative processes. Two such processes are

a) Auger processes

b) Deep centres

a) Auger processes

Non-radiative Auger processes

The energy released due to electron-hole recombination, instead of being carried away by a photon, is transferred as kinetic energy to a third particle (electron or hole), bound or free.

b) Deep centres

Doubly charged deep centres are capable of binding two particles. Any recombination with such a centre will not result in the emission of a photon because the excess energy will be transferred to the other trapped carrier.

2.4 Types of Damage introduced by ion bombardment

2.4.1 Physical properties

The damage produced by an incident particle may be of various forms.

a) Vacancy - Interstitial Pair (The Frenkel defect).
A Frenkel defect is produced by removing an atom from its lattice site and placing it in a nearby interstitial position. Both the vacancy and the interstitial atom may play important roles in the formation of other defects, depending upon their mobility. Morrison et al have shown that the gallium interstitial is mobile below room temperature in GaAs\textsuperscript{49}.

Vook and Stein\textsuperscript{50} attribute the growth of more complicated defects such as vacancy-oxygen pairs and vacancy-vacancy pairs to the liberation of vacancies from defect clusters, and their subsequent recombination with themselves or other defects. Much less is known about the motion of the interstitial atom. It can migrate through the lattice until it encounters an impurity atom, which is then displaced into an interstitial site. The substitutional impurity is therefore converted to an interstitial impurity; this conversion is known as the Watkins replacement mechanism.\textsuperscript{51}

b) Vacancy-impurity pairs
These defects form by the diffusion of a simple vacancy to a lattice site adjacent to an impurity atom.

c) Divacancy.

Divacancies may form directly if an incident ion succeeds in displacing adjacent atoms; and simple vacancies may also combine to form divacancies.

d) Dislocation lines and loops

Dislocation lines and loops can grow either by the agglomeration of simple defects, or as a result of strain fields that accompany the damage. If we have a line of simple defects figure (2.9)(1) in a crystal pinned at either end by an impurity, then, under stress (say due to volume expansion of the damaged region) the line bows figure (2.9)(2). Under some conditions the stress required for continued bowing decreases as the bowing increases, so that eventually the dislocation loop will curl back on itself and surround the pinning points figure (2.9)(3). The two
ends may then unite so that a closed dislocation loop is formed, and the segment between the primary points may straighten out to its original condition figure (2.9)(4).

The dislocation loops thus formed will continue to grow under applied stress - and the pinned segment will continue to generate successive loops.

**Dislocation loop formation**

![Dislocation loop formation diagram]

**e) Vacancy and interstitial platelets**

**Types of platelet**

![Types of platelet]

- *Vacancy platelet*
- *Interstitial platelet*

![Figures 2.9 and 2.10]

The platelets grow by the accumulation of implantation generated vacancies and interstitials. They anneal out in the region 500–600°C.
f) Heavy disorder

If a large number of atoms are displaced in a sufficiently small volume (called displacement spikes by Brinkman)\textsuperscript{52} the characteristics of the material will change towards the amorphous state. This disorder consists of simple defects, dislocation loops and plates of interstitials and vacancies.

2.4.2. Electrical properties

The different types of damage (section (2.4.1)) may be electrically charged, so that they will then be capable of acting as carrier trapping or recombination centres.

If a carrier captured at a centre stays for a certain length of time in that state (known as the lifetime), before being ejected thermally, the centre is acting as a trap. If, however, before the thermal ejection can occur, a carrier of opposite type is trapped at the same centre, recombination takes place and it may be regarded as a recombination centre. Which role a centre plays depends upon the relative concentrations of majority and minority carriers and upon the relative capture cross-sections for these carriers.

Table (2.3) shows the different kinds of trapping centre and the capture process involved. The generation of carriers i.e. the release of carriers from trapping centres, is the reverse process of that indicated.
Trapping centre capture processes

<table>
<thead>
<tr>
<th>Type of centre</th>
<th>Carrier</th>
<th>Initial Trap State</th>
<th>Process</th>
<th>Final Trap State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attractive</td>
<td>electron</td>
<td>$N_T^+$</td>
<td>$N_T^+ + e \rightarrow N_T^0$</td>
<td>$N_T^0$</td>
</tr>
<tr>
<td>Neutral</td>
<td>electron</td>
<td>$N_T^0$</td>
<td>$N_T^0 + e \rightarrow N_T^-$</td>
<td>$N_T^-$</td>
</tr>
<tr>
<td>Repulsive</td>
<td>electron</td>
<td>$N_T^-$</td>
<td>$N_T^- + e \rightarrow N_T^{2-}$</td>
<td>$N_T^{2-}$</td>
</tr>
<tr>
<td>Repulsive</td>
<td>hole</td>
<td>$N_T^+$</td>
<td>$N_T^+ + h \rightarrow N_T^{2+}$</td>
<td>$N_T^{2+}$</td>
</tr>
<tr>
<td>Neutral</td>
<td>hole</td>
<td>$N_T^0$</td>
<td>$N_T^0 + h \rightarrow N_T^+$</td>
<td>$N_T^+$</td>
</tr>
<tr>
<td>Attractive</td>
<td>hole</td>
<td>$N_T^-$</td>
<td>$N_T^- + h \rightarrow N_T^0$</td>
<td>$N_T^0$</td>
</tr>
</tbody>
</table>

Table (2.3.)

There are indications that the vacancies $V_{Ga}$ and $V_{P}$ are both electrically active - $V_{P}$ acting as a donor producing a level $E_v - 0.07$ eV and $V_{Ga}$ acting as an acceptor producing a level $E_v + 0.19$ eV. (see section 2.3.3 and Table (2.1)).

The charge and related levels for interstitials divacancies etc. are unknown at present.

2.5. Surface preparation and contacts

Because ion implantation is basically a surface process, being limited to the first few microns into the materials, the surface preparation of specimens is of particular importance.

2.5.1. Dicing

Slices were cut up into 2.5 mm squares using a wire saw made by Production Techniques Limited. The wire, made by Laser Technology Incorporated, was 0.2 mm thick and impregnated with 45$\mu$m diamond. Laister$^{53}$ comments that surface damage resulting from cutting up slices using a diamond impregnated wheel can be fractions of a micron thick.
2.5.2. Polishing

To obtain a good surface finish and to remove any damage produced by cutting up the ingot, the surface to be implanted is first polished. Specimens are degreased with trichloroethylene and then washed in methanol in an ultrasonic bath. After this they are mounted using Apiezon-W wax (which melts at 50°C, allowing easy mounting and removing of specimens) onto a quartz disc. Once all traces of excess wax are removed, and after a further degreasing, the specimens are polished with 500 Å alumina powder on a Metaserv B polishing pad with 1% bromine/methanol solution acting as an etch and lubricant. The pressure applied to the specimen was in the region 150 - 200 gm/cm². Talystep measurements showed that this procedure gave a surface finish with a peak to valley distance of better than 200 Å.

The method is, in fact, a combination of several techniques which various authors have used successfully on GaAs. Meieron has polished GaAs with 1µ diamond paste which leaves damage estimated to extend 70 Å into the material; which he removed by a chemical polish of 0.5% bromine/methanol solution. Buiocchi, on the other hand, used 6µ diamond paste leaving damage 6000 Å deep, which was removed with 15% bromine/methanol solution. Fuller and Allison used 5% bromine/methanol to obtain a "high" polish on GaAs, whilst Sullivan and Kolb used various concentrations below 0.1% and applied pressure to the specimens, finding that a practical working pressure was 250 gm/cm².

The variables are, therefore:

- size of polishing powder
- concentration of bromine/methanol
- pressure.
It was found that coarser grade alumina powder than the 500 Å used, produced a greater peak to valley distance (0.1μ powder gave 2000 Å peak to valley), whilst finer grades gave no measurable improvement as measured by the Talystep, whilst increasing the time taken to obtain a satisfactory finish. The finer the powder used, however, the less the surface damage.

Bromine/methanol acts as a chemical polish. Too low a concentration will impede this polishing process, whilst too high a concentration will etch away the GaP without improving the surface finish. The 1% bromine/methanol used was found to give a good surface finish (200 Å peak to valley); without removing a lot of material, typically 5μ.

Simply placing a specimen in a rotating beaker, that is, no pressure is being applied, with 1% bromine/methanol solution and powder, gave a surface which under the microscope could be seen to be pitted. This indicated that preferential etching was taking place, the specimens being orientated in the (111) direction. On the other hand, too high a pressure, 400 gm/cm², produced a scratched surface.

Using Wronski's solution of 5 phosphoric acid/1% bromine/methanol solution as a polish for GaP, resulted in an undulating surface with a peak to valley distance of 2000 Å, as measured by a Talystep surface profile.

2.5.3. Etching

Numerous authors have suggested etchants for GaP. Some of these are:
Etchants for GaP

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Ratio</th>
<th>Etch rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃, HCL (boiling)</td>
<td>1,3</td>
<td>30 μ/min</td>
<td>59</td>
</tr>
<tr>
<td>Chlorine saturated methanol</td>
<td></td>
<td>30 μ/min</td>
<td>56</td>
</tr>
<tr>
<td>H₂SO₄ : H₂O₂ : H₂O</td>
<td>3:1:1</td>
<td>0.01 μ/min</td>
<td>60</td>
</tr>
<tr>
<td>H₂SO₄ : HNO₃ : HF</td>
<td>3:6:1</td>
<td>2-3 μ/min</td>
<td>61</td>
</tr>
<tr>
<td>plus a few drops of bromine at 50°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF : HNO₃</td>
<td>1:1</td>
<td>0.5 μ/min</td>
<td>62</td>
</tr>
</tbody>
</table>

Table (2.4.)

Not all the etchants were used as it was found that a short etch (10 seconds) in a warm aqua regia at 50°C left a surface finish not measurably changed from the unetched material. Thus, after polishing, specimens were given a short etch in aqua regia to remove any remaining traces of damage.

2.5.4. Ohmic contacts

Ohmic contacts were made to both the n-type and high resistivity bulk material by alloying in tin at 230°C in an atmosphere of HCl vapour, a process which takes 2 - 3 minutes. Tin is convenient to use, as it alloys at low temperatures so that there is little or no change in the composition of the GaP during contacting. A gold-tin alloy (4% tin) was also used occasionally, but this requires an alloying temperature of approximately 400°C.

The limitations of alloyed contacts, namely, the depth to which contacts penetrate (1 - 2μ, which is large compared to implantation ranges) and lack of control over contact area can be overcome by evaporating contacts through a mask, followed by heat treatment. Tin was also used for this method. Evaporating
tin directly onto the surface gave a rectifying contact, whilst heat treatment resulted in the tin melting. Good ohmic contacts could be obtained, however, by evaporating a layer of nickel (melting point $1455^\circ$C) over the tin, and then heat treating.

2.5.5. Schottky contacts

1.5 mm diameter gold dots were evaporated onto the gallium phosphide to produce Schottky barrier contacts. B. L. Smith$^{65}$ has measured the diffusion voltage of the Au-GaP interface to be $1.31 \pm 0.02$V. Cowley$^{66}$ discusses the effects of a small interfacial layer. If the layer is 10 Å thick, the apparent diffusion voltage, as measured by the C-V method will be 1.4V increasing to 2.4 V for one 20 Å thick.

Before a specimen was placed in the evaporator it was degreased and washed in iso-propyl alcohol. Each sample was held on a stainless steel mask with silver conducting paint. The gold was evaporated at a pressure in the region $5 \times 10^{-6}$ torr. No difficulty was experienced in obtaining diodes with diffusion voltages of less than 1.4 V, using this method. In cases where this voltage was higher, the gold was removed, the surface cleaned and a new contact evaporated.

2.5.6. Removal of Schottky contacts.

Mercury was found to be convenient way of removing gold Schottky contacts; the solubility of gold in mercury being 0.13 atomic % at room temperature$^{67}$. However, the method often left small traces of gold behind, clearly visible under an optical microscope. The process was followed, therefore, by placing specimens in a 10% potassium cyanide solution. Any gold dissolves to form potassium aurocyanide, hydrogen cyanide gas being evolved$^{68}$. 
Chapter 3

EXPERIMENTAL TECHNIQUES AND APPARATUS

3.1 General Introduction

The initial sections of this chapter outline the accelerator facilities and the way in which specimens were implanted. Another sample processing procedure, that is annealing, is then discussed.

Later sections describe firstly the experimental techniques employed to determine some of the properties of the centres produced by the ion bombardment and secondly the corresponding pieces of apparatus. The methods used were:

1) Thermally stimulated current (TSC), providing information on the capture cross-sections, concentrations and associated energy levels of the trapping centres.

2) Capacitance measurements as a function of
   (a) voltage (C-V): enabling the majority carrier concentration to be determined
   (b) frequency (C-f): indicating the number of deep levels, and
   (c) time (C-t): also allowing the energy level values to be calculated.

All these methods employ metal/semiconductor rectifying contacts (Schottky barriers). The limitations of such barriers are discussed in section (3.4.4.2.). Method (1) is only possible if the reverse bias junction current is very low < $10^{-9}$ A so that carriers released from traps are not swamped by the leakage current. For highly doped material the leakage current may be in the range $10^{-9} - 10^{-6}$ A, in this case capacitance as a function of time (C-t) proved to be a more practical method.

The last section provides details of the capacitance bridges.
3.2 Implantation facilities

3.2.1. The accelerator

Implantations were carried out using the department's 600 keV heavy ion accelerator, which has been described in detail by Cracknell et al.\(^6^9\) Figure (3.1) shows the facility schematically. All implantations were made on the 90° exit beam line from the analysing magnet, the maximum mass-energy product from this line being 45 a.m.u. MeV. The stability of the electrostatic generator (SAMES) was better than 1% (this determines the stability of the whole system, as the magnet stability is 0.1%). The stability of the generator has recently (Feb. 75) been improved to better than 0.2% and further modifications are planned.

3.2.2. Ion species

For a given accelerator voltage variation of the magnet current results in ions of different mass entering the target chamber. By monitoring the beam current a spectrum of current versus mass can be obtained. The ion of interest can then be identified either by comparison with previous spectra obtained with known ion species in the accelerator, or by comparison with published isotope abundance data.

3.2.3. Beam uniformity

The beam in the 90° line is firstly de-focused and then electrostatically scanned at a frequency of 200 Hz → 2 kHz in both x and y directions. The x direction is usually swept at a faster rate than the y direction to obtain good coverage of the specimen.

3.2.4. Dosimetry

It is assumed that each incident ion falling on the specimen and specimen plate contributes one unit of charge to the beam current. This will be in error if secondary electrons are emitted from the sample surface. This emission may be minimised by
having a negatively biased suppressor in front of the specimen. As the suppression voltage is increased the collected current falls to the same constant value which is assumed to be due to the positive ions only.

A potential of 300 V (corresponding to an electric field of 100 V/cm) was found to provide more than adequate suppression. The measured current had dropped to a constant value by about 150 V.

Possible sources of error are
1. the neutral component of the beam. This may be minimised by reducing the pressure in the beam lines to as low a value as possible. The pressure in the target chamber was typically \(10^{-6} - 10^{-7}\) torr.
2. doubly charged species, created in the beam line after the magnet
3. leakage currents in the target chamber.

3.2.5. Adjustable parameters

The parameters available are:
1. Energy of incident ion; so determining the depth of implantation.
   The energy range used was 15 keV - 400 keV.
2. Dose. Greater than \(10^{10}\) cm\(^{-2}\). Very small doses are difficult to measure accurately because of the very small time that the beam is on the specimen.
3. Ion species. The work concentrated on protons, but a few sulphur implantations were also carried out.
4. Dose rate. This depends on the ion species. For protons the dose rate could be varied over the range 30 - 150 nA.
5. The temperature at which the specimen was implanted. This could be in the range 20 - 200°C. In all cases the specimens were implanted at room temperature.
6. The orientation of the crystal to the beam. All specimens were orientated at 7° off the <111> direction to avoid significant channelling.

3.2.6. Mounting of specimens for implantation

Specimens were mounted onto a stainless steel holder using silver conducting paint to provide a good electrical and thermal contact. Slits defined the area to be implanted and samples could be orientated 7° off the <111> direction to avoid channelling. The holder assembly fitted into a sliding carriage (which could be controlled from outside the target chamber) so that up to five different implantations could be carried out, without letting the target chamber up to air.

3.3. Annealing of specimens

The annealing behaviour of the proton damage was investigated in two temperature regions (sections 5.5.4.). Specimens to be annealed below 250°C had a tin contact alloyed on before implantation and annealing, whilst those to be annealed at 300°C or above were implanted and annealed before contacting. (The temperature limit of 250°C was determined by the fact that tin melts at 280°C). This latter group of samples were coated with SiO₂ before annealing. In each case specimens were placed face down on a similar slice of GaP in a quartz boat, a method used by Hunsperger and Marsh for annealing GaAs. Argon gas was passed over the samples whilst in the furnace at a rate of 5 ft³/hr, nitrogen not being used as it is a dopant in GaP. The anneal temperature could be calculated from the known profile along the furnace and the known relationship between the area of maximum temperature and the temperature set on the control unit. In every case the annealing time was 30 minutes. Each specimen was annealed at only one temperature i.e. not at a series of increasing temperatures.
Deposition of Silicon Dioxide

Flowmeters

Specimens

Reduced Pressure Enclosure

Rotatable Holder with Heater

Rotary Pump

\[ \text{SiH}_4 \]

\[ \text{N}_2 \]

\[ \text{O}_2 \]

Fig (3.2)
The SiO₂ films were grown using the technique of Goldsmith and Kern, in which silane (SiH₄) reacts with oxygen at a temperature of approximately 300°C - 350°C. The reaction is:

$$\text{SiH}_4 + 2\text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}$$

Specimens to be coated were placed on a hot plate inside a bell jar, as shown in figure (3.2). The deposition rate is an increasing function of temperature, typical rates being 450 Å/cm at 310°C, and 800 Å/cm at 330°C. Grown films were approximately 5000 Å thick as judged by the colour of the interference fringes, and after annealing could be removed with 40% hydrofluoric acid.

3.4. Electrical measurements and apparatus

3.4.1. Introduction

The electrical properties of semiconductor materials are not only determined by their physical structure but by the presence of small quantities of impurities and/or imperfections in the crystal lattice. For this reason electrical measurements on semiconductors are very sensitive to irradiation damage compared to say Rutherford backscatter techniques; consequently, electrical methods were used extensively. The techniques available for determining some of the properties of deep levels were:

(1) Hall and resistivity measurements as a function of temperature

(2) Thermally stimulated current (TSC)

(3) Reverse biased metal/semiconductor junction capacitance measurements as a function of frequency.

(4) Reverse biased metal/semiconductor junction capacitance measurements as a function of time.

Methods (1) and (3) are of only limited application. Method (1) is difficult to
analyse in cases where many deep levels are present. Furthermore, Hall measurements have to be confined to the implanted region alone which means that the method can only be applied to cases in which the implantation either produces, or the ions penetrate straight through, a thin epitaxial layer which is mounted on a semi-insulating substrate.

Method (3) provides a qualitative indication of the number of deep levels. It was used for this purpose in section (5.4.3.). It is difficult to determine any quantitative information from this technique.

Methods (2) and (4) are the most easily applied. Method (2) is particularly useful as energy levels can be readily resolved, simplifying the analysis. The technique relies on the current across a reverse biased metal/semiconductor junction being small, that is of the order of $10^{-9}$ A. For highly doped ($10^{17}$ cm$^{-3}$) material this current is exceeded for even low biases, so swamping any current generated by the release of carriers from trapping centres. In this case, however, provided the current is less than 1 $\mu$A, the C-t method can be used. Method (4) was applied to the measurement of deep levels in the medium and low resistivity materials (sections (5.4.5.)) where the TSC method was limited by leakage currents. The analysis of C-t curves, however, is difficult if many deep levels are present.

In all these techniques Schottky barriers have been employed. These are discussed in section (3.4.4.2.).

Other capacitance measurements C-V and Copeland, used to determine the majority carrier concentration of regions close to the semiconductor surface are described in sections (3.4.4.3.) and (3.4.4.4.).

For each experimental method the apparatus used is also outlined.
3.4.2. The thermally stimulated current experiment

3.4.2.1. General method

The experimental method may be summarised as follows:

(a) Cool the specimen to some convenient temperature, in this case the boiling point of nitrogen, 77°K.

(b) Ensure that trapping centres are filled. This may be achieved using optical excitation or suitable biasing.

(c) Warm up the specimen at a constant heating rate, monitoring the current as a function of temperature.

If it is known which energy levels are present in the bandgap, it should be possible to choose lower and upper temperatures such that the levels of interest may be examined. In practice, however, the method is usually employed to establish which levels are present, and the temperature limits adjusted from experimental experience. In this work, the lower limit (77°K) was set by the equipment available, the upper limit 323 - 373°K by the temperature at which the thermal generation of carriers swamped any trapping effects.

3.4.2.2. Filling of the traps

3.4.2.2.1. By optical excitation

The specimen is firstly cycled several times, between 77°K and room temperature, in the dark and under constant reverse bias. This ensures that trapping centres with energy levels in the upper part of the bandgap are empty, the Fermi level under these conditions being close to the centre of the bandgap. Any thermally stimulated current obtained with the specimen in this state is referred to as the "dark" or "background" current. If the specimen is now illuminated either with white light or a helium/neon laser, electrons are excited from the valence band into empty trapping centres and from full trapping centres into the conduction band. Depending upon the light’s wave-
Trapping centre occupancy as a function of temperature, for traps in various bandgap positions.

The effect of changing the bias upon trapping centre occupancy.

(a) Metal-semiconductor junction

The effect of changing the bias upon trapping centre occupancy.

(b) Zero bias

(c) Reverse bias (at the same temperature)

Fig(3.3)
length and intensity an equilibrium condition is reached in which some proportion of deep trapping centres are filled at any instant; the equilibrium state being "frozen-in" when the illumination is removed. As some trapping centres in the upper part of the bandgap will now be full, the Fermi level will have moved closer to the conduction band as a result of this excitation. Upon raising the temperature trapped carriers are released into the conduction and/or valence bands. The effects of temperature upon trapping centres in various bandgap positions, labelled 1 - 3 in figure (3.3(a)), are summarized in table (3.1.). The release of an electron from a donor-like trap or the release of a hole from an acceptor-like trap (as defined in table 2.3) will both contribute to the measured current.

3.4.2.2.2. By variation of the bias

A specimen is first cooled under zero or low reverse bias in the dark, figure (3.3)(b), as in the previous section. Once the low temperature limit is reached, the bias on the specimen is changed to a higher value of reverse bias. The situation is then as in figure (3.3(c)). Trapping centres in the upper part of the bandgap, at the edge of the depletion region are filled and in a state of non-equilibrium, so that, with a rise in temperature, they release their carriers into the conduction band. Other centres remain empty. The main contribution, therefore, to any thermally stimulated currents will be as a result of carriers being released from "levels" in the upper part of the bandgap. Comparison of TSC curves obtained after optical excitation with those obtained after variation of the bias have been used to determine energy level bandgap positions in sections (5.3.2.).
<table>
<thead>
<tr>
<th>Increase</th>
<th>Increase</th>
<th>Increase</th>
<th>Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Full</td>
<td>empty</td>
<td>pH</td>
</tr>
<tr>
<td>no change</td>
<td>Full</td>
<td>Full</td>
<td>no change</td>
</tr>
<tr>
<td>e</td>
<td>empty</td>
<td>empty</td>
<td>e</td>
</tr>
</tbody>
</table>

Table (5.1)

<table>
<thead>
<tr>
<th>Increase</th>
<th>Increase</th>
<th>Increase</th>
<th>Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>current</td>
<td>section</td>
<td>change in</td>
<td>released</td>
</tr>
<tr>
<td>spice</td>
<td>line</td>
<td>high</td>
<td>carrier</td>
</tr>
<tr>
<td>no change</td>
<td>low</td>
<td>temperature</td>
<td></td>
</tr>
<tr>
<td>Carrier</td>
<td>Occupacy</td>
<td>Occupancy</td>
<td>Type of center</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(see table 2.3(3))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bandgap position</td>
</tr>
</tbody>
</table>

Temperature centre occupancy as a function of temperature for centres in various bandgap positions.
The temperature at which the current peak occurs as a function of heating rate for various energy levels.
The temperature at which the current peak occurs as a function of heating rate, for a level 0.6eV below the conduction band.
3.4.2.3. Effect of the heating rate

The variation of the temperature at which a current maximum occurs, as a function of heating rate can be calculated from

\[
\beta = \frac{N_s <v> S_T T_m^2}{E_T \exp \left( \frac{E_T}{kT_m} \right)} \quad \text{... reference (75)}
\]

- \(T_m\) - temperature at which the current maximum occurs
- \(E_T\) - trap energy level
- \(\beta\) - heating rate
- \(S_T\) - capture cross-section of the trap.

Increasing the heating rate moves the current maximum positions to higher temperatures. A change of \(+10\%\) in the heating rate about the usual value of \(0.3\,\text{K/sec}\) will cause \(T_m\) to move by \(+0.3\,\text{K}\) for a shallow level (e.g. 0.2 eV), and by \(+0.9\,\text{K}\) for a deeper level (e.g. 0.75 eV) figure (3.4). Figure (3.5) shows the variation of \(T_m\) with \(\beta\), for an \(E_T\) of 0.6 eV, in greater detail.

\(T_m\) is not strongly dependent upon \(\beta\), so that

a) by varying the heating rate it is not possible to separate closely spaced current peaks.

b) the good separation of the peaks, found in the experiments, meant that the choice of heating rate was not critical.

Whatever value of heating rate is chosen, however, it must remain constant over the period of time which it takes for one set of trapping centres to empty, typically 1 - 2 mins.

3.4.2.4. Separation of the current peaks

If two energy levels having the same concentration of trapping centres are close to each other in the bandgap then they can be separated, provided they are not closer than 0.01 eV at low temperatures (77°K) and 0.06 eV at room temperature.
Depletion region capacitance as a function of specimen temperature (computer plot)

Fig(36)
Thermal quenching can be used to separate peaks experimentally. As soon as the first peak has reached its maximum value, liquid nitrogen is poured into the cryostat. The temperature will not fall immediately because of thermal inertia. Any delay ensures that all trapping centres are completely emptied. After cooling, the temperature is raised without any re-filling of traps. Only the second peak is now seen.

3.4.2.5 Concentration measurements

By measuring the Schottky contact capacitance as a function of temperature (C-T) the depletion region width and therefore the volume being examined (as the contact area is known \(1.767 \times 10^{-2} \text{ sq. cm}\)) at each current peak can be determined. Figure (3.6) shows a C-T curve. The area under the current peak is proportional to the number of centres in the measured volume. If \(n\) is the number of carriers

\[
n = \frac{\Delta}{q} \int_{T_1}^{T_2} I \frac{dT}{\beta}
\]

where the current peak occurs in the temperature range \(T_1 - T_2\). The integral term is then the area under the current peak. If it is assumed that each centre releases only one carrier, then \(\Delta = 1\).

3.4.2.6 Detection limits

The minimum number of trapping centres detectable was approximately \(10^8 - 10^9\), which corresponds to a concentration of \(10^{13} - 10^{14} \text{ cm}^{-3}\), that is a detection limit of 0.001 ppm. It should, therefore, be possible to measure the impurity concentrations in as grown material, typical values of which are given in section (2.2).
Effect of the electric field upon the numbers of carriers collected

The electric field affects the number of carriers collected in several ways.

1) the probability of a carrier, emitted from a centre, being re-captured, decreases as the field increases. Dussel and Bube have shown this experimentally.

2) the capture cross-section of a trap is field dependent, varying as $E^{-3/2}$. At the low temperatures at which the trapping centres are filled, however, this field dependence is negligible compared to that of the temperature dependence, this varying as $T^{-n}$, where $n$ is greater than 2.9 (see results table (5.2.)).

3) the Coulombic potential barrier of the trap may be lowered, resulting in carriers being more easily trapped. This is known as the Poole-Frenkel effect. To experience this effect, the trap must be either positively charged when empty and neutral when occupied, or, neutral when empty and negative when filled. Figure (3.7) shows the effect of increasing the electric field upon the trap potential barrier. For zero or very low fields (less than 100V/cm) the emission from a trap is by thermal processes only. At moderate fields ($10^2 - 10^5$V/cm) thermal emission over a reduced barrier ($E_T - \Delta E_T$) takes place. At high fields tunnelling can occur, and at still higher fields the trap becomes de-localised.

The barrier height for a trap, experiencing a Poole-Frenkel type of barrier lowering, varies as $E^{1/2}$. The change in barrier height ($\Delta E_T$) for an electric field ($E$) is given by

$$\Delta E_T = -\left(\frac{3E}{\pi \varepsilon_0 \varepsilon_r}\right)^{1/2}$$

The maximum field value measured in this work was $2 \times 10^4$V/cm corresponding to a value of $\Delta E_T$ of 0.0007 eV, a change of only $\frac{1}{2}$% in the barrier height for the shallowest level, and an increase in the thermal emission rate of 9%. The field
The effect of increasing the electric field upon the trap potential barrier.

Low field
Thermal re-emission

Moderate field
Thermal re-emission with reduced barrier

High field
Tunnelling

Very high field
Trap delocalization

Fig (3,7,.)
Specimen Geometry

(a) Implanted regions

(b) Mesa structure
   evaporated gold top contact (Schottky)
   alloyed tin bottom contact (Ohmic)

(d) Fig (3.8)
variation resulting from the Poole-Frenkel effect, therefore, is negligible. Consequently, the predominant effect of the electric field is in determining the number of carriers collected, i.e., number 1). In the results which follow, the number of damage centres at each level have been normalised to the appropriate field saturation value, or in some cases e.g., minority trapping centres, to a fixed field value.

3.4.2.8. Effect of the specimen geometry and the contacts

A few specimens were implanted with 300 keV protons at various doses \((10^{13} - 10^{15}) \text{ cm}^{-2}\) using the geometry of figures (3.8 (a) and (b)). Contacts A and B were formed by alloying tin dots, or evaporating either tin or gold, whilst contact C was always an alloyed tin dot. In each case, independent of the material used for the contacts, TSC measurements indicated the presence of the same band-gap energy levels. The number of measured trapping centres, however, did appear to depend upon the type of contact, that is, upon whether the contact(s) were ohmic, reverse biased rectifying, or forward biased rectifying. Subsequently it was found that the samples which included a forward biased rectifying contact (so that carriers were being injected into the implanted layer) gave results which were not consistent with the results in which the other types of contact were used. Therefore, either two ohmic contacts (alloyed tin) or one ohmic and one reversed biased (evaporated gold) contact were used throughout as in figure (3.8(c)).

When using the geometry of figures (3.8(a) and (b)) the levels present in the unimplanted material could be obtained by measuring either across A - C or B - C, whilst any additional levels produced by the implantation could be measured across A-B. With this geometry, however, any high-resistivity buried layer produced by the protons was shunted by the lower bulk resistance. In order to ensure that the current paths were through the implanted region it was necessary to either mesa etch samples
The geometry of figure (3.8(d)) was the one adopted for all further implantations as it includes no forward biased contacts and the irradiation can be across the whole of the specimen surface.

3.4.3. TSC apparatus

3.4.3.1. Vacuum equipment

A diffusion pump system exhausted a cryostat for thermally stimulated current work as well as two other cryostats for Hall and resistivity measurements. (See photographs (3.9, 3.10). The rotary pump was equipped with a phosphorus pentoxide trap to prevent oil and water vapour streaming back, and a liquid nitrogen trap above the diffusion pump served the same purpose, as well as increasing its pumping efficiency. A typical working pressure was $5 \times 10^{-6}$ torr.

3.4.3.2. Specimen mounting

Each sample was held on a thin aluminium baseplate with silver conducting paint. This baseplate was electrically insulated, but not thermally, from the cryostat's cold finger, by a piece of sapphire ($\alpha$Al$_2$O$_3$). Gold probes were used to make contact to the specimen; the circuit to the back contact being completed via a gold film evaporated onto the sapphire. The probes were isolated by thin sheets of PTFE and the connections taken out through PET sockets. A cold shield surrounded the sample, except for a small hole through which it could be illuminated. PTFE sleeving was used on all leads so that leakage currents to earth were reduced to less than $10^{-12}$ amps. (See figure (3.11) and photograph (3.12)). To prevent water vapour condensing on the specimen when cooling, a small amount of power could be fed into the heater located in the cold finger, so that the cold finger was a few degrees warmer than its surroundings. Any water vapour in the system preferentially condensed on the colder areas.
Thermally Stimulated Current Apparatus
I. Control and Measurement

- A. Temperature Controller
- B. Power supply for cryostat heater
- C. DVM thermocouple millivolts
- D. XY recorder current temperature
- E. Electrometer
- F. Cryostat
- G. Specim bias
- H. Light source, tungsten bulb or laser

Fig (3.9)
Thermally Stimulated Current Apparatus
II. Vacuum System

- Magnets for Hall measurements
- Rotary pump used to depress the boiling point of liquid nitrogen

Fig(3.10)
Specimen Mounting

Fig(3.11)
Specimen Mounting

thermocouples

specimen

gold probe
+ Be Cu holder

PTFE insulation

sapphire plate
+ evaporated gold

Al specimen holder

base connector

Fig(3.12)
Thermocouple Calibration Curve
thermocouple: Chromel—Alumel
reference junction at 0°C

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>Thermocouple Millivolts</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-10</td>
</tr>
<tr>
<td>150</td>
<td>-8</td>
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<tr>
<td>200</td>
<td>-6</td>
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<td>250</td>
<td>-4</td>
</tr>
<tr>
<td>300</td>
<td>-2</td>
</tr>
<tr>
<td>350</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig (3.13)

Intensity/wavelength relationship of light sources used in TSC experiments

Relative Intensity

- tungsten filament lamp
- He/Ne laser 6328 Å

Fig (3.15)
3.4.3.3. Cryostat heating

A small 50W heater in the cold finger, was used to raise the temperature at a maximum rate of 0.5°/sec. Usually a rate of 0.3°/sec was employed. A Chromel-Alumel thermocouple, which is almost linear over the temperature range of interest, figure (3.13) was mounted on the sapphire block as close to the sample as possible. A second thermocouple was attached to the top of the cold finger. Crushed ice was used to provide the cold junction reference temperature. The output from the specimen thermocouple fed directly into the x input of an Advance HR 2000 plotter.

By reducing the pressure over the liquid nitrogen, using a rotary pump, its boiling point could be lowered from 77°K at atmospheric pressure to 65°K at 10^-3 torr. This extension of the temperature range was useful in cases where thermally stimulated current peaks were generated in the range 77°K - 90°K. Because of the non-linear heating rate in this region, energy levels appeared to be deeper in the band gap than they really were. This error could be eliminated by starting the heating up process from a lower temperature.

3.4.3.4. Electrical circuit

![Diagram](image)

Fig. (3.14)

Great care was taken to avoid unnecessary leakage currents at every point in
the circuit. The battery box was lined with PTFE sheet and the variable
potentiometer (1M\(\Omega\)) was also mounted on PTFE. The leads to the specimen were
kept as short as possible and firmly secured in place to avoid generating charge
by movement of the cable. Currents, measured with a Keithley Type 602
electrometer, could be in the pico-amp range. The voltage applied to the speci-
men was continuously variable over 0 - 120 volts.

3.4.3.5. Optical stimulation

A quartz window allowed specimens to be irradiated either with a tungsten
filament bulb, the intensity/wavelength relationship of which is shown in figure
(3.15), or with a He/Ne laser (wavelength 6328\(\lambda\)).

3.4.4. Capacitance measurements

3.4.4.1. Introduction

Capacitance measurements were used extensively in the work. Capacitance
as a function of voltage either using the normal C-V techniques section (3.4.4.3)
or Copeland section (3.4.4.4) enabled the majority carrier concentration, in a
region close to the semiconductor surface to be determined. The variation of the
specimen capacitance as a function of measuring frequency (C-f) gave an indica-
tion of the number of deep levels section(3.4.4.5) whilst the same capacitance as
a function of time (C - t), after changing from forward to reverse bias, allowed
some of the deep level properties to be evaluated section (3.4.4.6).

Another area in which capacitance measurements were used was in
determining the trapping centre concentrations in the TSC experiments section
(3.4.2.5.).

The following sections discuss each type of capacitance technique and des-
cribe the relevant apparatus. The final section shows how the specimen capaci-
tance is related to the measured capacitance together with details of the capacitance
bridges used.
Variation of the reverse breakdown voltage ($V_{BR}$) of GaP with doping concentration.

Data taken from ref. (83)
3.4.4.2. Schottky barriers

In every case it is the capacitance of a metal/semiconductor rectifying junction which is being measured. The physics of such Schottky barrier contacts and their use in various capacitance techniques is well documented in the literature. An inherent experimental limitation, however, results from avalanche mechanisms within the space-charge layer of the test junction. Avalanche breakdown limits the maximum voltage that can be applied to the junction, and therefore, the region of the specimen which can be examined. This maximum voltage ($V_{BR}$) not only limits C-V measurements but determines the maximum fixed bias which can be applied whilst C-f and C-t data is being obtained.

The reverse breakdown voltage ($V_{BR}$) for an abrupt junction in GaP has been calculated by Sze and Gibbons to be

$$V_{BR} = \left( \frac{\varepsilon_{r} \varepsilon_{0} E_{m}}{2qN_{D}} \right)^{2}$$

$N_{D}$ is the donor doping concentration cm$^{-3}$.

$E_{m}$ is the electric field at which breakdown occurs.

A similar expression exists for p-type material. Figure (3.16) shows $V_{BR}$ as a function of $N_{D}$. This theoretical curve, taken from reference (83) is the upper limit for the breakdown voltage. It is lowered by surface leakage currents, effects of any implanted region, tunnelling and direct field ionisation of carriers. The figure shows that capacitance techniques are most suitable for investigations of specimens with doping concentrations < $5 \times 10^{16}$ cm$^{-3}$.

3.4.4.3. Capacitance - Voltage measurements and apparatus

The reverse bias (d.c.) of a Schottky contact is slowly increased whilst the capacitance of the junction is measured by superimposing an a.c. signal on the steady d.c. The amplitude of this measuring signal is kept as small as possible.
D.C. bias supply for the C-V apparatus

battery or power supply

\[ VR = 10 \text{ kohms} \]
\[ L = 5 \text{ H, 2.90 ohms} \]

Fig (3.17)
(≈ 25 mV) so that the resulting movement of the depletion region is less than 6L^D
section (4.3.3.). Measurements at high or low frequencies can be made section
(3.4.5.2., 3.4.5.3.). The circuit for applying the d.c. bias is shown in figure
(3.17).

Samples are held on an aluminium base plate with silver conducting paint,
there being a small depression into which the protruding tin back contact fits. A
gold probe makes contact to a gold Schottky barrier. This top contact is 1.5 mm
in diameter so limiting the edge capacitance (C_e) to 0.1 pf; a factor of 1% compared
to the smallest values measured. The whole assembly is enclosed to eliminate the
effects of daylight. The majority carrier concentration can be determined from such
C-V measurements. (see section (4.3)).

3.4.4.4. Copeland measurements and apparatus

This was built in the department to a Mullard Research Laboratories design
based on the work of Copeland. The technique involves driving a Schottky barrier
diode with a small constant RF current; a few hundred microamps at 5.7 MHz. At
this operating frequency, carriers in trapping levels down to approximately 0.15 eV
below the conduction band will respond. The width of the depletion layer (w) is varied
by changing the d.c. bias, so that a profile can be obtained by monitoring the voltage
across the diode at the fundamental frequency, which is proportional to the depth (w),
and the second harmonic voltage which is proportional to \( \frac{1}{N(w)} \) (the inverse of the
carrier concentration). When measuring GaP specimens the sample holder
is covered to eliminate light effects.

The depth scale can be calibrated by replacing the sample with capacitors of
known values since \( w = \varepsilon A/C \), A being the Schottky barrier area.
The concentration axis can be calibrated in one of two ways, either
a) specimens of known concentration values can be used to obtain reference points or
b) the output voltage is measured and knowing the transfer characteristic of the profiler, is related back to a concentration value.

Method (a) was normally employed. The Copeland apparatus was used to determine the high frequency carrier concentration of the medium and low resistivity Te-doped GaP materials in section (5.4.3).

3.4.4.5 Capacitance-Frequency measurement and apparatus

The thermal emission rate of a trapping centre is inversely proportional to its position in the band gap \( E \), eqn (1). The deeper the trap, the longer it takes to empty, or fill as the case might be. A shallow trap will be able, therefore, to respond to a higher frequency signal than a deeper one. Figure (3.18) (above) shows the frequency response of a semiconductor with a shallow level at \( E_s \) and a deep level at \( E_d \). The deep trapping centres are able to respond at the lower frequency and so contribute to the capacitance.
The C-f method was used to give an indication of the number of deep levels in the medium and low resistivity Te-doped materials section (5.4.3).

3.4.4.6. Capacitance-time measurements and apparatus

The analysis and theory of C-t data is discussed in section (4.4). The measurements were made at the Mullard Research Laboratories Redhill. Specimens were mounted on transistor headers (TO5) which were then attached to a cryostat cold finger. As the cryostat was not equipped with a heater and controller only a few fixed temperatures could be obtained. These were liquid nitrogen 77°C, liquid freon 246°C and in the region of 300°C i.e. room temperature. Samples were first forward biased in order to fill any trapping centres, then the bias was reversed instantaneously, that is in less than 1μs. This ensured that only the shallow levels would respond immediately. The change of capacitance with time was measured using a Boonton automatic bridge, the measuring frequency being 1592Hz \( (2\pi f=10^4) \). By comparing the specimen capacitance with a standard capacitance an accuracy of better than 0.1% could be obtained. Results were plotted on an X-t recorder.

3.4.5. Capacitance bridge measurements and bridges

3.4.5.1. Bridge measurements

Figure (3.19)(a) is the electrical representation of a reverse biased metal semiconductor junction as shown in figure (3.19)(c). The depletion region is represented as a capacitance (C) and a resistance (R) in parallel. In series with these is a resistance \( (R_s) \) associated with the bulk of the material. In the case of low resistivity material \( R_s \ll R \) and \( R \) will determine the current through the specimen under reverse bias. The bridge, however, measures a single capacitance \( C_m \) and a single conductance \( G_m \) figure (3.19)(b).
Specimen equivalent circuit for bridge measurements

\[ R = \frac{1}{G} \]

\[ R_m = \frac{1}{G_m} \]

Figure (3.19)

Deery\(^{35}\) expanding the work of Goodman\(^{36}\) showed that

\[ G_m = \frac{R + R_s (1 + w^2 C^2 R^2)}{R^2 + 2RR_s + R_s^2 (1 + w^2 C^2 R^2)} \]

and

\[ C_m = \frac{CR^2}{R^2 + 2RR_s + R_s^2 (1 + w^2 C^2 R^2)} \]
Bridge measurements as a function of frequency

$G = 2 \times 10^{-6}$ mho

$C = 1.25$ nF

$C_m$ & $G_m$: measured capacitance and conductance

$C$ & $G$: actual capacitance and conductance

Fig (3.20)
Three separate frequency regions can be considered viz:-

1) \( wCR \ll 1, R_s \ll R \) then \( Gm \propto \frac{1}{R} \) and \( C_m \propto C \).

2) \( wCR \gg 1, R_s \ll R, wCR \ll 1 \)
then \( G_m \propto w^2 C^2 R_s \) and \( C_m \propto C \).

3) \( wCR \gg 1, R_s \ll R, wCR \gg 1 \)
then \( G_m \propto \frac{1}{R_s} \) and \( C_m \propto \frac{1}{w^2 CR_s^2} \).

This means that at high frequencies the measured capacitance falls with a slope proportional to \( w^{-2} \).

Further, as \( R_s \) is independent of \( V \), the slope of the \( \frac{1}{C_m} \) versus \( V \) curve will not differ from that of the \( \frac{1}{C} \) versus \( V \) curve but the intercept on the voltage axis will. If the intercept of \( \frac{1}{C_m} \) is \( V_{Bm} \) (the apparent barrier height) the actual barrier height \( V_B \) is given by

\[
V_B = V_{Bm} - 2R_s w^2 \left[ \frac{d \left( \frac{1}{C_m} \right)}{dV} \right]^{-1}
\]

The correction term only becomes important at high frequencies, 1 MHz and above, due to its \( w^2 \) dependence.

Take for example a Schottky barrier diode made from \( 2 \times 10^{17} \text{ cm}^{-3} \) Te doped material. Measured values are \( R_s = 0.6 \Omega, R = 8 \times 10^5 \Omega, C = 1250 \text{ pf} \).

Then \( wCR \gg 1, R_s \ll R \) and \( wCR \ll 1 \) over the frequency range \( 10^5 \text{ Hz} \) to \( 10^7 \text{ Hz} \). Figure (3.20) shows the values of \( G_m \) and \( C_m \). \( C_m \) changes by less than 0.1% over the total frequency range whilst \( G_m \) differs appreciably from \( G_m \) above \( 10^5 \text{ Hz} \).

3.4.5.2. Low Frequency Bridge

A Wayne Kerr audio frequency signal generator covering the range 10Hz - 120 kHz in conjunction with the Wayne Kerr Universal bridge type B221.
Transformer ratio-arm bridge

Fig(3.21)
and the STC 90616 selective null detector make up the system.

The bridge is of the transformer ratio-arm type, figure (3.21). At balance, with Zs adjusted to give a null indication on the detector, the voltages across the unknown and the standard are Ex and Es. The balance condition is

\[ Z_x = \left( \frac{N_x}{N_s} - \frac{m_x}{m_s} \right) Z_s. \]

In order to apply a d.c. bias to the specimen the circuit of figure (3.17) was used.

### 3.4.5.3 High Frequency Bridge

This used a Wayne Kerr SR 268 source and detector covering the range 100kHz - 100 MHz, and a Wayne Kerr B602 bridge covering the range 15kHz - 5MHz. Accuracy of the bridge is 1% up to 3 MHz then 2% up to 5 MHz. The same d.c. bias circuit was used as for the low frequency bridge. To apply bias to a specimen the sample had to be placed in series with two large capacitors, one either side, in order to isolate it, d.c. wise, completely. Provided the capacitors used were far larger in value than that of the specimen, the change in measured capacitance varied little from the actual capacitance of the specimen.
### 4.1 Nomenclature

#### 4.1.1 TSC theory

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Specimen or junction area</td>
</tr>
<tr>
<td>$\beta$</td>
<td>heating rate</td>
</tr>
<tr>
<td>$\delta$</td>
<td>capture coefficient of an empty trap for a free charge carrier</td>
</tr>
<tr>
<td>$E$</td>
<td>electric field</td>
</tr>
<tr>
<td>$E_F$</td>
<td>energy level value of the Fermi level</td>
</tr>
<tr>
<td>$E_m$</td>
<td>mean value of a normal (Gaussian) distribution of energy level values</td>
</tr>
<tr>
<td>$e_n$</td>
<td>thermal emission rate of a carrier from a trapping centre</td>
</tr>
<tr>
<td>$E_T$</td>
<td>energy level value of trapping centres (either below the conduction band or above the valence band)</td>
</tr>
<tr>
<td>$\Delta E_T$</td>
<td>standard deviation of a normal (Gaussian) distribution of energy levels</td>
</tr>
<tr>
<td>$f$</td>
<td>density of recombination centres</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>capture coefficient of recombination</td>
</tr>
<tr>
<td>$h$</td>
<td>density of free charge carriers</td>
</tr>
<tr>
<td>$H$</td>
<td>density of trapping centres</td>
</tr>
<tr>
<td>$I$</td>
<td>specimen current</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann's constant ($8.63 \times 10^{-5} \text{eV}/\text{K}$)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>carrier mobility</td>
</tr>
<tr>
<td>$n$</td>
<td>density of trapped charge carriers</td>
</tr>
<tr>
<td>$n_c$</td>
<td>density of carriers in the conduction band</td>
</tr>
<tr>
<td>$N_c$</td>
<td>effective density of states in the conduction band</td>
</tr>
<tr>
<td>$n_o$</td>
<td>initial density of trapped carriers</td>
</tr>
<tr>
<td>$N_T$</td>
<td>density of trapping centres having an energy level value of $E_T$</td>
</tr>
</tbody>
</table>
70

$q$  electronic charge
$S_T$  capture cross-section of a trap (energy level value $E_T$) for a free carrier
$\tau$  recombination lifetime
$t$  time
$T$  temperature
$T_m$  temperature at which the current maximum occurs
$T_0$  initial (or lower) temperature
$T_{1/2}$  temperature at which the TSC peak is one half of its maximum height on the low temperature side

4.1.2. **C-V and C-t theory**

$A$  area of metal/semiconductor junction
$C$  capacitance
$C_e$  edge capacitance
$C_0$  capacitance at time $t = 0$
$C_t$  capacitance at time $t > 0$
$C_\infty$  value of capacitance as $t$ becomes very large
$\varepsilon_0$  permittivity of free space
$\varepsilon_r$  relative permittivity
$E_F$  energy level value of the Fermi level
$e_n$  thermal emission rate of the $n$th level
$E_{tn}$  energy level value of the $n$th level
$L_D$  Debye length
$N_A$  concentration of acceptor trapping centres
$N_D$  concentration of donor trapping centres
$N_I$  concentration of ionized impurity centres
\( N_{tn} \) concentration of trapping centres at the nth level

\( N_{tot} \) total number of trapping centres

\( n(w) \) local concentration of mobile majority carriers at the space charge layer edge.

t time

\( V \) applied reverse bias voltage

\( V_d \) diffusion voltage

\( w \) depletion region width

\( y \) perimeter of the contact.

### 4.1.3. Range Theory

\( a \) screening length of the Thomas-Fermi potential

\( a_0 \) Bohr radius \((5.29 \times 10^{-9} \text{ cm})\)

\( e \) electronic charge

\( \epsilon \) dimensionless energy parameter (LSS)

\( E \) particle energy

\( E_d \) displacement energy

\( E_R \) Rydberg energy

\( E_{RC} \) mean recoil energy

\( m \) mass of an atom (Northcliffe and Schilling)

\( M_1, M_2 \) mass of projectile and target atoms (LSS).

\( N \) number of atoms per unit volume

\( N_{Av} \) average atom concentration

\( N(D) \) implanted dose

\( N(E) \) number of displaced atoms produced by a particle of energy \( E \)

\( \rho \) dimensionless range parameter (LSS)
\( r \)  
\text{distance from the nucleus}

\( R \)  
\text{range}

\( R_p \)  
\text{projected range}

\( \Delta R_p \)  
\text{root mean square fluctuation in the range}

\( \sigma_p \)  
\text{primary collision cross-section}

\( S_e \)  
\text{electronic stopping cross-section (LSS)}

\( S_n \)  
\text{nuclear stopping cross-section (LSS)}

\( v \)  
\text{velocity of the particle}

\( V(r) \)  
\text{interatomic potential}

\( Z_1, Z_2 \)  
\text{atomic number of projectile and target atoms}
4.2 Thermally Stimulated Current Theory

4.2.1 Introduction

The theory relating to the thermally stimulated current (TSC) experiment, outlined in section (3.4.2.) will now be examined in detail. The basic equations as derived by Randall and Wilkins\textsuperscript{88} for the case of no re-trapping, and by Garlick and Gibson\textsuperscript{89} for the case where there is some re-trapping, are presented. By making suitable mathematical approximations these equations can be solved to obtain the following trapping centre properties:

i) an energy level value
ii) a capture cross-section
iii) the concentration of trapping centres.

In some cases the variation of the capture cross-section with temperature can also be determined using the analysis of Keating\textsuperscript{90}.

Both Randall and Wilkins and Garlick and Gibson assume that the traps produce discrete energy levels. For high concentrations of defects this may not be the case. I expanded the theories, therefore, to include bands of levels where each band was assumed to have a Gaussian intensity distribution centred about its mean value. This expansion was used (section (6.3.1.2)) to determine the breadth of the energy levels as a function of proton dose.

4.2.2 Derivation of the basic equations

4.2.2.1 General

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Bandgap_figure_for_general_TSC_theory.png}
\caption{Bandgap figure for general TSC theory.}
\end{figure}

\textit{at temperature }T\textit{ at temperature }T_0
Suppose a specimen, doped n-type, has a density $N_T$ of electron traps at an energy level $E_T$ (eV) below the conduction band, and that at some temperature $T$ the Fermi level lies below this energy level at $E_F$ (eV), Fig. (4.1). Then in order to obtain the thermally stimulated current (TSC) curve the specimen is first cooled to a temperature $T_o$ ($T_o << T$) and the trapping centres filled by optical stimulation or suitable biasing. The number of full centres per unit volume will be $n_o$ where $n_o \leq N_T$. $E_F$ now lies above $E_T$. The specimen is then heated up, at a constant rate $\beta$ deg/sec, to the original temperature $T$ and any carriers released into the conduction band are measured as a change in current section (3.4.2.2.). The resulting current/temperature relationship can be analysed to obtain information about the traps. At a fixed temperature $T$, the rate of change of density of trapped carriers is

$$\frac{dn}{dt} = -ne_n + \delta h (H-n) \quad \text{eqn. (1)}$$

$-ne_n$ being the rate of emission of carriers

and $\delta h (H-n)$ being the rate of capture of carriers

where

$e_n$ = thermal emission rate of carriers from the trap

$n$ = density of trapped charge carriers

$h$ = density of free charge carriers

$H$ = density of trapping centres

and $\delta$ = capture coefficient of an empty trap for a free charge carrier.

Similarly, the rate of change of density of free charge carriers is:

$$\frac{dh}{dt} = ne_n - \delta h (H-n) - \gamma hf \quad \text{eqn. (2)}$$

the last term ($-\gamma hf$) taking into account the effect of recombination centres

where $\gamma$ = capture coefficient of recombination,

and $f$ = density of recombination centres.
The thermal emission rate \( e_n \) of electrons from the trap is given by:

\[
e_n = N_c < v > S_T \exp \left( - \frac{E}{kT} \right) \quad \text{ref. (91)}
\]

There are too many unknowns in eqns. (1) and (2) to be able to integrate them (with respect to time and temperature) to solve for the variables in which we are particularly interested, namely \( E_T \) and \( S_T \). The more limited cases, therefore, of no-retrapping and re-trapping in the presence of recombination centres, have to be considered.

4.2.2.2. No re-trapping (Randall and Wilkins equation)

This case has been considered in detail by Randall and Wilkins. They assume that the number of free carriers is small compared to the number of trapped carriers, and remains so, i.e. \( h \ll n \) and \( \frac{dn}{dt} \ll \frac{dn}{dt} \).

The capture term of eqn (1) is therefore zero and

\[
\frac{dn}{dt} = - n N_c < v > S_T \exp \left( - \frac{E_T}{kT} \right) \cdot
\]

These theoretical constraints imply that only results obtained from semi-insulating material, or the depletion region of reversed-biased junctions, can be analysed in this way.

Now if the temperature of the specimen is changing in a linear fashion, such that

\[
dt = \frac{dT}{\beta}
\]

then equation (1) becomes

\[
\frac{dn}{n} = - N_c < v > S_T \exp \left( - \frac{E_T}{kT} \right) \frac{dT}{\beta}
\]

Integrating over the temperature range \( T_0 \to T \)

\[
n = n_o \exp \left( \frac{-N_c < v > S_T}{\beta} \int_{T_0}^{T} \exp \left( - \frac{E_T}{kT} \right) dT \right)
\]
and \[ \frac{dn_c}{dT} = \frac{n_c N_c}{\beta} \exp \left( \frac{E_T}{kT} \right) - \frac{N_c}{\beta} \int_{T_0}^{T} \exp \left( \frac{-E_T}{kT} \right) dT \]

Now the density of carriers in the conduction band \( (n_c) \) will change with time as:

\[ \frac{dn_c}{dt} = -\frac{n_c}{\tau} - \frac{dn_c}{dt} \]

it being assumed that any recombination processes can be described by a term \(-\frac{n_c}{\tau}\), that is there exists a constant recombination lifetime \( \tau \). If this lifetime is very short such that \( \frac{dn_c}{dt} \ll \frac{n_c}{\tau} \) then \( n_c = -\frac{dn_c}{dt} \).

As \( \frac{dn_c}{dt} = \frac{dT}{t} \),

\[ n_c = -\beta \frac{dn_c}{dT} \]

Substituting for \( \frac{dn_c}{dT} \)

\[ n_c = \tau n_o N_c \langle \nu \rangle_S T \exp \left( -\frac{E_T}{kT} \right) - \frac{N_c}{\beta} \int_{T_0}^{T} \exp \left( \frac{-E_T}{kT} \right) dT \].

For several \( i \) energy levels with energies \( E_{T_i} \) and capture cross-sections \( S_{T_i} \),

\[ n_c = \sum_i A_i \exp \left( -\frac{E_{T_i}}{kT} \right) - \frac{N_c}{\beta} \int_{T_0}^{T} \exp \left( \frac{-E_{T_i}}{kT} \right) dT \].

The density of carriers in the conduction band can, therefore, be expressed in terms of some of the properties \( (E_T, S_T) \) of the trapping centres in the bandgap and in terms of the absolute temperature.

It is convenient to relate the carrier density either to the specimen conductivity or to the specimen current. Consequently, any change in temperature, assuming \( \beta \) is a constant, will produce a change in specimen current such that

\[ I = C \exp \left( \frac{-E_T}{kT} \right) - \frac{N_c}{\beta} \int_{T_0}^{T} \exp \left( \frac{-E_T}{kT} \right) dT \] \hspace{1cm} \text{equ. (3)}

where \( C = AE \nu n_o N_c \langle \nu \rangle_S T \).
A is the specimen, or junction area

E is the electric field across the specimen

and \( \mu \) the mobility of carriers.

The general form of equation (3) is known as Randall and Wilkins equation \(^88\).

4.2.2.3. Some re-trapping (Garlick and Gibson's Equation)

This analysis was proposed by Garlick and Gibson \(^89\). They also make the assumption that the number of free carriers is small compared to the number of trapped carriers but they provide for the possibility of re-trapping by assuming that there are recombination centres present. If, the density of recombination centres is assumed to be the same as the density of trapped carriers, i.e. each has density \( n \) then the probability that an escaping carrier will not be re-trapped is \( \frac{n}{H} \) and eqn. (1) is modified so that

\[
\frac{dn}{dt} = -n \left( \frac{n}{H} \right) e^n.
\]

Proceeding in the same way as Randall and Wilkins they obtained

\[
I = \frac{C \exp \left( -\frac{E_T}{kT} \right)}{H \left[ 1 + \frac{N}{e^{\frac{S_T}{H\beta}} \int_{T_0}^{T} \exp \left( -\frac{E_T}{kT} dT \right)^2 } \right]} \tag{eqn (4)}
\]

The problem of finding a value for \( E_T \) and \( S_T \) now reduces to that of solving either eqn (3) or eqn (4) for these variables.

4.2.3. Solutions to the basic equations

Nicholas and Woods \(^92\) discuss the most widely used methods for obtaining a solution of equation (3) or (4). Most involve further approximations or assumptions, usually of a mathematical nature. Some of those examined were:

1. Grossweiner's method \(^93\)
2. Heating rate method \(^75\)
3. Initial rise method \(^89\)
4. Numerical (computer) methods \(^94\)
Methods (1) and (2) are limited in their application either by mathematical or experimental constraints and can only be used where there is no re-trapping. Methods (3) and (4), however, are independent of the trapping kinetics. All the methods allow an energy level value to be obtained. In addition method (2) can provide information on the size of the trap capture cross-section and method (4) the size of the trap capture cross-section and the trapping centre concentration. Because this last method provides the greatest amount of information, it was used throughout, except for the analysis of TSC curves obtained when the trapping centre concentration was very small or the centres were empty. In these cases a current peak is not produced and the initial rise method has to be employed.

4.2.3.1. Grossweiner's method

By simplifying Randall and Wilkins equation, (eqn (3)), and therefore, assuming no re-trapping Grossweiner obtained:

\[ E_T = \frac{1.51 k T_m T_{\frac{3}{2}}}{(T_m - T_{\frac{3}{2}})} \]

where \( T_m \) - peak temperature

\( T_{\frac{3}{2}} \) - temperature at which the curve is one half its peak height on the low temperature side

provided \( E_T/kT > 20 \)

\[ \frac{N_s T_{<\psi>}}{\beta} > 10^7 \]

The first constraint means the method is only suitable for traps deeper than 0.15eV.

4.2.3.2. Heating-rate method

The method involves measuring the TSC curve of a specimen at various heating rates (\( \beta \)). The temperatures at which the current peaks occur (\( T_m \)) will then be shifted. The disadvantages of the technique are firstly, the many TSC curves
which have to be obtained, and secondly the difficulty of separating closely spaced energy levels, and therefore, of obtaining values for $E_T$.

Differentiating eqn. (3) (and so assuming no retrapping) to find the conditions for a current maximum yields

$$\exp \left( \frac{E_T}{kT_m} \right) = \frac{N <\nu> S_T kT_m^2}{\beta E_T}$$

This may be re-written as

$$\log \left( \frac{\frac{T^2}{m}}{\beta} \right) = \frac{E_T}{kT_m} - \log \left( \frac{N <\nu> S_T k}{E_T} \right)$$

Plotting $\log \left( \frac{\frac{T^2}{m}}{\beta} \right)$ as a function of $\frac{1}{T_m}$ yields a straight line of slope $E_T/k$ and hence a value for $E_T$, while the intercept on the $y$-axis can be used to find a value for $S_T$.

4.2.3.3. Initial-rise method

The method depends on the fact that when the traps begin to empty as the temperature is raised, the integrals in eqn (3) and (4), are small and so

$$I = I_o \exp \left( - \frac{E_T}{kT} \right)$$

This means that only the initial portion of the curve need be measured.

TSC curves obtained from specimens where there was no distinct current peak, i.e. when the trapping centre concentration was small or the traps were empty, were analysed in this way (section (5.4.4.2.)).

4.2.3.4. Numerical (computer) methods

One such method, due to Chen and Mohan, was that adopted for the analysis of the TSC curves. The integral term in eqn (3) can be expressed as an asymptotic series.
\[ \int_{T_0}^{T} \exp\left(- \frac{E_T}{kT} \right) dT \approx T \exp\left(- \frac{E_T}{kT} \right) \sum_{n=1}^{\infty} \left( \frac{kT}{E_T} \right)^n \frac{(-1)^{n-1}}{n!} \]

By using just the first two terms of this series, a good approximation to eqn (3) can be obtained, viz.

\[ I \approx C \exp\left(- \frac{E_T}{kT} \right) - B \exp\left(- \frac{E_T}{kT} \right) \left( \frac{kT}{E_T} \right)^2 \]

where

\[ B = \frac{N_{<\gamma>E_T}}{\beta k} \]

B can be approximated by

\[ B \approx \exp\left(- \frac{E_T}{kT\mu}\right) - \left(\frac{E_T}{kT}\right)^3 / \left(\frac{E_T}{kT} + 2\right) \]

The best fit theoretical curve can then be matched to an experimental curve, with \( E_T \) as the variable. The advantages of fitting the whole curve in this way are that one can obtain

a) a value for \( E_T \)

b) a value for the area under the curve, and so the number of trapping centres at any level. The method is particularly useful, where only the low temperature side of the peak is available experimentally, most of the peak on the high temperature side not being recorded due to thermal quenching.

c) a value for the capture cross-section of the trap

d) the properties of shallower trapping levels than is possible by other methods, particularly Grosswein's.

Similar numerical methods can be used to obtain the best fit values to curves of the form of equation (4). In practice the usual method was to obtain a best fit to the experimental curve, first excluding re-trapping i.e., using equation (3), and then with re-trapping using equation (4). A measure of the closeness of each fit was then calculated by summing the squares of the differences between
the experimental points and the corresponding theoretical values. The same
criterion as used by Chen and Mohan for determining $E_T$ was then applied, i.e.
the closer fit, (the smaller total difference), indicated the value of $E_T$, as well as
showing whether re-trapping needed to be taken into account for the centres con-
cerned.

For these reasons, the method was used for the analysis of all TSC curves
where distinct current peaks were obtained.

4.2.4 Keating's analysis

In the derivation of eqn (3), it is assumed that $N_c S_T <\psi>$ is independent
of temperature. But $N_c \propto T^{3/2}$ and $<\psi> \propto T^{1/2}$. Keating takes $N_c S_T <\psi>$ to be
proportional to $T^b$ and $S_T \propto T^{-a}$ where $a = 2-b$. If $N_c S_T <\psi> = GT^b$ then equation
(3) becomes:

$$I = DGT^b \exp \left( -\frac{E_T}{kT} \right) - \int_{T_0}^{T} \frac{GT^b}{\beta} \exp \left( -\frac{E_T}{kT} \right) dT.$$  \text{eqn (5)}

The C of eqn (3) being replaced by $DGT^b$.

Using the asymptotic series

$$\int_{T_0}^{T} T^b \exp \left( -\frac{E_T}{kT} \right) dT \approx \frac{kT^{b+2}}{E_T} \left( 1 - \eta \right) \exp \left( -\frac{E_T}{kT} \right),$$

where

$$\eta = \frac{(b+2) kT}{E_T},$$

equation (5) becomes, taking the log

$$-\ln \left( \frac{1}{DG} \right) = \frac{E_T}{kT} - b \ln T + \left( \frac{T}{T_m} \right)^{b+2} \left( 1 + \frac{b kT_m}{E} \right) (1 - \eta) \ln T - \frac{E_T}{kT}.$$
In the two cases where \( I = \frac{1}{2} \) max at temperatures \( T_1 \) and \( T_2 \) if
\[
\alpha_1 = \frac{T_m - T_1}{T_m}, \quad \text{and} \quad \alpha_2 = \frac{T_2 - T_m}{T_m}
\]
then
\[
(1 - \eta) (1 + \frac{b T_m}{E_T}) + \ln 2 = -\psi - b \ln (1 + x) + (1 + x)^{b+2} (1 + \frac{b T_m}{E_T}) (1 - \eta) \exp \psi \quad \text{eqn (6)}
\]
where
\[
x = \alpha_1 \quad \text{or} \quad \alpha_2
\]
\[
\psi = \frac{E_T}{k T_m} \left( \frac{x}{1 + x} \right)
\]

Provided a value for \( E_T \) is known, equation (6) can be solved numerically to obtain a value for \( b \), and provided \( \frac{E_T}{k T_m} > 10 \), the use of the asymptotic series for the integral term introduces an error of less than 3%. A computer program was written to obtain values of \( b \) from experimental data.

4.2.5. Distributed energy levels

Both Randall and Wilkins and Garlick and Gibson assume that the trapping centre energy levels are discrete. For a highly doped semiconductor, however, this will not be the case. As the donor, or acceptor, concentration increases the associated energy level broadens, eventually overlapping the conduction, (or valence)band. This overlapping produces the so-called band tails. The broad energy level distribution is, in most cases, a normal (Gaussian) distribution.

The implantation of protons results in high damage centre concentrations at the end of the proton range. If each proton creates one vacancy then a dose of \( 10^{15} \text{cm}^2 \) will produce an average vacancy concentration of \( 8 \times 10^{19} \text{cm}^{-3} \), (using the formula given in section (4,5,9,)). This is sufficient to cause energy level broadening of tenths of an eV. I modified the basic theories, therefore, to include Gaussian distributed energy levels and applied the new analysis to the
TSC curves obtained after specimens had been implanted with proton doses in the range $10^{13} - 10^{15} \text{cm}^{-2}$, section (6.3.1.2).

If $N$ is the total number of trapping centres in a Gaussian distribution of energy levels, centred on $E_m$ with a standard deviation of $\Delta E_T$,

\begin{equation}
\int_{-\infty}^{\infty} N(E) \, dE = \int_{-\infty}^{\infty} \text{exp} \left( - \frac{(E - E_m)^2}{2\Delta E_T^2} \right) \, dE
\end{equation}

then

\begin{equation}
N = M \int_{-\infty}^{\infty} \text{exp} \left( - \frac{(E - E_m)^2}{2\Delta E_T^2} \right) \, dE
\end{equation}

where $M$ is a normalization constant. If the distribution is approximately $6 \Delta E_T$ wide, then Randall and Wilkins equation becomes

\begin{equation}
I = C \int_{E_m - 3\Delta E_T}^{E_m + 3\Delta E_T} \text{exp} \left( - \frac{(E - E_m)^2}{2\Delta E_T^2} \right) \left[ \text{exp} \left( - \frac{E}{kT} - \frac{N_c \langle v \rangle}{\beta} \right) \right] \, dE \int_{T_0}^{T} \exp \left( - \frac{E}{kT} \right) \, dT \, dE
\end{equation}

and Garlick and Gibsons equation becomes:

\begin{equation}
\text{eqn. (7)}
\end{equation}
The variation of current peak shape with breadth of energy level.

<table>
<thead>
<tr>
<th>E_T value assuming energy level is discrete (eV)</th>
<th>Breadth of energy level assuming the centre of the distribution is at 1.0 eV (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>10</td>
</tr>
<tr>
<td>o</td>
<td>0.7</td>
</tr>
<tr>
<td>□</td>
<td>0.4</td>
</tr>
<tr>
<td>△</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Fig (4.3)
\[ I = C \left\{ \int_{E_m - 3 \Delta E_T}^{E_m + 3 \Delta E_T} \exp \left( -\frac{(E_m - E)^2}{2 \Delta E_T^2} \right) \left( \frac{\exp \left( \frac{-E}{kT} \right)}{N_c S <\nu> n_0} \right) \int_{T_0}^{T} \exp \left( \frac{-E}{kT} \right) dT \right\} dE \]  

(eqns. 8)

In either case if a value of \( E_m \) is known, then the breadth of the level can be calculated using a curve-fitting program.

Figure (4.3) shows how the TSC peak changes for a level, assumed discrete, 1.0 eV below the conduction band as it broadens in energy. The TSC peaks obtained from the distributed level appear, if they are analysed using eqn (3), to be closer to the conduction band than is actually the case. For example, if the 1.0 eV level is 0.04 eV in width, it would result in a discrete \( E_T \) value of 0.1 eV.

4.2.6 Summary

Analytical expressions for the analysis of TSC curves have been derived by Randall and Wilkins for the case of no re-trapping, and by Garlick and Gibson in cases where there is some re-trapping. These basic equations can be solved using a curve-fitting program, similar to that of Chen and Mohan, to obtain the following trapping centre properties:

1. the energy level value
2. the size of the capture cross-section
3. and the trapping centre concentration.

The variation of the capture cross-section with temperature can also be obtained using Keating's analysis, provided there is no re-trapping and the energy level position is known. The basic theories have been expanded so that the energy level width can be determined from TSC current peaks. It is assumed
that as the damage centre concentration increases, the associated energy level broadens out in the form of a Gaussian distribution.

4.3 C - V Theory

4.3.1 Introduction

C-V measurements on reverse biased metal/semiconductor junctions were used to measure the majority carrier concentration of specimens before and after bombardment (see section (5.4.3.)). The basic theory and the assumptions which are made are outlined in the following section. It is shown that the largest error involved, in such measurements, is in the uncertainty in the width of the depletion region. C-V measurements at different frequencies were used to give an indication of the presence of deep levels in section (5.4.3.).

4.3.2 Basic Theory

The small signal capacitance \( C \) of a reverse biased \( p-n \) junction arises from the charge circulating within the external biasing circuit due to an incremental change of applied bias \( dV \),

\[
C = \frac{1}{dV} \int_{0}^{\infty} i(t) \, dt
\]

The magnitude of the charge is dependent upon the quantity of mobile electrons either removed or added, due to a change in the space charge layer width. This quantity of mobile electrons is \( n(w) \, dw \) where \( n(w) \) is the local concentration of mobile electrons at the space charge layer edge and \( dw \) is the change in the space charge layer width due to the application of \( dV \).

Consequently

\[
C = \frac{1}{dV} \int_{0}^{\infty} i(t) \, dt = qn(w) \frac{dw}{dV} \quad \text{A}
\]
I-V characteristics of Schottky barriers made on proton implanted and unimplanted GaP.

- Implanted (protons, $10^{13}$ cm$^{-2}$, 400 keV)
- Unimplanted
- Medium resistivity Te-doped GaP gold Schottky barriers
Now as

\[ C = \frac{\varepsilon_r \varepsilon_0}{w} \quad A \cdot \frac{dw}{dV} = -\frac{\varepsilon_r \varepsilon_0}{C^2} \quad A \frac{dC}{dV} \]

\[ n(w) = -\frac{C^3}{qA^2 \varepsilon_r \varepsilon_0} \quad \left( \frac{dC}{dV} \right)^{-1} \]

as

\[ \frac{d(C^{-2})}{dV} = -\frac{2}{C^3} \frac{dC}{dV} \]

\[ n(w) = \frac{2}{q\varepsilon_r \varepsilon_0} \frac{A^2}{d\left(\frac{1}{C^2}\right)} \frac{dV}{d\left(\frac{1}{C^2}\right)} \]

which is the normal C-V equation\(^95,96\).

Note that \( n(w) \) is the majority carrier concentration and not the impurity carrier concentration.

The assumptions that have been made are:-

i) one side of the junction is doped to an impurity concentration which is several orders of magnitude greater than the other side. In Schottky barriers this is the case, the depletion region then being almost completely in the low doped side.

ii) the space-charge region

a) contains no mobile carriers, i.e., \( n(w) = 0 \).

This is a valid assumption provided that the electric field across the depletion region is sufficiently high, i.e., greater than \( 10^9 \text{V/cm} \).

b) is free from recombination

Comparison of the I-V characteristics of unimplanted and implanted specimens shows (figure (4.4)) that this is not the case. Radiation damage produces recombination centres which lower \( n(w) \).

iii) terminates abruptly.

The depletion region, however, terminates in a distance approxi-
Variation of Debye length with doping concentration

Debye length m

Doping concentration cm⁻³

Variation of Debye length with temperature

Debye length μm

Temperature °K

for a room temperature doping concentration of $10^{13}$ cm⁻³
nately $6L_D$ where $L_D$ is the extrinsic Debye length defined as

$$L_D = \left( \frac{kT}{q} \frac{\epsilon_r \epsilon_0}{qN} \right)^{\frac{1}{2}}$$

(ref. 97)

where $N = N_D$ or $N_A$. The amplitude of the measuring signal should be less than $kT/q \approx 25$ mV to ensure that the modulation of the edge of the layer does not exceed $6L_D$. It is also seen that the higher the doping concentration the smaller $L_D$. Figure (4.5) plots $L_D$ versus $N$ for GaP. For example, $L_D$ for a specimen doping concentration of $3 \times 10^{17}$ cm$^{-3}$ is $60^\circ$A. For a typical depletion region width of $2000^\circ$A, the uncertainty in $w$ is $\pm 10\%$. The variation of $L_D$ with temperature is shown in figure (4.6). The lower the temperature, the smaller $L_D$.

iii) the dielectric constant $\epsilon_r \epsilon_0$ remains the same for implanted and unimplanted specimens. At the frequencies at which measurements have been carried out, this is the case.

iv) edge capacitance is negligible.

Goodman$^{36}$ has derived the expression for the edge capacitance as $C_e = \epsilon_r \epsilon_0 \pi y/2$ where $y$ is the perimeter of the contact.

For Schottky barriers of $1.5$ mm diameter, which were used throughout, $C_e \approx 0.1$pf which is less than $1\%$ of the smallest capacitance value measured.

v) all the deep levels have responded.

The case where deep levels are present is discussed in section (4.4.2.). Therefore the largest uncertainty in capacitance measurements is in the definition of the space charge layer width provided $A$ is known accurately and the number of recombination centres is small.
4.4 C-t Theory

4.4.1 Introduction

In the above discussion of C-V measurements it has been assumed that at each voltage change $dV$ all the impurity levels respond immediately, implying that only shallow donors or acceptors are present. In the case where deep levels are present, the instantaneous application of a large reverse bias will extend the depletion region to a width which depends upon the ionized shallow levels. At any given time later, however, some fraction of the deep traps will have responded and the depletion region will have moved.

By measuring the capacitance as a function of time ($C-t$), at different temperatures, the energy level values, thermal emission rates and trapping centre concentrations of some of the deep traps can be determined. The analysis, presented in the following section, is by Wronski\(^{58}\). He assumes that at any given temperature the emission of carriers is predominantly from only one level i.e. $e_n << e_{n-1} << e_{n-2} \ldots$ The number of levels contributing to any one C-t curve is found by graphical techniques.

4.4.2 Basic theory (due to Wronski)

Suppose we have a series of deep trapping levels characterised by

- $N_{tn}$ - the number of trapping centres
- $E_{tn}$ - the energy of the level below the conduction band
- $e_n$ - the thermal emission rate for the trap.
at time $t$, the net concentration of ionized impurity centres will be

$$N_I = (N_D - N_A) + N_{tn} (1 - \exp(-e_n t)) + N_{tn-1} (1 - \exp(-e_{n-1} t)) \ldots$$

at $t = 0$

$$C_0^2 = \frac{q \epsilon_r \epsilon_0 A^2}{2(V_d-V)} (N_D - N_A)$$

at $t = \infty$

$$C_{\infty}^2 = \frac{q \epsilon_r \epsilon_0 A^2}{2(V_d-V)} \left( (N_D - N_A) + N_{tn} + N_{tn-1} \ldots \right)$$

if $e_n < e_{n-1}$ then for large $t$ we have

$$C_t^2 = \frac{q \epsilon_r \epsilon_0 A^2}{2(V_d-V)} \left( (N_D - N_A) + N_{tn} (1 - \exp(-e_n t)) + N_{tn-1} \ldots \right)$$

Rearranging this expression gives:

$$C_t^2 = \frac{q \epsilon_r \epsilon_0 A^2}{2(V_d-V)} (N_D - N_A) + \frac{q \epsilon_r \epsilon_0 A^2}{2(V_d-V)} (N_{tn} + N_{tn-1} \ldots)$$

$$- \frac{q \epsilon_r \epsilon_0 A^2}{2(V_d-V)} \cdot N_{tn} \exp(-e_n t)$$
Let $N_{\text{tot}} = N_{\text{tn}} + N_{\text{tn-1}} + N_{\text{tn-2}} \ldots$

then $C_\infty^2 - C_o^2 = \frac{q\varepsilon_0 A^2}{2(V_d-V)}N_{\text{tot}}$

and $C_t^2 = C_o^2 + (C_\infty^2 - C_o^2) - N_{\text{tn}} \exp(-e_n t) \frac{q\varepsilon_0 A^2}{2(V_d-V)}$

rearranging

$$\frac{C_\infty^2 - C_t^2}{C_\infty^2 - C_o^2} = \frac{N_{\text{tn}}}{N_{\text{tot}}} \exp(-e_n t)$$

$$\ln\left(\frac{C_\infty^2 - C_t^2}{C_\infty^2 - C_o^2}\right) = -e_n t + \ln\left(\frac{N_{\text{tn}}}{N_{\text{tot}}}\right)$$

thus if $\ln\left(\frac{C_\infty^2 - C_t^2}{C_\infty^2 - C_o^2}\right)$ is plotted as a function of $t$ the intercept gives

$$\ln\left(\frac{N_{\text{tn}}}{N_{\text{tot}}}\right)$$

and hence $N_{\text{tn}}$, and the gradient gives $e_n$ (ref. 58).

Similarly if $e_n-1 < e_n$ then

$$\ln\left(\frac{C_\infty^2 - C_t^2}{C_\infty^2 - C_o^2}\right) = \frac{N_{\text{tn}}}{N_{\text{tot}}} \exp(-e_n t)) = -e_n t + \ln\left(\frac{N_{\text{tn-1}}}{N_{\text{tot}}}\right)$$

and so on.

A value for $E_{\text{tn}}^-\text{m}

\text{ay now be obtained by making capacitance-time measurements at different temperatures. As } e_n = N_c <\psi> S_T \exp\left(-\frac{E_{\text{tn}}^-}{kT}\right) \text{ so that}$

$$\ln(e_n) = -\frac{E_{\text{tn}}^-}{kT} + \ln(N_c <\psi> S_T) \text{ any plot of } \ln(e_n) \text{ as a function of } 1/T$$

is a straight line with a gradient of $-E_{\text{tn}}^-/k$. The gradient, therefore, yields a value

for $E_{\text{tn}}^-\text{m}. \text{ Again this assumes that } N_c, <\psi> \text{ and } S_T \text{ do not vary with temperature.}$

Alternatively a best fit plot to a curve of the form
\[ e_n = \frac{C}{T^b} \exp \left( - \frac{E_{\text{in}}}{kT} \right) \] could be used.

where \( b > 0 \)

As \( N_c S_T \langle \nu \rangle \) is proportional to \( T^b \), if \( S_T \) does not vary with temperature then \( b = 2 \).

4.5 Range Theory

4.5.1 Introduction

The general range theory of Lindhard, Schiøtt and Scharf\(^{99}\) (LSS) is presented. Their predictions of the heavy ion ranges in compound semiconductors are found to be in good agreement with experimental results. For light ions, \( Z < 10 \), however, their theory seriously overestimates the extent of the elastic collisions, in consequence of which the range is seriously underestimated. Calculations by J. F. Janni\(^{100}\) and Northcliffe and Schilling\(^ {101}\) predict proton ranges for energies \( \geq 100 \) keV with better accuracy.

In the case of light ions most of the nuclear energy loss occurs close to the ion range. If it is assumed that only the elastic collisions produce atomic displacements then the damage and ion ranges (and profiles) will be coincident. The extent of this damage can be estimated using a modification by Sigmund\(^ {111}\) of the theory of Kinchin and Pease\(^ {102}\). This is outlined in section (4.5.10).

4.5.2 Energy loss processes

The energy loss of a charged particle moving through matter with keV energy is determined by screened Coulomb interactions with the target atoms.

There are three main energy loss processes:
a) elastic collisions between the incident ion and the target nuclei \( \frac{dE}{dx} \) 

b) inelastic or electronic processes in which the incident ion excites or ejects atomic electrons \( \frac{dE}{dx} \) 

c) charge exchange processes \( \frac{dE}{dx} \) 

The total stopping power will be 

\[
\left( \frac{dE}{dx} \right)_{\text{tot}} = \left( \frac{dE}{dx} \right)_n + \left( \frac{dE}{dx} \right)_e + \left( \frac{dE}{dx} \right)_{\text{ce}}
\]

Elastic collisions involve large, discrete energy losses and cause significant angular deflection of the ion trajectory. This results in the creation of lattice disorder. Processes (b) and (c), involving much smaller energy losses per collision, produce little disorder.

The relative importance of the two main mechanisms, a) and b), changes rapidly with the energy and atomic number of the incident ion. In general, nuclear stopping, (a), pre-dominates for low energy and high atomic number; whereas electronic stopping, (b), pre-dominates for high energy and low atomic number.

4.5.3. The Interatomic Potential

At a distance \( r \) from the nucleus, charge \( Ze \), the potential due to the nucleus, is reduced by the screening effect of the orbital electrons.

In general, 

\[ V(r) = \frac{Ze}{r} \cdot \psi \left( \frac{r}{a} \right) \]

where \( \psi \left( \frac{r}{a} \right) \) is the screening function and \( a \) the screening length.

At small separation distances the potential is repulsive and a Bohr screening function \( \psi \left( \frac{r}{a} \right) = \exp \left( -\frac{r}{a} \right) \) can be used. At large separations, the Coulomb law describes the interaction. For ion implantation, however, the ion-atom separation is between these two cases. In this region the potential can be best described by Bohr's equation, modified using Thomas-Fermi statistics\(^{103,104} \) which gives
\[ V(r) = \frac{Z_1 Z_2 e^2}{r} \phi_{T.F.}(r/a) \]

where \( V(r) \) is the interatomic potential, and \( a \) is the screening length measured in units of \( a = 0.8853a_0 \left( Z_1^{2/3} + Z_2^{2/3} \right)^{-1/2} \).

4.5.4. Ion ranges (LSS)

Lindhard, Scharf, Schiott\(^{99,106}\) (LSS), based their calculations on a universal nuclear stopping cross-section \( S_n \), calculated from a Thomas-Fermi model of the interaction between heavy ions, and an electronic stopping cross-section \( S_e \), proportional to the velocity, \( v \), of the incoming particle. Energy and range are expressed as the dimensionless parameters \( \varepsilon \) and \( \rho \), where

\[ \varepsilon = \frac{E a M_2}{Z_1 Z_2 e^2 (M_1 + M_2)} \]

\[ \rho = \frac{R N M_2 4\pi a^2 M_1}{(M_1 + M_2)^2} \]

Then, the nuclear stopping power \( \frac{d\varepsilon}{d\rho} \) is a function of \( \varepsilon \) only and the electronic stopping power is represented by \( \frac{d\varepsilon}{d\rho} \varepsilon = k \varepsilon^{3/2} \),

where

\[ k = \frac{0.0793 Z^{1/3} M_{3/2} (M_1 + M_2)^{3/2}}{(Z_1^{2/3} + Z_2^{2/3})^{3/4} M_1^{3/2} M_2^{1/2}} \]

Johnson and Gibbons\(^{107}\) have produced a set of tables based on this theory. Predictions of the range for heavy ions in compound semiconductors are found to be in good agreement with the experimental results. However, in the case of light ions, \( Z \leq 10 \), the LSS theory overestimates the extent of the inelastic collisions; in consequence of which the range is seriously underestimated figure (4.8).
4.5.5. Proton ranges

4.5.5.1. Northcliffe and Schilling

Northcliffe and Schilling have generated a set of semi-empirical stopping power curves from which the calculated range-energy relations for proton energies $\geq 100$ keV are in good agreement with the available range data. The basis of their stopping-power curves is the assumption that the relative stopping power of two materials is independent of ion identity at a given ion velocity. If the subscripts $A$, $B$, denote two different materials and the subscripts $p$, $q$ denote different ions, it is assumed that at equal ion velocities:

where $E_p$, $E_q$ is the energy and $m_p$, $m_q$ are the masses of the particles.

$$\frac{E_p}{m_p} = \frac{E_q}{m_q}$$

and

$$\frac{(dE/dx)_{p,A}}{(dE/dx)_{p,B}} = \frac{(dE/dx)_{q,A}}{(dE/dx)_{q,B}}$$

In addition it is assumed that the relative stopping power varies smoothly with material $Z$ and ion $E/m$, and that the stopping power varies smoothly with the ion atomic number and $E/m$.

By applying these assumptions to a set of experimentally determined stopping power curves for various ions into aluminium, stopping power curves for various ions into other materials were generated. Range data was then obtained by calculating an "electronic range"

$$R(E) = \int_0^E \left( -\frac{dE}{dx} \right)^{-1} dE$$

where $-\frac{dE}{dx} = kE^{\frac{3}{2}}$, the constant $k$ being chosen to fit experimental data for small $E$. 
Projected range as a function of energy for protons into gallium phosphide.

Fig 4B

Energy keV

Projected Range μm

Janni (ref 100)

Northcliffe (ref 101) & Schilling

LSS, (ref 99)
The effective charge of a low energy proton in air

Effective proton charge

from J.F. Janni ref (100)

Energy eV

Fig (4.9)
A nuclear stopping correction based on the LSS tables was then applied. This gives good agreement with the available experimental data above 100keV.

4.5.5.2. J. F. Janni

J. F. Janni\(^{100}\) has also produced a set of proton range data, for energies \(\geq 100\text{keV}\), using a similar approach to Northcliffe and Schilling. He found that below 1MeV the proton capture cross-section for atomic electrons increases significantly, so that a proton transversing matter may have a rapid exchange of electrons with the nearby atoms of the absorber. This has the net effect of reducing the effective charge of the proton to a value which is less than unity. Figure (4.9) shows the effective charge of a proton at different energies in air. Even taking this charge effect into account, however, Janni obtained poor agreement between his theoretical range predictions (using the Bethe\(^{108}\) equation) and the experimental results available. He, therefore, smoothed and interpolated as much experimental information as he could find in order to predict proton ranges for energies 0.1 - 1.0 MeV.

4.5.6. Summary of range data

Figure (4.8) shows the ranges as a function of energy, predicted by the different theories or calculations, for protons into GaP.

The results of Northcliffe and Schilling and J. F. Janni are seen to be similar. The LSS range data was calculated using the computer program published in the set of tables by Johnson and Gibbons. This program was adapted to the University ICL 1905F machine by M. Deery\(^{85}\).

4.5.7. The Projected range

![Particle trajectory diagram](image-url)

**Fig. 4.10**
The conversion factor necessary to obtain the projected range \( R_p \) from the total range \( R \) is

\[
R = R_p \left(1 + \frac{bM_2}{M_1} \right),
\]

where \( b \) is a slowly varying function of energy and range. If the incident particle was to suffer no inelastic processes then \( R_p = R \) and \( b = 0 \). If nuclear stopping predominates, and \( M_1 > M_2 \), then \( b = 1/3 \) (ref. 98).

4.5.8. Standard deviation of the ion range

Because of the random nature of the collision processes, there will be a spread in range about the mean, approximately following a Gaussian distribution. Lindhard gives the following expression for the relative "straggling" where nuclear stopping pre-dominates i.e.

\[
\frac{\Delta R_p}{R_p}^2 = \frac{2M_1M_2}{3(M_1 + M_2)^2}
\]

where \( \Delta R_p \) is the root mean square fluctuation in the range. Again, the LSS theory, because it overestimates the amount of nuclear stopping, overestimates \( \Delta R_p \). This can be seen from Table 4.1. which lists the range and projected range, (with associated standard deviation) for protons at various energies using the LSS theory, and the projected range and standard deviation from Janni's theory.

**Proton range data**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.212μ</td>
<td>0.847μ</td>
<td>1.14μ</td>
<td>89A</td>
<td>1212A</td>
<td>300A</td>
</tr>
<tr>
<td>200</td>
<td>1.733μ</td>
<td>1.35μ</td>
<td>2.09μ</td>
<td>92A</td>
<td>1299A</td>
<td>400A</td>
</tr>
<tr>
<td>300</td>
<td>2.14μ</td>
<td>1.75μ</td>
<td>3.12μ</td>
<td>93A</td>
<td>1334A</td>
<td>500A</td>
</tr>
<tr>
<td>400</td>
<td>2.48μ</td>
<td>2.08μ</td>
<td>4.30μ</td>
<td>93A</td>
<td>1352A</td>
<td>600A</td>
</tr>
</tbody>
</table>

Table (4.1.)
Table (4,2) shows the projected ranges and standard deviations, in brackets, at different energies for important dopants in gallium phosphide.

The values (in Ångstroms) were calculated using the LSS program, adapted to the University computer by M. Deery.

### LSS range data for various ions into GaP

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (keV)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td></td>
<td>1787</td>
<td>3526</td>
<td>5100</td>
<td>6556</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(654)</td>
<td>(1010)</td>
<td>(1242)</td>
<td>(1410)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td>2047</td>
<td>3875</td>
<td>5708</td>
<td>7286</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(731)</td>
<td>(1094)</td>
<td>(1324)</td>
<td>(1484)</td>
</tr>
<tr>
<td>Sulphur</td>
<td></td>
<td>868</td>
<td>1752</td>
<td>2639</td>
<td>3524</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(331)</td>
<td>(577)</td>
<td>(774)</td>
<td>(946)</td>
</tr>
<tr>
<td>Tellurium</td>
<td></td>
<td>330</td>
<td>578</td>
<td>820</td>
<td>1059</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(82)</td>
<td>(140)</td>
<td>(192)</td>
<td>(241)</td>
</tr>
<tr>
<td>Cadmium</td>
<td></td>
<td>343</td>
<td>610</td>
<td>871</td>
<td>1132</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(92)</td>
<td>(157)</td>
<td>(216)</td>
<td>(272)</td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td>475</td>
<td>902</td>
<td>1347</td>
<td>1801</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(159)</td>
<td>(280)</td>
<td>(394)</td>
<td>(500)</td>
</tr>
</tbody>
</table>

Table (4,2)
4.5.9. Average atom concentration

The average implanted atom concentration $N_{Av'}$ in the region around $R_p$, assuming that an approximately Gaussian distribution is produced, can be estimated using the formula

$$N_{Av'} \approx \frac{N(D)}{2.5\Delta R_p}$$

where $N(D)$ is the implanted dose.

4.5.10. Displacement theory

A lattice atom will recoil from its site if the energy it acquires from an incident particle is greater than its displacement energy ($E_d$). If this primary recoil energy is sufficiently large then further atomic collisions will occur ejecting other (secondary) atoms and producing a damage cascade of vacancy-interstitial pairs. For a light energetic ion the primary interaction can be described in terms of a simple Coulomb collision. Rutherford's scattering law, therefore, applies. Thompson\textsuperscript{110} has shown that using this law, the cross-section ($\sigma_p$) for an initial displacement at energy $E$ is:

$$\sigma_p = \frac{4\pi a_0^2 M_1 Z_1^2 Z_2^2 E^2}{E M_2} \left(1 - \frac{E_d}{AE}\right)$$

and the mean recoil energy $E_{RC}$ is:

$$E_{RC} = \frac{Ed \log \frac{AE}{E_d}}{1 - \frac{E_d}{AE}}$$

where $\Lambda = \frac{4M_1 M_2}{(M_1 + M_2)^2}$ and $E_R$ is the Rydberg energy.

The number of secondary displacements can then be estimated using the formula:\textsuperscript{11}

$$N(E) = \frac{E_{RC}}{2Ed}$$
where $g$ is a factor $< 1$, and depends upon the atomic interaction $^{112,113}$.

This formula is a modification of an equation by Kinchin and Pease $^{102}$ in which the following assumptions were made.

1) there is no recombination of closely spaced vacancy-interstitial pairs
2) there is no spatial variation in $E_d$ due to existing damage centres
3) an atom recoiling with energy $T$ is displaced if $T > E_d$.
4) no energy is lost if $T > E_d$; whilst all the energy is lost if $T < E_d$.
5) they are elastic collisions involving hard spheres.

These approximations mean that $N(E)$ is an overestimation and so the value of $N(E)$ obtained is an upper limit.

The equations above were used to estimate the extent of the proton damage as a function of energy in section (6.3.2.).
Chapter 5

RESULTS

5.1 Introduction

In this chapter the experimental results are presented. They will be discussed in chapter 6. Measurements were made on specimens cut from three different slices of gallium phosphide purchased from the Mining and Chemical Products Ltd. (MCP).

Table (5.1) summarizes the properties of the slices.

<table>
<thead>
<tr>
<th>Material Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. No.</td>
</tr>
<tr>
<td>GPC 328</td>
</tr>
<tr>
<td>GPC 270</td>
</tr>
<tr>
<td>GPC 400</td>
</tr>
</tbody>
</table>

Table (5.1)

All the specimens were polished on the (111) i.e. the B(P) face and were implanted at 7° off the <111> to avoid any major channel.

The majority of specimens were implanted with protons for reasons discussed in section (1.2.4). The first set of results sections (5.3) and (5.4) are of measurements made on the three types of material to evaluate some of the properties of the deep levels present before and after the proton implantation.
An investigation of the number of deep centres introduced into the semi-insulating material as a function of proton dose, section (5.5.2) and proton energy, section (5.5.3), is then presented. The annealing behaviour of the damage was also examined section (5.5.4). The final section (5.6) describes the type of damage produced by a medium Z ion, sulphur, when implanted into the medium resistivity material. A comparison can then be made between the damage produced by protons and that produced by sulphur ions.

The techniques described in section (3.4) were used to measure some of the properties of the deep levels. The TSC method was employed in the case of the semi-insulating material whilst for the medium and low resistivity materials, although a few TSC measurements were made, the capacitance-time method, for reasons already discussed, was found to be the most suitable.

5.2 Implantation of specimens

Samples were implanted using the 600 keV accelerator described in section (3.2.1).

Implantation energies were in the range 15 - 400 keV and implanted doses in the range $2 \times 10^{10} - 10^{15}/\text{cm}^2$. Picraux and Vook\textsuperscript{114} have shown by Rutherford Backscatter techniques\textsuperscript{115, 116} that the amount of damage produced in silicon by various ions depends not only upon the ion energy and dose but upon the implantation temperature and the dose rate. Consequently samples were bombarded at a fixed temperature, i.e., room temperature, and at a proton dose rate of $50 \pm 10\text{nA/cm}^2$. All specimens were orientated 7° off the $<111>$ to avoid major channelling directions.

5.3 Trapping centres in semi-insulating GaP

5.3.1 Deep energy levels

All the measurements were made using the TSC technique. An example of a TSC curve is shown in figure (5.1). A total of eight different current peaks,
A thermally stimulated current curve obtained from proton implanted (300 keV, $10^{13}$/cm$^2$) GaP

Each current peak indicates the presence of trapping centres which produce a corresponding energy level as shown.

- Curve A: traps filled by optical excitation at 77K
- Curve B: traps empty

Thermocouple reference junction at 273K
Thermocouple (mV) Temperature (°K)

Fig(5.1)
and therefore of eight different deep levels, were found in the 44 specimens examined.

Using the analysis of section (4.2.2 and 4.2.3.) some of the properties of these deep levels are tabulated below (table (5.2)). Ninety per cent of the energy level values obtained were within the limits shown, whilst the majority (70%) of the capture cross-sections were to within (plus or minus) half an order of magnitude of the values indicated. Although there is this spread in the capture cross-section values they can still be used to indicate the type of trapping centre by comparing them with the bands (usually a few orders of magnitude) of cross-section sizes defined by Lax section (6.2.2.1.).

In some cases the table also includes the variation of the capture cross-section with temperature section (4.2.4.). These were calculated using the mean energy level values shown in the first column.

<table>
<thead>
<tr>
<th>Energy level (eV)</th>
<th>Capture cross-section at 300K (cm^2)</th>
<th>The capture cross-section is proportional to T^-n where n =</th>
<th>Temperature at which current peak occurs, for a heating rate of 0.3°K/sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19 ± 0.03</td>
<td>1.0 x 10^-14</td>
<td>3.2</td>
<td>84.1</td>
</tr>
<tr>
<td>0.22 ± 0.02</td>
<td>5.0 x 10^-16</td>
<td>4.5</td>
<td>115.4</td>
</tr>
<tr>
<td>0.35 ± 0.03</td>
<td>5.0 x 10^-12</td>
<td>3.2</td>
<td>140.5</td>
</tr>
<tr>
<td>0.43 ± 0.03</td>
<td>1.0 x 10^-11</td>
<td>4.4</td>
<td>159.1</td>
</tr>
<tr>
<td>0.48 ± 0.03</td>
<td>1.0 x 10^-12</td>
<td>4.5</td>
<td>167.2</td>
</tr>
<tr>
<td>0.75 ± 0.04</td>
<td>5.0 x 10^-15</td>
<td>2.9</td>
<td>291.9</td>
</tr>
</tbody>
</table>

Table (5.2)
The TSC curves obtained from an implanted specimen using different methods to fill the trapping centres.

Current scales (amps): --- max $8 \times 10^{-11}$ A --- max $2.4 \times 10^{-10}$ A --- max $8 \times 10^{-12}$ A ---

- Curve (a): traps filled by optical excitation at 77 K.
- Curve (b): traps filled by increasing the bias at 77 K.
- Curve (c): traps empty.

Thermocouple reference junction at 294 K.

Thermocouple (mV) vs Temperature (°K):

Fig (5, 2)
5.3.2. Energy level positions in the bandgap

An indication of the bandgap position of the energy levels (i.e. whether the levels are in the lower or upper halves of the bandgap) can be obtained by the experimental method described in section (3.4.2.2.).

Figure (5.2) shows the TSC curves, for an implanted specimen, obtained after optical excitation at 77°K, (curve (a)) and after increasing the bias at 77°K (curve (b)). In the latter case the bias applied during cooling down was such that the depletion region was less than the proton range, whilst the bias applied during warming up was greater than the proton range. The energy levels produced by the implantation would, therefore, be included in the change of depletion region width. Comparison of the two curves indicates (section 3.4.2.2.2.) that the 0.19, 0.22 and 0.61 eV levels lie in the upper half of the bandgap.

5.3.3. Comparison of implanted with unimplanted material

Measurements on unimplanted material showed that traps which produced energy levels of 0.19, 0.22, 0.35, 0.4, 0.48 and 0.61 eV's were present. The implantation of protons increased the number of trapping centres producing the 0.19, 0.4 and 0.61 eV levels and introduced additional levels at 0.24 and 0.75 eV.

5.4. Trapping centres in medium and low resistivity GaP

5.4.1. Introduction

Initial measurements on unimplanted material indicated the maximum depth into the materials which could be examined by Schottky barrier techniques and, therefore, the maximum proton energy which could be used in each case. For medium resistivity material this was 400 keV, for low resistivity material 15 keV. (Section (5.4.2.)). A qualitative examination of the deep levels in both
unimplanted and implanted materials section (5.4.3.) using C-f techniques is followed by measurements (TSC and C-t) which yield more quantitative information about the trapping centres responsible (sections (5.4.4. and 5.4.5.)). A total of eight specimens were examined; two unimplanted and two implanted for both types of material.

5.4.2. Initial measurements

Capacitance-voltage measurements confirmed the majority carrier concentration values as stated by MCP (table (5.1)), whilst G-V measurements provided experimental values for the reverse breakdown voltages $V_{BR}$.

Table (5.3) shows typical experimental reverse breakdown voltages ($V_{BR}$) for the different slices, together with the corresponding depletion width ($w$).

The reverse breakdown voltage and the depletion region width for metal/semiconductor junctions made from medium and low resistivity GaP.

<table>
<thead>
<tr>
<th>Material</th>
<th>Theoretical $V_{BR}$ from ref. (83)</th>
<th>Experimental $V_{BR}$ in the range</th>
<th>Maximum Depletion Width ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium Resistivity</td>
<td>850</td>
<td>25-30</td>
<td>4.0</td>
</tr>
<tr>
<td>Material</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Resistivity</td>
<td>30</td>
<td>7-10</td>
<td>0.2</td>
</tr>
<tr>
<td>Material</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (5.3)

From this table, assuming no compensation effects take place, the maximum implantation energy for protons, which ensures that the resulting distribution is all within the maximum depletion region, is $\sim 400$ keV for the medium resistivity material and $\sim 15$ keV for the low resistivity material. The whole of the distribution can be analysed, therefore, using capacitance techniques. The implant-
The capacitance as a function of frequency for both unimplanted and implanted medium resistivity material.
The capacitance as a function of frequency for both unimplanted and implanted low resistivity material.
The majority carrier concentration as a function of frequency for unimplanted low resistivity material.
$1/C^2-V$ relationships at different frequencies for proton implanted medium resistivity material

Implant: 400 keV
2 x 10^{-10} cm$^2$

Fig (5,6)
tation of some species, protons in particular, compensate n-type material,
increasing $V_{BR}$ so that a region as deep as the ion range can be examined, even
if this is larger than the maximum depletion depth for unimplanted material. For
example, a 400 keV implant (range 4.3μ) into medium resistivity material increased
$V_{BR}$ (experimental) from 25 to 35 volts.

5.4.3 Capacitance - Frequency measurements

Figures (5.3, 5.4) show the results from a set of 4 specimens i.e. the
capacitance as a function of frequency for medium and low resistivity materials,
unimplanted and implanted. By making $C - V$ measurements at different frequen-
cies it was possible to plot the majority carrier concentration as a function of
frequency figures(5.5, 5.6). Table (5.4) summarizes the results. The Copeland
apparatus was employed to make measurements at 5.7 MHz.

<p>| Majority carrier concentration measurements on medium and low resistivity GaP |
|-------------------------|-------------------------------|-------------------------------|-------------------|
| Carrier concentration  | Carrier concentration         | Introduction rate          |</p>
<table>
<thead>
<tr>
<th>cm$^{-3}$</th>
<th>Unimplanted material</th>
<th>Implanted Material</th>
<th>cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium Resistivity</td>
<td>1 kHz</td>
<td>$2.2 \times 10^{15}$</td>
<td>$3.41 \times 10^{16}$</td>
</tr>
<tr>
<td>Material</td>
<td>100 kHz</td>
<td>$1.8 \times 10^{15}$</td>
<td>$2.13 \times 10^{16}$</td>
</tr>
<tr>
<td></td>
<td>5.7 MHz</td>
<td>$1.0 \times 10^{15}$</td>
<td>not measurable</td>
</tr>
<tr>
<td>Low Resistivity Material</td>
<td>1 kHz</td>
<td>$3.97 \times 10^{17}$</td>
<td>$5.42 \times 10^{17}$</td>
</tr>
<tr>
<td></td>
<td>100 kHz</td>
<td>$3.49 \times 10^{17}$</td>
<td>$3.83 \times 10^{17}$</td>
</tr>
<tr>
<td></td>
<td>5.7 MHz</td>
<td>$3.0 \times 10^{17}$</td>
<td>not measurable</td>
</tr>
</tbody>
</table>

The table shows that

a) the number of deep trapping centres has increased after implantation

b) the number of majority carriers, at high frequencies, was below the detection
   limit of the Copeland apparatus, which is $5 \times 10^{14}$ cm$^{-3}$.
Thermally stimulated current curves obtained from proton implanted (10^9 cm^-2, 15 keV) low-resistivity GaP with zero-bias across the metal/semiconductor junction.

The current peak indicates the presence of trapping centres which produce a corresponding energy level as shown.

Curve A: traps filled by optical excitation at 77 K.
Curve B: traps empty.

Thermocouple reference junction at 273 K.

Thermocouple (mV)

Temperature (°K)

Fig (5,7)
5.4.4. Thermally Stimulated Current Measurements

5.4.4.1. TSC results

The same specimens as were used for the capacitance-frequency measurements, were also examined by thermally stimulated current techniques. Employing a gold Schottky barrier, it was possible to apply reverse biases of a few volts, to the medium resistivity material, before leakage currents swamped trapping level effects; whilst for the low resistivity material, only half a volt could be used. In general, currents of $10^3 - 10^6$ times greater than those in the semi-insulating material were obtained, the diodes also being very much more noisy.

Figure (5.7) shows a TSC curve. Using the same experimental techniques (as for the semi-insulating material), table (5.5) below summarizes the results.

Some properties of the trapping centres found in medium and low resistivity GaP using the TSC technique

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy Level (eV)</th>
<th>Capture cross-section at 300°K (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium Resistivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unimplanted</td>
<td>0.69 $\pm$ 0.03</td>
<td></td>
</tr>
<tr>
<td>Implanted</td>
<td>0.59 $\pm$ 0.03</td>
<td>$1.0 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>0.71 $\pm$ 0.02</td>
<td>$5.0 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low resistivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unimplanted</td>
<td>0.02 $\pm$ 0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.45 $\pm$ 0.03</td>
<td>$5.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>Implanted</td>
<td>0.04 $\pm$ 0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.35 $\pm$ 0.02</td>
<td>$5.0 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Table (5.5)
The natural logarithm of the current through a metal-semiconductor junction plotted against the reciprocal of the temperature (computer printout).

Fig 5.8

- slope gives $E = 0.31\,\text{eV}$
- slope gives $E = 0.05\,\text{eV}$

low resistivity GaP implanted with protons $15\,\text{keV}, 10^6\,\text{cm}^{-2}$. 

Log Current $- 1/T$
5.4.4.2. Further analysis

In cases where no current peaks are present, for example, where the number of trapping centres is very low, or the trapping centres are empty, the current/temperature relationship can be described approximately by

\[
I = I_0 \exp \left( \frac{-E_T}{kT} \right)
\]

section (4.2.3.3.).

Plotting the natural logarithm of the current against the reciprocal of the temperature, an example of which is shown in figure (5.8), energy levels in the band gap can be determined. Table (5.6) shows the results obtained from each specimen using this method.

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy levels (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium resistivity</td>
<td></td>
</tr>
<tr>
<td>Unimplanted</td>
<td>0.09, 0.09</td>
</tr>
<tr>
<td></td>
<td>0.19, 0.18</td>
</tr>
<tr>
<td>Implanted</td>
<td>0.19, 0.20</td>
</tr>
<tr>
<td></td>
<td>0.22, 0.23</td>
</tr>
<tr>
<td>Low resistivity</td>
<td></td>
</tr>
<tr>
<td>Unimplanted</td>
<td>0.007, 0.005</td>
</tr>
<tr>
<td></td>
<td>0.012, 0.018</td>
</tr>
<tr>
<td></td>
<td>0.04, 0.03</td>
</tr>
<tr>
<td></td>
<td>0.13, 0.16</td>
</tr>
<tr>
<td>Implanted</td>
<td>0.015, 0.018</td>
</tr>
<tr>
<td></td>
<td>0.06, 0.07</td>
</tr>
<tr>
<td></td>
<td>0.3, 0.3</td>
</tr>
</tbody>
</table>

Table (5.6)
The capacitance of a metal/semiconductor junction as a function of time.

(time reverse bias is applied at t=0)

Medium resistivity material implanted with protons 400 keV, 2 x 10^13 cm^-2 bias -40 V, temperature 8°C.
The electron thermal emission rate ($e_p$) for a trapping centre having a level 0.09 eV below the conduction band as a function of temperature.

**EMISSION CONSTANT VERSUS TEMPERATURE** (computer printout)

- low resistivity GaP
- unimplanted

**Fig 5.10**
5.4.4.3. Position in the band gap

In the case of the medium resistivity material, a 0.22 eV level is introduced by the implantation process; for the low resistivity material a 0.3 eV level. Changing the reverse bias of the Schottky barrier at low temperatures, the 0.22 eV level was determined to be in the upper half of the band gap, the 0.3 eV level in the lower half.

5.4.5. Capacitance - Time measurements

The method, analysis and apparatus have already been described, section (3.4.4.6.). From the capacitance time curves, an example of which is shown in figure (5.9), the thermal emission rate \( e_n \) of the traps can be calculated; the variation of the different \( e_n \) with temperature figure (5.10) enables energy level values to be obtained section (4.4.2.).

Two specimens of each kind were examined (i.e., two implanted and two unimplanted). The energy level values for each specimen are given in table (5.7).

Results of capacitance - time measurements

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy Levels (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium resistivity</td>
<td></td>
</tr>
<tr>
<td>Unimplanted</td>
<td>0.33, 0.4</td>
</tr>
<tr>
<td></td>
<td>0.45, 0.44</td>
</tr>
<tr>
<td></td>
<td>0.64, 0.61</td>
</tr>
<tr>
<td>Implanted</td>
<td>0.61, 0.63</td>
</tr>
<tr>
<td></td>
<td>0.7, 0.69</td>
</tr>
<tr>
<td>Low resistivity</td>
<td></td>
</tr>
<tr>
<td>Unimplanted</td>
<td>0.05, 0.06</td>
</tr>
<tr>
<td></td>
<td>0.09, 0.085</td>
</tr>
<tr>
<td>Implanted</td>
<td>0.24, 0.23</td>
</tr>
<tr>
<td></td>
<td>0.31, 0.32</td>
</tr>
</tbody>
</table>

Tables (5.7)
The number of full trapping centres as a function of optical stimulation time (each curve is labelled according to the energy level produced by the centres).

Number of full trapping centres

Optical stimulation time (seconds)

Fig(5.12)
5.5 Trapping centre concentration measurements on semi-insulating GaP

5.5.1 Reproducibility

5.5.1.1 Introduction

By integrating the area under each current peak curve (section 3.4.2.5.) the number of trapping centres for each level can be estimated. If each centre releases only one carrier then the actual number of centres can be determined. On the other hand if the number of carriers released from each centre is unknown then the absolute number of centres is also unknown. The relative concentrations of centres as a function of proton dose or energy, however, will not be affected.

Each specimen was thermally cycled several times until the TSC curves obtained were reproducible. Factors which then affect the area under the current peaks are

a) the initial number of centres which are full. This is determined by the optical excitation time and the optical intensity.

b) the proportion of the carriers which are not re-trapped. This will depend upon the electric field across the specimen.

5.5.1.2 Effect of optical excitation time and optical intensity

Measurements made on a specimen implanted with a proton dose of \(10^{13} \text{cm}^{-2}\) at 300 keV, figures(5.11, 5.12), shows that the number of full trapping centres (for each type of centre) as a function of optical excitation time reaches a saturation value after about 50 seconds. An illumination time of 300 seconds was used in all subsequent experiments to ensure total occupancy. The number of levels observed was not dependent upon the excitation time; an effect which has been reported for GaAs.

The same intensity of illumination was used for all experiments.
TSC curves as a function of electric field across the depletion region.

Current scale: $10^3 \text{ s.d.}$

Average electric field over temperature range of curve A is approx $4 \times 10^3 \text{ V/cm}$

B : 50

C : 75

All curves from the same proton implanted (300 kV 10^16 cm^-2) specimen.

Fig (5.13)
The number of carriers collected from the centres responsible for each energy level as a function of the electric field across the depletion region.
The number of carriers collected, from the traps responsible for the 0.61eV and 0.75eV levels, as a function of the electric field across the metal-semiconductor depletion region.
5.5.1.3. Effect of the electric field

The ways in which the electric field can affect the number of centres measured has been discussed already in section (3.4.2.7.). The variation of the number of full trapping centres as a function of electric field, for a specimen implanted with a proton dose of $10^{13}$ cm$^{-2}$ at 300 keV, is shown in figures (5,13-15). It was assumed that all of the voltage applied to the specimen appeared across the reverse biased metal/semiconductor depletion region, the width of which was found by measuring its capacitance section (3.4.2.5.). Under all field conditions the depletion region width was greater than the proton range. Any change in width was taken into account when constructing the curves for centres which were present in the bulk material. The number of centres, producing the 0.19, 0.24, 0.35, 0.48 and 0.61 eV levels, reach saturation values for fields greater than $6 \times 10^3$ V/cm. The traps producing the 0.22 eV level show little field dependence whilst the numbers of centres, producing the 0.4 and 0.75 eV levels, show no indication of approaching any saturation values.

The higher the electric field the higher the carrier velocity and, therefore, the lower the probability that a carrier, released from a centre, will be re-trapped. This elimination of re-trapping has been shown to be the primary effect of the electric field, section (3.4.2.7). The velocity of the carriers is independent of the number of carriers but may depend upon the number of trapping and/or recombination centres in the material. The electric field dependence of the number of centres in figures (5,13-15) may, therefore, be dose dependent. To test this proposition, electric field measurements were also made on specimens implanted with doses of $10^{12}$ cm$^{-2}$ and $10^{15}$ cm$^{-2}$, and compared with the results from the specimen implanted with a dose of $10^{13}$ cm$^{-2}$ (tables (5.8, 5.9, 5.10, 5.11)). In each case, the...
TSC curves from two different specimens after similar proton implantations

- S.I.16 [300 keV, $10^{14}$ cm$^{-2}$ protons]
- S.I.15 [300 keV, $10^{14}$ cm$^{-2}$ protons]

Fig(5.16)
number of centres measured at the highest value of electric field is taken as the reference point. The number of centres at lower field values are then compared with the highest field values in terms of a percentage. In each case the variation of the number of centres with electric field is to within ±5% of the variation found in the specimen implanted with a dose of $10^{13}$ cm$^{-2}$ for the levels introduced by the implantation. The field dependence results in figures (5.13-15) were used, therefore, to compare the trapping centre concentrations in different specimens, independent of the implanted dose. For each type of centre, results were normalized to the same field value.

5.5.1.4. Comparison of specimens

Tables (5.12-16) compare the number of centres introduced by the implantation for several specimens implanted on different occasions under the same implantation conditions. Table (5.12) compares specimens implanted with a dose of $10^{13}$ cm$^{-2}$ at 300 keV; table (5.13) those implanted with a dose of $10^{15}$ cm$^{-2}$ at 300 keV, whilst table (5.14) compares specimens implanted with a dose of $10^{13}$ cm$^{-2}$ at 200 keV. Table (5.15) compares two specimens which were annealed at the same temperature of 300°C after being implanted with a dose of $10^{13}$ cm$^{-2}$ at 300 keV; while table (5.16) compares unimplanted specimens. After taking the electric field effect into account the number of centres introduced into the specimens agreed to within a worst case of ±11%. In the following groups of results, the dose dependence section (5.5.2.), the energy dependence section (5.5.3), and the annealing behaviour section (5.5.4), the error based on the results above was estimated to be ±10%. This is small compared to the order of magnitude changes which are brought about by increases in the proton dose etc.

Some specimens in which the trapping centre concentrations did not follow the general trend of the other specimens in the set were repeated as a check. Figure (5.16) shows the TSC curves obtained from two specimens implanted with $10^{13}$ cm$^{-2}$ 300keV protons.
Field dependence of the number of centres producing the 0.19 eV level in specimens implanted with doses of $10^{13} \text{ cm}^{-2}$ and $10^{12} \text{ cm}^{-2}$.

<table>
<thead>
<tr>
<th>Electric field (V/cm)</th>
<th>$10^{13} \text{ cm}^{-2}$</th>
<th>$10^{12} \text{ cm}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of centres</td>
<td>%</td>
</tr>
<tr>
<td>$2.7 \times 10^3$</td>
<td>$6.5 \times 10^8$</td>
<td>100</td>
</tr>
<tr>
<td>$2.0 \times 10^3$</td>
<td>$5.0 \times 10^8$</td>
<td>76.9</td>
</tr>
<tr>
<td>$1.4 \times 10^3$</td>
<td>$3.4 \times 10^8$</td>
<td>52.3</td>
</tr>
<tr>
<td>$0.7 \times 10^3$</td>
<td>$2.0 \times 10^8$</td>
<td>30.7</td>
</tr>
</tbody>
</table>

Table (5.8)

Field dependence of the number of centres producing the 0.61 eV level in specimens implanted with doses of $10^{13} \text{ cm}^{-2}$ and $10^{12} \text{ cm}^{-2}$.

<table>
<thead>
<tr>
<th>Electric field (V/cm)</th>
<th>$10^{13} \text{ cm}^{-2}$</th>
<th>$10^{12} \text{ cm}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of centres</td>
<td>%</td>
</tr>
<tr>
<td>$3.9 \times 10^3$</td>
<td>$9 \times 10^9$</td>
<td>100</td>
</tr>
<tr>
<td>$2.7 \times 10^3$</td>
<td>$4 \times 10^9$</td>
<td>44.4</td>
</tr>
<tr>
<td>$2.0 \times 10^3$</td>
<td>$3 \times 10^9$</td>
<td>33.3</td>
</tr>
<tr>
<td>$1.4 \times 10^3$</td>
<td>$2 \times 10^9$</td>
<td>22.2</td>
</tr>
<tr>
<td>$0.7 \times 10^3$</td>
<td>$1.8 \times 10^9$</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Table (5.9)
Field dependences of the number of centres producing the 0.61 eV level in specimens implanted with doses of $10^{13}$ cm$^{-2}$ and $10^{15}$ cm$^{-2}$

<table>
<thead>
<tr>
<th>Electric field (V/cm)</th>
<th>$10^{13}$ cm$^{-2}$</th>
<th>$10^{15}$ cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of centres</td>
<td>%</td>
</tr>
<tr>
<td>$7.2 \times 10^3$</td>
<td>$2.8 \times 10^{10}$</td>
<td>100</td>
</tr>
<tr>
<td>$4.8 \times 10^3$</td>
<td>$1.5 \times 10^{10}$</td>
<td>54</td>
</tr>
<tr>
<td>$1.2 \times 10^3$</td>
<td>$2 \times 10^9$</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Table (5.10)

Field dependences of the number of centres producing the 0.75 eV level in specimens implanted with doses of $10^{13}$ cm$^{-2}$ and $10^{15}$ cm$^{-2}$

<table>
<thead>
<tr>
<th>Electric field (V/cm)</th>
<th>$10^{13}$ cm$^{-2}$</th>
<th>$10^{15}$ cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of centres</td>
<td>%</td>
</tr>
<tr>
<td>$7.4 \times 10^3$</td>
<td>$2.2 \times 10^{10}$</td>
<td>100</td>
</tr>
<tr>
<td>$4.7 \times 10^3$</td>
<td>$1.8 \times 10^{10}$</td>
<td>81.8</td>
</tr>
<tr>
<td>$1.2 \times 10^3$</td>
<td>$8.3 \times 10^9$</td>
<td>37.7</td>
</tr>
</tbody>
</table>

Table (5.11)
Comparison of the number of centres introduced for four specimens implanted with $10^{13}$ cm$^{-2}$, 300 keV protons

<table>
<thead>
<tr>
<th>Level (eV)</th>
<th>Specimen ref. no.</th>
<th>S.I.15</th>
<th>S.I.16</th>
<th>328 /9</th>
<th>M9/2</th>
<th>Average no. of centres</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td></td>
<td>1.28x10$^9$</td>
<td>1.3x10$^9$</td>
<td>1.2x10$^9$</td>
<td>1.34x10$^9$</td>
<td>1.28x10$^9$</td>
</tr>
<tr>
<td>0.61</td>
<td></td>
<td>1.84x10$^{10}$</td>
<td>1.73x10$^{10}$</td>
<td>1.6x10$^{10}$</td>
<td>1.47x10$^{10}$</td>
<td>1.66x10$^{10}$</td>
</tr>
<tr>
<td>0.75</td>
<td></td>
<td>3.0x10$^{10}$</td>
<td>3.3x10$^{10}$</td>
<td>-</td>
<td>3.1x10$^{10}$</td>
<td>3.13x10$^{10}$</td>
</tr>
</tbody>
</table>

Table (5.12)

Comparison of the number of centres introduced for two specimens implanted with $10^{15}$ cm$^{-2}$, 300 keV protons

<table>
<thead>
<tr>
<th>Level (eV)</th>
<th>Specimen ref. no.</th>
<th>S.I.14</th>
<th>S.I.33</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.48</td>
<td></td>
<td>8.06x10$^7$</td>
<td>8.6x10$^7$</td>
</tr>
<tr>
<td>0.61</td>
<td></td>
<td>7.93x10$^9$</td>
<td>7.43x10$^9$</td>
</tr>
<tr>
<td>0.75</td>
<td></td>
<td>6.5x10$^8$</td>
<td>6.1x10$^8$</td>
</tr>
</tbody>
</table>

Table (5.13)
Comparison of the number of centres introduced for two specimens implanted with $10^{13}$ cm$^{-2}$ 200 keV protons

<table>
<thead>
<tr>
<th>Level (eV)</th>
<th>Specimen ref. no.</th>
<th>No. of centres</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S.I. 6.</td>
<td>M2/9</td>
</tr>
<tr>
<td>0.19</td>
<td>$3.46 \times 10^9$</td>
<td>$3.37 \times 10^9$</td>
</tr>
<tr>
<td>0.61</td>
<td>$2.45 \times 10^{10}$</td>
<td>$2.3 \times 10^{10}$</td>
</tr>
<tr>
<td>0.75</td>
<td>$9.19 \times 10^{10}$</td>
<td>$9.24 \times 10^{10}$</td>
</tr>
</tbody>
</table>

Table (5.14)

Comparison of the number of centres introduced for two specimens implanted with $10^{13}$ cm$^{-2}$ 300 keV protons and annealed at 300°C

<table>
<thead>
<tr>
<th>Level (eV)</th>
<th>Specimen ref. no.</th>
<th>No. of centres</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S.I.17.</td>
<td>GaP 10</td>
</tr>
<tr>
<td>0.19</td>
<td>$5.08 \times 10^9$</td>
<td>$4.7 \times 10^9$</td>
</tr>
<tr>
<td>0.24</td>
<td>$1.87 \times 10^9$</td>
<td>$1.44 \times 10^9$</td>
</tr>
<tr>
<td>0.61</td>
<td>$3.88 \times 10^{10}$</td>
<td>$4.2 \times 10^{10}$</td>
</tr>
</tbody>
</table>

Table (5.15)
Comparison of the number of centres in three unimplanted specimens.

<table>
<thead>
<tr>
<th>Specimen ref. no.</th>
<th>S.I.23</th>
<th>S.I.32</th>
<th>GaP/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level (eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.19</td>
<td>7.5 x 10^9</td>
<td>7 x 10^9</td>
<td>6.92 x 10^9</td>
</tr>
<tr>
<td>0.4</td>
<td>8.1 x 10^8</td>
<td>8.3 x 10^8</td>
<td>-</td>
</tr>
<tr>
<td>0.61</td>
<td>1.23 x 10^10</td>
<td>1.18 x 10^10</td>
<td>1.3 x 10^10</td>
</tr>
</tbody>
</table>

Table (5.16)

5.5.2. Variation of the number of trapping centres with proton dose

5.5.2.1. Resistivity measurements

Figure (5.17) shows the resistivity of the implanted layer as a function of dose. The results were obtained by measuring the resistance of each specimen under forward bias. Knowing the area of the Schottky barrier contact, the proton range and the resistivity of the unimplanted material, the resistivity of the implanted region can then be calculated. The figure also shows, for comparison, the results of Spitzer and North.\(^\text{11}\)

5.5.2.2. TSC Measurements

Figure (5.18) shows the total number of trapping centres introduced by the implantation as measured by the TSC method as a function of dose. For comparison, the resistivity/dose curve is also included. At low doses <5 x 10^{13} \text{/cm}^2 a
The resistivity of the implanted layer as a function of proton dose.

Resistivity ($\Omega \cdot \text{cm}$)

- Resistivity of unimplanted material: $10^6 \Omega \cdot \text{cm}$.
- Data from ref (11).

For both sets of data the proton energy was 300 keV.

Proton dose/cm$^2$

Fig (5.17)
The total number of trapping centres compared with the resistivity of the implanted layer, as a function of proton dose.

Resistivity of implanted layer ($\Omega \cdot \text{cm}$)

Total number of trapping centres

Proton dose/$\text{cm}^2$

Estimated error±30%

Fig (5.18)
The number of trapping centres, producing the different levels, as a function of proton dose

Implantation energy 300keV
Dose rate 50nA/cm²

Estimated error ±10%

<table>
<thead>
<tr>
<th>Proton Dose/cm²</th>
<th>Number of trapping centres</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^8$</td>
<td>$10^9$</td>
</tr>
<tr>
<td>$10^9$</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>$10^{10}$</td>
<td>$10^{11}$</td>
</tr>
</tbody>
</table>

Fig(5,19)
large increase in the number of trapping centres (x50) results in only a small increase in the resistivity (x1.6). Taking into account the area of the specimen, the introduction rate is 0.125 trapping centres per proton, and each proton removes 38 carriers assuming that there is no change in the mobility. Over the dose range $5 \times 10^{13} - 10^{15} \text{cm}^2$, although the resistivity increases, the total number of measured trapping centres decreases. This implies that different centres may be responsible for the carrier removal at these high doses compared to the low dose situation.

Figure (5.19) shows the number of trapping centres, producing the different levels, as a function of dose. It can be seen that

(a) the number of centres producing the 0.19 eV level, increases with dose up to $10^{14}/\text{cm}^2$, and then rapidly decreases; no centres being measurable at a dose of $10^{15}/\text{cm}^2$.

(b) the population of traps, responsible for the 0.61 eV level, is large, even after a dose of only $10^{12}/\text{cm}^2$. There is a slight increase in numbers over the range $10^{12} - 5 \times 10^{13}/\text{cm}^2$ followed by a decrease, again only slightly, from $5 \times 10^{13}/\text{cm}^2$ to $10^{15}/\text{cm}^2$.

(c) the centres causing the 0.75 eV level, are introduced rapidly up to a dose of $10^{13}/\text{cm}^2$; then more slowly over the range $10^{13} - 10^{14}/\text{cm}^2$, and at higher doses they have been substantially reduced in numbers.

(d) the centres responsible for the level at 0.4 eV are introduced in measurable numbers for doses greater than $5 \times 10^{13}/\text{cm}^2$, but the numbers decrease as the dose increases up to $10^{15}/\text{cm}^2$.

5.5.3. Variation of the number of trapping centres with proton energy

Specimens were implanted at various energies over the range 50-300 keV. In each case the dose was $10^{13}/\text{cm}^2$, this value being chosen so that the implanted region did not become amorphous, (section (5.5.2.2)). The other implantation conditions have already been described in section (5.2). Figure (5.20)
The number of trapping centres, producing the different levels, as a function of the proton energy.

Estimated error ±10%

In each case, the dose was $10^{18}\text{cm}^{-2}$.

![Graph showing the number of trapping centres as a function of proton energy for different energies (0.75 eV, 0.61 eV, 0.19 eV). The graph includes error estimates and labels for each energy level.](image)
shows how the number of trapping centres producing the different levels, vary with proton energy. In each case the number of centres decreases as the energy increases. Table (5.1) (below) presents the same information, but in terms of the introduction rate (i.e., the number of damage centres per proton).

**Trapping centre introduction rate as a function of proton energy**

<table>
<thead>
<tr>
<th>Proton energy (keV)</th>
<th>Centres producing the 0.19 eV level</th>
<th>0.61 eV level</th>
<th>0.75 eV level</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-</td>
<td>0.73</td>
<td>-</td>
<td>0.73</td>
</tr>
<tr>
<td>75</td>
<td>0.073</td>
<td>0.43</td>
<td>10.0</td>
<td>10.50</td>
</tr>
<tr>
<td>100</td>
<td>0.043</td>
<td>0.29</td>
<td>1.25</td>
<td>1.58</td>
</tr>
<tr>
<td>200</td>
<td>0.028</td>
<td>0.136</td>
<td>0.54</td>
<td>0.70</td>
</tr>
<tr>
<td>300</td>
<td>0.021</td>
<td>0.10</td>
<td>0.48</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Table (5.17)

**5.5.4. Annealing behaviour of the trapping centres**

**5.5.4.1. Introduction**

The annealing behaviour of the trapping centres was examined in two separate regions i.e., room temperature - 200°C and 300°C - 650°C. This was necessary because tin, which was used to form the ohmic back contact to the specimens, melts at 280°C. Consequently those specimens which were to be annealed below 280°C were contacted before implantation, whilst those to be annealed above 280°C were implanted and annealed before contacting. In the latter case the temperature of the contacting process was controlled so that it did not rise above 300°C. In the latter case also, specimens were coated with SiO₂ before annealing (section (3.3)). The temperature at which the coating was carried out was in the region 300 - 310°C.
For convenience the trapping centres responsible for a level E will be referred to as centres (E).

5.5.4.2. Unimplanted material

Figure (5.21) shows the concentration of trapping centres, producing the 0.19, 0.22, 0.61 and 0.75 eV levels, as a function of anneal temperature. The centres (0.19), centres (0.22) and centres (0.61) all increase rapidly in the region room temperature to 200°C. The concentration of centres (0.22) at 200°C could not be measured, the TSC peak being obscured by the peak of the 0.19 eV level. Assuming, however, that the concentration of centres (0.22) increases as rapidly over the region 100°C -> 200°C as it did over the range 20°C -> 100°C, the concentration at 200°C would be approximately $3 \times 10^{13} / \text{cm}^3$. An anneal at 300°C (with encapsulation) reduces the numbers of the centres (0.19), centres (0.22) and centres (0.61). At 430°C there is a slight increase in the concentrations of the centres (0.19) and centres (0.22) but by 650°C the numbers have been reduced substantially. The 0.75 eV level appears after an anneal of 430°C, but again the concentration falls as the anneal temperature ($T_A$) increases. In the case of the centres (0.61), however, the concentration of these increases over the range 540°C - 650°C. [The concentration at 300°C could not be measured]. Figures (5.22 and 5.23) compare the behaviour of the centres (0.24), centres (0.35), centres (0.4) and centres (0.48) before and after implantation. Considering the unimplanted material the numbers of the centres (0.24), centres (0.35) and centres (0.48) all increase from 20°C to 200°C. [The centres (0.4) were obscured by other levels close by.] At higher temperatures the number of centres (0.24) and centres (0.35) are reduced by the anneal at 300°C whilst the number of centres (0.4) and centres (0.48) are both increased. All the centres are reduced in concentration over the range 300°C - 650°C except for the centres (0.4) which increase by over an order of magnitude from 540°C - 650°C.
The annealing behaviour of the centres (0.19, 0.22, 0.61) and (0.75) in unimplanted material.

Trapping centre concentration (cm$^{-2}$)

Estimated error ±10%

SiO$_2$ encapsulation

Fig (5.21)
The annealing behaviour of the centres (0.35) and (0.4) in both unimplanted and implanted material.

Trapping centre concentration (cm$^3$)

Estimated error ±10%

Annealing Temperature (°C)

- Implantation material
  - 300 keV protons 10$^{13}$/cm$^2$

- No encapsulant
- SiO$_2$ encapsulation

Fig(5.22)
The annealing behaviour of the centres (0.24) and (0.48) in both unimplanted and implanted material.

Estimated error ±10%

Trapping centre concentration (cm$^3$)

Annealing Temperature ($^\circ$C)

Implanted material: 300 keV protons $10^3$/cm$^2$.
The number of centres (0.19), (0.61) and (0.75) for both unimplanted and implanted material as a function of annealing temperature.

Number of trapping centres

Unimplanted, Implanted

Estimated error ±10%

Anneal Temperature (°C)

Fig(5.24)
The annealing behaviour of the trapping centres responsible for the different levels.

Number of trapping centres

- No encapsulation
- With SiO₂ encapsulation

Anneal time: 30 mins
Estimated error ±10%

Anneal temperature (°C)

Fig (525)
The majority carrier concentration as a function of annealing temperature for both unimplanted and implanted material.

- Implanted (300 keV, $10^{15}$/cm$^2$)
- Unimplanted

![Graph showing the majority carrier concentration as a function of annealing temperature for both unimplanted and implanted material.](image)

**Fig (5.26)**
5.5.4.3. Implanted material

The same figures (5.22) and (5.23) show the annealing behaviour of the centres (0.24), centres (0.35), centres (0.4) and centres (0.48) in implanted material. At low temperatures (20–200°C) there is little difference between the implanted and unimplanted material, except for the centres (0.24), which are introduced by the bombardment, but have annealed out by 100°C. At higher temperatures, \( T_A = 300°C \), the numbers of centres (0.24) have increased, but decrease again for higher values of \( T_A \). The concentration of centres (0.48) is a little less than for the unimplanted case, whilst for the centres (0.35) a small concentration increase after an anneal at 300°C is quickly annealed out. The behaviour of the centres (0.4) eV was obscured by other TSC peaks over some of the temperature range. Figure (5.24.) shows the annealing behaviour of the total number of centres after implantation, together with the behaviour of the unimplanted material in the same region. For clarity, figure (5.25) shows just the behaviour of the centres introduced by the implantation. In each case there is an initial decrease in numbers from \( T_A = 20-150°C \), followed by an increase at \( T_A = 300°C \). By \( T_A = 650°C \) a second annealing out has occurred, except in the case of the centres (0.75) where the concentration increases over the range 540–850°C.

5.5.4.4. Annealing behaviour

C-V measurements were made (as in section 5.4.3.) on each annealed specimen. The majority carrier concentration as a function of anneal temperature is shown in figure (5.26).

5.6 Sulphur implantation into medium resistivity material

5.6.1. Introduction

A few measurements (far less detailed than in previous sections) were made on
A thermally stimulated current curve obtained from sulphur implanted \(200\text{keV},10^3\text{cm}^{-3}\) GaP

Each current peak indicates the presence of trapping centres which produce a corresponding energy level as shown.

Curve A: traps filled by optical excitation at \(77^\circ\text{K}\)
Curve B: traps empty

Thermocouple reference junction at \(273^\circ\text{K}\)
Thermocouple (mV)
Temperature (°K)


gg
E=12eV E=0.44eV
E=0.9eV

Fig(5.27)
The current through an implanted specimen as an inverse function of temperature.

Medium resistivity GaP implanted with sulphur: 200keV, $10^{13}/cm^2$.

Fig (5.26)
The majority carrier concentration resulting from medium resistivity material being implanted with sulphur at various doses.
sulphur-implanted material, so that the damage centres produced by a heavier ion could be compared with those resulting from proton bombardment. Specimens of medium resistivity Te-doped GaP were bombarded with 200 keV $^{32}$S, at a dose rate of 10 nA/cm$^2$, and 7° off the <111> direction. Using a reverse-biased metal/semiconductor (Au/GaP) junction, TSC and C-V data was obtained from three samples, implanted with doses of $3 \times 10^{12}$/cm$^2$, $10^{13}$/cm$^2$ and $3 \times 10^{13}$/cm$^2$.

5.6.2. TSC measurements

Figure (5.27) shows the TSC curve obtained after implanting a sulphur dose of $10^{13}$/cm$^2$. Three current peaks, indicating the presence of three deep energy levels, and therefore three types of damage centre, are seen to be present. Further, by plotting the logarithm of the current produced with no optical excitation against the inverse of the temperature (i.e. log I vs $\frac{1}{T}$), (figure (5.28)), the energy level values of two other centres can also be determined. Table (5.18) summarises the properties of all the damage centres found, the properties of the centres produced by proton bombardment (into the same type of material) are included for comparison.

5.6.3. C-V measurements

Figure (5.29) shows the majority carrier concentration as a function of dose. The peak sulphur concentration, occurring at the ion range, is also given calculated from the formula of section (4.5.9.). The increase in the concentration with dose suggests that deep donors are primarily produced in this particular dose range.

5.6.4. Annealing behaviour

After a dose of $10^{13}$/cm$^2$ the majority carrier concentration (determined using C-V measurements) had risen to $5.6 \times 10^{16}$/cm$^3$ from the bulk material value of $3 \times 10^{15}$/cm$^3$. However, after a half hour anneal (in an argon atmosphere at 200°C) it had dropped to $4.3 \times 10^{15}$/cm$^3$ i.e. over an order of magnitude difference.
<table>
<thead>
<tr>
<th>Method</th>
<th>Energy Level (eV)</th>
<th>Cross-section and Capture Cross-section Coefficient (cm²)</th>
<th>Temperature Coefficient (°C⁻¹)</th>
<th>Experimental Value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSC</td>
<td>1.0 x 10⁻¹²</td>
<td>0.05</td>
<td>0.27</td>
<td>0.72 x 10⁻¹²</td>
</tr>
<tr>
<td>TSC</td>
<td>1.0 x 10⁻¹²</td>
<td>0.05</td>
<td>0.27</td>
<td>0.72 x 10⁻¹²</td>
</tr>
<tr>
<td>Log-I</td>
<td>0.2 x 20</td>
<td>0.05</td>
<td>0.27</td>
<td>0.72 x 10⁻¹²</td>
</tr>
<tr>
<td>Log-I</td>
<td>0.2 x 20</td>
<td>0.05</td>
<td>0.27</td>
<td>0.72 x 10⁻¹²</td>
</tr>
<tr>
<td>Log-I</td>
<td>0.2 x 20</td>
<td>0.05</td>
<td>0.27</td>
<td>0.72 x 10⁻¹²</td>
</tr>
</tbody>
</table>

Material: Sulfur Implant proton medium resistivity
Chapter 6

DISCUSSION OF RESULTS

6.1 Introduction

The results of chapter 5 are now discussed. The energy levels produced by ion bombardment are first compared for all three types of GaP in tables (6.1, 6.2). This is followed by a section on the trapping centre capture cross-sections. The trapping centre concentrations as a function of dose, energy and anneal temperature are then examined section (6.3.1, 6.3.2, 6.3.3). Finally the measurements on the sulphur implanted material are contrasted with those from the proton bombarded material.

At the end of each section the results are compared with other data reported in the literature. Very few papers have appeared, as far as I am aware, on the proton implantation of GaP. There has been a little correspondence on electron and heavy ion bombardment of GaP and these together with results from other III-V cpds, in particular GaAs, have been drawn on heavily. There are dangers, however, in doing this. Thommen attributed an annealing stage at 520°C in GaAs to the gallium vacancy as it was similar to behaviour which had been observed in GaSb. Potts and Pearson, however, have produced more conclusive evidence to suggest that this stage in GaAs is associated with the arsenic vacancy.

With no direct experimental evidence, in this work or in the literature, for the properties of the trapping centres associated with the simple defects such as \( V_{Ga} \), \( I_{Ga} \), \( V_{p} \), \( I_{p} \), let alone the more complex centres, any deductions from the measurements in this direction are necessarily tentative and should be treated as such. Some of the literature gives the impression that the evidence for, for example the temperature at which \( V_{Ga} \) anneals out in GaAs, is far more conclusive than it actually is; authors drawing on each others only tentative suggestions.
6.2 Trapping centre properties.

6.2.1. Comparison of the energy levels found in the three different types of GaP material

In this section tables (6.1, 6.2) compare the energy level values found in the different materials for both unimplanted and proton implanted specimens.

6.2.1.1. Unimplanted specimens

Table (6.1) shows the energy levels measured, by the various methods, for unimplanted material.

The energy levels found to be present in the different GaP slices before implantation

<table>
<thead>
<tr>
<th>Energy Levels</th>
<th>Method</th>
<th>Energy Levels</th>
<th>Method</th>
<th>Energy Levels</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.007</td>
<td>Conductivity</td>
<td>0.012</td>
<td>Conductivity</td>
<td>0.02</td>
<td>T.S.C.</td>
</tr>
<tr>
<td>0.04</td>
<td>Conductivity</td>
<td>0.05</td>
<td>C-t</td>
<td>0.09</td>
<td>Conductivity</td>
</tr>
<tr>
<td>0.14</td>
<td>Conductivity</td>
<td>0.19</td>
<td>Conductivity</td>
<td>0.38</td>
<td>C-t</td>
</tr>
<tr>
<td>0.4</td>
<td>C-t</td>
<td>0.45</td>
<td>T.S.C.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.61</td>
<td>T.S.C.</td>
<td>0.69</td>
<td>T.S.C.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (6.1)

The levels in the medium resistivity material of 0.19, 0.38, 0.4 and 0.64 eVs compare with those in the semi-insulating material of 0.19, 0.35, 0.4 and 0.61 eVs.

The tellurium level at 0.09 eV is evident in both the medium and low resistivity materials. Of the many shallow levels in the latter material, the one at 0.007 eV could
be due to nitrogen (reported as $E_c - 0.008$) and the 0.04 - 0.05 level may be carbon.

6.2.1.2. Implanted specimens

Similarly for implanted material:

The energy levels found to be present in the different GaP slices after proton implantation:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.012</td>
<td>Conductivity</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>T.S.C.</td>
<td></td>
<td>0.19</td>
<td>Conductivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>T.S.C.</td>
<td></td>
<td>0.22</td>
<td>Conductivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>T.S.C.</td>
<td></td>
<td>0.59</td>
<td>T.S.C.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.61</td>
<td>T.S.C.</td>
<td></td>
<td>0.61</td>
<td>C - t</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>T.S.C.</td>
<td></td>
<td>0.71</td>
<td>T.S.C.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>Conductivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>T.S.C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>Conductivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>C - t</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>Conductivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.32</td>
<td>C - t</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>T.S.C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (6.2)

The levels introduced by proton bombardment of the medium resistivity and semi-insulating materials are similar, implying that the same trapping centres are responsible.

The levels introduced into the low resistivity material, however, do not follow the same pattern. Two deep levels were measured i.e. at 0.24 eV and 0.32 eV. The 0.24 eV level compares with similar levels found in the other materials. The 0.32 level, in the bottom half of the band gap, is probably
the same level as the 0.35 eV level measured using TSC techniques. This level may be already present in the material (c.f. the semi-insulating material table (6.1)) or it may be introduced by the implantation. If the latter is the case then it could be the same level as the 0.4 eV level introduced, for doses $> 5 \times 10^{13} / \text{cm}^2$ into the semi-insulating material. The difference in energy level value of 0.05 eV, however, is rather large. Hamilton and Smith$^{122}$ have reported an $E_v + 0.4$ eV level in n-type GaP.

The 0.24 eV and 0.4 eV levels found to be introduced into the semi-insulating material were not examined quantitatively in sections (5.5 and 6.3) because the 0.24 eV level was often obscured by other levels closely, the introduction rate being calculated as 0.01 centres/proton, whilst the 0.4 eV level was only detectable for doses $> 5 \times 10^{13} / \text{cm}^2$.

6.2.1.2. Energy levels introduced by proton implantation

In a binary compound such as GaP the displacement of an atom can result in the formation of several energy levels. There will be a level associated with each type of vacancy and also with each type of interstitial. In the latter case the resulting level may depend upon the position of the atom relative to the other lattice atoms. It is thought,$^{147}$ however, that interstitials anneal out below room temperature so that the levels created by a room temperature implantation are primarily connected with the vacancies. The gallium vacancy produces a level 0.19 eV above the valence band, the phosphorus vacancy a level 0.07 eV below the conduction band. The energy levels caused by divacancies are unknown at present. Vacancy complexes with other lattice atoms, including the tellurium dopant ($E_c - 0.09$ eV), will produce even more levels e.g. $V_{Ga}^{-} - 2Te_p$ and $V_{Ga}^{-} - 3Te_p$ which are discussed in the annealing section (6.3.3.2).

Toyama and Ikoma$^{123}$ have suggested that a level ($E_c - 0.15$) eV found in GaAs is produced by a complex containing two arsenic atoms. The experimental results in this work suggest that the 0.19 eV level may
be a complex containing two phosphorus vacancies. Similar types of centre may, therefore, be responsible.

6.2.1.4. Comparison with other work

In most cases the type of damage centre responsible for a particular deep level is unknown and the levels, together with some of their properties, are simply reported. The levels found by B.L. Smith and those by E. Fabre et al, who both used TSC techniques, are listed in the following table (6.3) together with the levels measured in this work. B.L. Smith used LEC grown Te-doped and liquid phase epitaxial grown (LPE) S-doped $10^{16} - 10^{17}/\text{cm}^3$ material, E.F. Fabre et al examined L.E.C. grown, Te, Se, and S doped $10^{17}/\text{cm}^3$ materials, (in both these cases only the levels found to be present in the Te-doped and undoped material have been included in the table), whilst the GaP used in this work was also LEC grown Te-doped, but compensated with chromium.

Only the results from the semi-insulating material are given as the deep energy levels in the other materials are similar (tables 6.1, 6.2).

Comparison of energy level values with values reported in the literature

<table>
<thead>
<tr>
<th>B.L. Smith</th>
<th>E. Fabre</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>0.24</td>
<td>0.27</td>
</tr>
<tr>
<td>0.22</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>0.43</td>
<td>0.48</td>
<td>0.5</td>
</tr>
<tr>
<td>0.54</td>
<td>0.61</td>
<td>0.72</td>
</tr>
<tr>
<td>0.93</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

Table (6.3)
The three sets of energy level values are similar. The defects which were found in the particular material which was used are, therefore, similar to those found in LEC grown Te-doped GaP generally. The relative concentrations of defects, however, would be expected to vary.

Some of the other authors who have measured deep levels in GaP are Kamath and Bowman, who reported an acceptor level at 0.35 eV in vapour phase n-type material (c.f. the \((E_v + 0.35)\) eV level in this work), and Young and Bass, who showed there were donor levels at \((E_c - 0.2)\) eV, \((E_c - 0.25)\) eV, \((E_c - 0.47)\) eV and \((E_c - 0.55)\) eV in semi-insulating material (c.f. the \((E_c - 0.19)\) eV; \((E_c - 0.22)\) eV and \((E_c - 0.61)\) eV levels in this work) which they attributed to oxygen complexes.

Again these levels are very similar to those in the table.

As far as I am aware there are no reported measurements of the energy levels introduced into GaP by proton implantation, although the change in conductivity and optical absorption after bombardment has been investigated. Logan examined the effects of \(\gamma\) radiation (Co) on GaP EL diodes and found that non-radiative donor trapping centres were introduced. H. Schade et al electron irradiation (1 MeV) GaAs\(_{1-x}\), P. EL diodes and discovered that as the phosphorous content increased (up to a maximum of \(x = 0.5\)) the levels produced became deeper, lying in the range \(0.2 \rightarrow 0.35\) eV.

Aukermann lists the energy levels introduced into GaAs by electron, or \(\gamma\), and neutron irradiation whilst Coates and Mitchell have examined neutron irradiated GaAs, see table (6.4).
Energy levels introduced into GaAs by different types of radiation.

<table>
<thead>
<tr>
<th>Type of radiation</th>
<th>Levels</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron or γ</td>
<td>E(_c) - 0.13</td>
<td>Aukermann</td>
</tr>
<tr>
<td></td>
<td>E(_c) - 0.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E(_c) - 0.52</td>
<td></td>
</tr>
<tr>
<td>Neutron radiation</td>
<td>E(_c) - 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E(_c) - 0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E(_v) + 0.6</td>
<td></td>
</tr>
<tr>
<td>Neutron</td>
<td>E(_v) + 0.35</td>
<td>Coates and Mitchell</td>
</tr>
<tr>
<td></td>
<td>E(_v) + 0.73</td>
<td></td>
</tr>
</tbody>
</table>

From Aukermann's results it would appear that some of the levels introduced are similar, independent of the type of bombardment (compare the E\(_c\) - 0.13, E\(_c\) - 0.1, and E\(_c\) - 0.52, E\(_c\) - 0.5 eV levels) although in the case of the neutron irradiation one level (and in Coates and Mitchell's work several levels) closer to the valence band is also created.

The E\(_v\) + 0.35 eV and E\(_v\) + 0.73 eV levels found in neutron bombarded selenium doped GaAs are very similar to the E\(_v\) + 0.4 and E\(_v\) + 0.75 eV levels in the semi-insulating GaP. The annealing results section (6.3.3.) imply that gallium vacancies connected with the tellurium dopant are responsible for these latter levels, so that the same type of centres, but connected with the selenium dopant may be responsible for the GaAs levels. In the appendix the potential energy between two charged atoms on different lattice sites has been calculated. It is interesting to note that the values obtained in several cases are in good
agreement with the values of the energy levels measured, possibly indicating the positions of the atoms which make up the trapping centres.

6.2.2. Capture cross-sections

6.2.2.1. Types of centre

Lax has calculated the following sizes for the capture cross-sections of repulsive, neutral and attractive centres:

- repulsive \(10^{-24} - 10^{-22} \text{ cm}^2\)
- neutral \(10^{-17} - 10^{-15} \text{ cm}^2\)
- attractive \(10^{-15} - 10^{-12} \text{ cm}^2\)

The attractive centres can be either

- singly charged \(10^{-15} - 5 \times 10^{-14} \text{ cm}^2\)
- or "giant" traps \(5 \times 10^{-14} - 10^{-12} \text{ cm}^2\)

The "giant" traps may be produced by

1) doubly or even triply charged centres
2) clustering of centres
3) excited states of centres. Centres with a long range Coulomb attractive potential possess a series of such states\(^{117}\). Carriers captured into an excited state may lose their energy by multiphonon transitions, or by the emission of radiation.

Comparison of the experimental cross-sections with the values of Lax suggests that in the semi-insulating material the traps which produce the

- 0.19 eV level are attractive and singly charged
- 0.22 " " neutral
- 0.24 " " "
- 0.35 " " attractive and "giant"
0.4 eV level are attractive and "giant"

0.48 " " " " "

0.61 " " " " "

0.75 " " neutral or attractive and singly charged.

Similarly from the TSC results on the medium and low resistivity materials

the traps which produce the

0.59 eV level are attractive and "giant" (medium)

0.71 " " " " " (medium)

0.45 " " " " " singly charged (low)

The cross-sections for the singly charged centres, are similar to those

reported for electron traps in GaAs. Ralph computed a value of \( 1.1 \times 10^{-14} \text{ cm}^2 \)
(at a temperature of 197°C) whilst Carballes and Lebailly quote \( 2.5 \times 10^{-15} \text{ cm}^2 \)
(at 293°C). Saunders and Jewitt report values as large as \( 10^{-10} \text{ cm}^2 \) (for trapping

centres in GaAs) which is over an order of magnitude greater than the largest

traps found in this work.

6.2.2.2. Variation of the capture cross-sections with temperature

The capture cross-section of a trap varies as an inverse function of

temperature i.e. \( S_T \propto T^{-n} \). Using Keating's analysis section (4.2.4) the variable

\( n \) was found to lie in the range 2.9 \( \rightarrow \) 4.5. At low temperatures therefore, the

probability of filling all the traps is large, and as the temperature is raised the

probability of carriers being re-trapped decreases.

The temperature coefficients are similar to those found in Bemski for

traps in silicon, where \( n \) had values up to 4. The larger traps also have the largest

temperature coefficients suggesting that they might be made up of groups of simpler

defects.
6.2.3. Observations from the capacitance-frequency results

6.2.3.1. Quantitative indication of the number of trapping centres

Examining the capacitance-frequency measurements made on both unimplanted low and medium resistivity materials, figures (5.4, 5.3), the "step" effect produced in such cases indicates that at least two deep energy levels are present in the specimens (section 3.4.4.5.). In the case of the implanted low resistivity material this "step" effect is no longer observed, but rather a gradual decrease in capacitance as the frequency is increased. This implies that other energy levels have been introduced into the bandgap which respond at comparable frequencies. The implanted, medium resistivity material, shows the same sort of behaviour but to a lesser extent. In each case the implanted material has a lower value of capacitance than the corresponding unimplanted material, indicating a larger depletion region, and that some compensation has taken place.

6.2.3.2. Majority carrier measurements

The majority carrier concentration after specimens have been bombarded will depend upon the types of centres introduced and their position in the bandgap.

An increase in the number of donors in the top half of the band gap will increase the majority carrier concentration and be reflected in the measured value of capacitance. Acceptor levels, however, will be empty provided they are above the Fermi level. These neutral trapping centres will not be detected.

Donors below the Fermi level, will be neutral and not detectable whilst acceptors, below the Fermi level, will reduce the carrier concentration.

Low frequency C-V measurements section (5.4.3.) indicate, therefore, that the increase in carrier concentration after implantation may be caused by
1) deep donors being introduced either into the upper half of the band gap or into the lower half, or both.

2) deep acceptors being introduced either into the top half of the band gap (and so are not detected) or if they are introduced into the lower half of the band gap, it is with a lower introduction rate than donors into the upper half.

Grimshaw has found that the electron irradiation of GaAs produced deep acceptor centres in the top half of the band gap, and deep donors in the bottom half. The results presented here may be interpreted in the same way.

Measurements at high frequencies show that shallow acceptors are introduced by the implantation which compensate the shallow donors.

6.2.3.3. Carrier removal

Copeland measurements suggested that the majority carrier concentration due to shallow donors had dropped below $5 \times 10^{14}$ cm$^{-3}$ in all the implanted specimens. I-V measurements showed that the resistivity of the bombarded region had increased to $2 \times 10^6$ Ω cm in the case of the low resistivity (0.1 Ω cm) material and to $5 \times 10^5$ Ω cm. in the case of the medium resistivity (50 Ω cm.) material, confirming the low majority carrier concentration values. The carrier removal rate i.e. the reduction in the number of majority carriers per implanted proton was estimated by assuming that in the bombarded region the majority carrier concentration was $5 \times 10^{14}$/cm$^2$. Then the reduction is approximately $3 \times 10^{17}$/cm$^3$ for the low resistivity material and $1.5 \times 10^{15}$/cm$^3$ for the medium resistivity material. Dividing, in each case, by the proton dose the figures in table (6.5) were obtained. The table also shows for comparison carrier removal
rates for proton implanted GaAs as reported in the literature.

### Carrier removal rates

<table>
<thead>
<tr>
<th>Material</th>
<th>Carrier Removal Rate</th>
<th>Energy (keV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low resistivity GaP, Te doped</td>
<td>$3 \times 10^4$</td>
<td>15</td>
<td>This work</td>
</tr>
<tr>
<td>Medium resistivity GaP Te doped</td>
<td>$7.5 \times 10^4$</td>
<td>400</td>
<td>This work</td>
</tr>
<tr>
<td>n-type GaAs</td>
<td>$8 \times 10^4$</td>
<td>60</td>
<td>157</td>
</tr>
<tr>
<td>n-type GaAs</td>
<td>$4 \times 10^4$</td>
<td>150</td>
<td>157</td>
</tr>
<tr>
<td>n-type GaAs</td>
<td>$4 \times 10^4$</td>
<td>150</td>
<td>154</td>
</tr>
</tbody>
</table>

Table (6.5.)

The similarity of the carrier removal rates suggest that the same processes are responsible for the production of semi-insulating regions in both GaAs and GaP.

6.3 Trapping centre concentration measurements

6.3.1 Trapping centre concentrations as a function of proton dose

6.3.1.1 Resistivity and TSC measurements

The resistivity of the implanted region is shown as a function of dose figure (5.17) together with similar results on low resistivity material by Spitzer and North. 

In both sets of results there is an initial increase in the resistivity by a factor of $10^7 - 10^8 \ \Omega \text{cm}$ at doses of $\approx 10^{12} / \text{cm}^2$, followed by a further increase in the dose range $5 \times 10^{14} / \text{cm}^2$. This further increase means that the resistivity of both materials approaches the intrinsic resistivity of GaP which is $5 \times 10^{16} \ \Omega \text{cm}$. The material used by Spitzer and North was n-type (Se doped) and p-type Zn doped LEC GaP with doping concentrations
in the region of $10^{17}$/cm$^3$. They obtained the same resistivity/dose curve with each type of material. In this work semi-insulating, but containing Te, LEC grown material was used. The same behaviour for differently doped materials suggests that simple defects such as $V_{Ga^+}$, $V_P$ may be responsible for the increase in resistivity.

The TSC results section (5.5.2.2.) and figure (5.19) indicate that for low dose implants $10^{12}$/cm$^2$ the centres producing the 0.61 eV level are dominant suggesting that these centres may be responsible for the plateau region of resistivity in the dose range $10^{12} - 5 \times 10^{13}$/cm$^2$. Other centres resulting in levels at 0.19 eV and 0.24 eV only become important in the range $10^{13} - 10^{14}$/cm$^2$ and, therefore, appear to be connected with the further increase in resistivity. At higher proton doses $10^{14}$/cm$^2$, all the introduced centres have been reduced substantially in number, except those associated with the 0.61 eV and 0.4 eV levels. The reduction could indicate the preferential production of more complex centres. No new levels, however, were detected at the highest dose implanted, but this does not exclude the possibility that levels shallower than 0.19 eV or deeper than 0.75 eV result from the association of the traps.

Dyment et al$^{135}$ have measured the resistivity of p-type GaAs as a function of proton dose and although there is no evidence of a plateau region (the lowest dose being $10^{14}$/cm$^2$), the resistivity does reach a maximum for a dose of $3 \times 10^{15}$/cm$^2$.

For the proton bombardment of n-type GaAs Pruniaux et al$^{154}$ found a maximum in the region $3 \times 10^{13} - 10^{14}$Ωcm, depending upon the initial resistivity of the starting material. No lower doses were examined. The electrical resistivity of proton bombarded material appears to be similar, (therefore) for these materials implying that the type of damage is also similar.
The build up in the number of damage centres with dose is sub-linear or linear in the case of the 0.19 and 0.61 eV levels up to a dose of $10^{13}/cm^2$. Above this value the number of centres falls below a linear increase. In the case of the 0.75 eV level the increase is super-linear up to $10^{14}/cm^2$. The general shape of the 0.19 and 0.61 eV dose curves is similar to the damage/dose curve of Carter et al. who implanted 20 keV Te ions into GaP; and similar to that of Haskell et al. after Zn and Se implants into GaP. In both cases RBS techniques (2 MeV He$^+$) were used for the analysis. Morehead and Crowder have proposed a model for the formation of amorphous silicon in which a critical point defect density, produced by the arrival of previous ions, is required before the damage surrounding a single ion track will become amorphous. The way in which damage builds up in a crystal as a function of ion dose will be affected, by this point defect density. If the dose required to produce the critical density is not too different from the dose required to produce saturation damage then the model predicts a slow variation of damage with dose, followed by a linear or super-linear rise to saturation. Although in the case in question ($H^+$ in GaP) the extent of the damage is small, the rapid build up of the number of centres in the 0.75 eV level in the region of $10^{13}/cm^2$ does suggest that a certain defect concentration is required before such centres are produced.

6.3.1.2. Broadening of the energy levels

As the dose increased, the positions in the band gap of some of the levels appeared to move towards the appropriate band edge. This was interpreted (section 4.2.5) as due to a broadening of the energy levels. Over the dose range $10^{12} - 10^{13}/cm^2$ any broadening of the energy levels was not measurable, i.e. less than 0.003 eV. Table (6.6) summarizes the broadening of the levels over the dose range $10^{13} - 10^{15}$ cm$^{-2}$. 
Energy level broadening

<table>
<thead>
<tr>
<th>Dose ( \text{cm}^2 )</th>
<th>( 10^{13} )</th>
<th>( 10^{14} )</th>
<th>( 10^{15} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy level (eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.19</td>
<td>0</td>
<td>0.012</td>
<td>level not detected</td>
</tr>
<tr>
<td>0.24</td>
<td>0</td>
<td>0.006</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.61</td>
<td>0</td>
<td>0.018</td>
<td>0.035</td>
</tr>
<tr>
<td>0.75</td>
<td>0</td>
<td>0.03</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Table (6.6.)

Although the distributions are not large, the broadening of the 0.19 eV level at a dose of \( 10^{14}/\text{cm}^2 \) causes it to approach the 0.22 eV level found in the unimplanted material. At a higher dose of \( 10^{15}/\text{cm}^2 \) the 0.19 eV level could not be detected. This suggests that these two levels have overlapped. If this also happens to any other shallow levels the nett result will be extended energy level tails at the band edges. The deep levels are sufficiently separate to prevent any overlapping occurring. As the dose increases, several stages can be defined.

(a) Simple defects.

These are produced at low doses; examples of which are \( V_{\text{Ga}}, V_{\text{P}}, Ga_1 \), and \( P_1 \). The centres producing the 0.61 eV level may be connected with a particular simple defect.

(b) Clusters of defects

These consist of small groups of defects which are significantly closer together
Band gap models of amorphous semiconductors.

Density of states →

d) C-F-O model

b) Mott-Davies

d) Crystalline GaP (for comparison)

c) Model for low dose proton implanted GaP from measurements

Fig(6.1)
than would be expected if the defects were distributed at random in the crystal. The effect of neighbouring defects may be viewed merely as a perturbation. This will effectively broaden out the energy levels. The results suggest that the centres responsible for the 0.19, 0.61 and 0.75 eV levels cluster with increasing proton dose.

(c) Association of defects

In this case the localized electronic levels belong to the group rather than the individual atoms. As the dose increased the 0.4 eV level became evident for doses greater than or equal to $5 \times 10^{13}$/cm$^2$. The association of simple defects may be responsible, therefore, for this level.

(d) Amorphicity

As the semiconductor approaches amorphicity the band structure will change towards that of an amorphous semiconductor. Two energy level models have been proposed for such semiconductors, these are the Cohen-Fritzsche-Ovshinsky (CFO) model and the Mott-Davis model. In the CFO model (figure (6.1(a)) extended energy level tails overlap near the centre of the band gap. This means that conduction is intrinsic and the transparency of the material is much reduced. The Mott-Davis model (figure (6.1(b)) on the other hand, proposes a narrow band of localized states near the centre of the band gap; conduction is extrinsic and the material is fairly transparent. The experimental results obtained in this work for a semiconductor which is approaching amorphicity suggest a band structure which is a combination of these two models. The shallow levels broaden sufficiently to overlap each other and will eventually merge with the nearest band edge. In this respect, therefore, proton implanted GaP (dose $10^{15}$ cm$^{-2}$) has extended energy level tails as in the CFO model. They do not, however, extend to the centre of the band gap, for several broadened deep energy levels were found. Consequently
the structure is also similar to the Mdt-Davis model, but differs in having several deep levels, rather than a single level, close to mid-band. The apparent band structure is shown in figure (6.1.c) along with the structure of crystalline GaP for comparison (figure 6.1.d).

"Band tails", that is, the broadening of energy levels so that they merge into the nearest band edge has also been observed by Pankey and Davey in neutron irradiated thin films of GaAs and GaP, and by Davey et al in argon bombarded GaP. In this latter case it was shown that for an argon dose of $10^{14}$/cm$^2$ (at 1.5 MeV) the optical edge shift was similar to an amorphous (cold deposited) film of GaP.

Channelling measurements on GaAs after proton bombardment do not show an increase in the number of backscattered particles, until a dose of the order of $10^{16}$/cm$^2$ (at 300 keV) have been implanted in a random direction. The optical absorption effects and electrical conductivity changes, therefore, produced after small doses, must be associated with small atomic displacements which cannot be detected by Rutherford Backscatter techniques. A channelled particle cannot detect displacements from lattice sites which are less than about 0.2Å.

6.3.1.3. Amorphicity

Amorphicity can be defined in several ways. Morehead and Crowder in proposing a method for calculating the dose required to produce an amorphous region ($D_{\text{amorphous}}$) assumed that such a layer is one in which every atom has been displaced, that is, long range order is destroyed.

The dose required is given by

$$D_{\text{amorphous}} = E n_2 \left( \frac{dE}{dx} \right)^{-1} \text{ref (10)}$$
Ed is the displacement energy of the lattice atom, \( n_2 \) is the number of target atoms per \( \text{cm}^3 \), and \( \left( \frac{\text{d}E}{\text{d}x} \right)_0 \) is the energy-independent nuclear loss per unit path length.

An approximation of the Nielson equation can be used to obtain values for this latter quantity. That is

\[
\left( \frac{\text{d}E}{\text{d}x} \right)_0 = 7 \times 10^8 \, \varepsilon_2 \, Z_1 \, \frac{M_1}{(M_1 + M_2)} \, \text{eV cm}^{-1}
\]

\( Z_1, \, M_1 \) are the atomic and mass numbers of the implanted ion

\( M_2 \) is the mass number of the target

\( \varepsilon_2 \) is the target density

Taking the average of \( M_{\text{Ga}} \) and \( M_{\text{P}} \) for \( M_2 \)

\[
\left( \frac{\text{d}E}{\text{d}x} \right)_0 = 1.2 \times 10^8 \, \text{eV cm}^{-1}
\]

and using a value of 10 eV for both the gallium and phosphorous displacement energies,

\[
D_{\text{am}} = 4.5 \times 10^{15} / \text{cm}^2
\]

This value is a lower limit as it neglects the effects of out-diffusion and annealing. Comparison with figure (5.18) shows that \( D_{\text{amorphous}} \) will be in a region where energy level broadening and overlapping is occurring.

An alternative definition of amorphicity is given by Polk. Describing a structural model for amorphous silicon and germanium he ascribes non-crystallinity to variations in bond lengths and bond angles as well as rotation about bonds. In this case long range order still exists. Such small changes would affect the optical and electrical properties of the material but would not be detected by RBS techniques.
This definition of amorphicity, therefore, is applicable to proton bombarded GaP.

Mazey and Nelson\(^{143}\) have studied electron diffraction patterns of GaAs after it had been bombarded with \(> 5 \times 10^{14} \text{ cm}^{-2}\) (40-100 keV) neon ions. They were able to calculate, from the diffuse Debye-Scherrer rings surrounding each diffraction spot, the first three nearest neighbour distances of the atoms in the amorphous region. The distances were to within 0.12\(\AA\) of the nearest neighbour distances in crystalline GaAs, indicating that 'small atomic displacements' had occurred.

6.3.2 Trapping centre concentrations as a function of proton energy

6.3.2.1 Introduction rates

The total number of atomic displacements as a function of bombardment energy can be calculated using equations (9, 10, 11) of section (4.5.10). If it is assumed that for each type of trap the number of centres is directly proportional to the total number of displaced atoms, then the trap/energy relationship will be of the same form as the atomic displacements/energy curve. The absolute value for the number of traps forming any particular level, however, cannot be calculated unless the kinetics of formation and the structure of the defect are known. Figure (6.2) shows

1) the number of damage centres producing the 0.61 eV level as a function of proton energy
2) as 1) but redrawn such that the peak damage concentration at each energy has been normalized, using the formula of section (4.5.9) to the peak damage concentration for a proton energy of 300 keV. This effect does not fully account for the difference between the experimental and theoretical curves as the number of traps still decreases with energy.
3) the total number of displaced atoms/proton energy calculated from equations (9, 10, 11) of section (4.5.10). The average number of
The number of trapping centres, responsible for the 0.61 eV level, as a function of proton energy.
displacements per proton is four

4) the number of traps responsible for the $E_0 - 0.61$ eV level assuming

an introduction rate of 0.01 centre/atomic displacement. This corresponds
to an introduction rate of approximately 0.04 centre/proton. The shape of
this curve is the same as 3).

6.3.2.2. Ionization processes

Several authors have suggested that the energy going into non-elastic
processes may affect the amount of damage produced. Oen\(^{144}\) has proposed that
the ionization of a lattice atom reduces its displacement energy so making it more
easily removed from its lattice site by any following ion. On the other hand, Picraux
and Vook\(^{114}\) have reported that the energy going into non-nuclear processes can
result in the annealing of defects. Their experiments were carried out with silicon.
Ionization, therefore, may either result in more damage being produced than
would be expected from purely elastic processes, or less damage occurring
because of annealing. The relative magnitude of these two competing processes
will depend upon other factors such as the implantation temperature.

Both the electron production process and the charge exchange mechanism
will result in target atoms becoming ionized viz: -

\[ H^+ + X \rightarrow H^+ + X^+ + e^- \] (electron production)

\[ H^+ + X \rightarrow H + X^+ \] (charge exchange)

Garcia et al\(^{145, 146}\) have calculated the cross-sections for these two mechanisms
for various elements undergoing proton bombardment. In general, the electron
production cross-section, $\sigma_{e.p.}$, first rises to a maximum at about 10 keV, and
then falls either as $\frac{1}{E}$, in the case of low Z target elements, or as $\frac{1}{\sqrt{E}}$, for
Data from figure (5.20) for 0.61 eV level.

\[ \frac{(N_{\text{tho}} - N_{\text{exp}})}{N_{\text{exp}} - N_{\text{tho}}} \] as functions of \( \frac{1}{E^2} \), LnE and \( E^{\frac{3}{2}} \).
medium to high Z elements \((Z > 30)\). The typical cross-section decreases by a factor of approximately four to five over the incident proton energy range of 50 - 300 keV. Charge exchange cross-sections, \(\sigma_{\text{c.e.}}\), however, have a maximum at much lower energies, less than 1 keV, thereafter falling as \(1/E^3\).

The ratio of the maximum values, i.e., \(\frac{\sigma_{\text{c.e.}}}{\sigma_{\text{e.p.}}}\) is in the range 5 \(\rightarrow\) 50.

For an ion of energy \(E\) the total ionization effects caused by the electron production process will be proportional to \(\int \frac{1}{E} \, dE\) or \(\int E^{-\frac{3}{2}} \, dE\) i.e. to \(\log E\) or \(E^\frac{1}{2}\). On the other hand the total ionization effects caused by the charge exchange mechanism will be proportional to \(\int E^{-\frac{3}{2}} \, dE\) i.e. to \(E^{-2}\).

The experimental curves figure (6, 2) show that with increasing energy the total amount of damage decreases implying that as the total amount of energy of the particle which goes into inelastic processes increases the amount of annealing also increases. The difference between the theoretical values, \(N_{\text{theo}}\), which takes into account the damage produced by atomic collisions and the experimental values, \(N_{\text{exp}}\), is a measure of any ionization effects. If the quantity \(N_{\text{theo}}\) is greater than \(N_{\text{exp}}\) then annealing is the predominant effect of any ionization and at even low energies the extent of the damage is less than the Kinchin and Pease model predicts.

If, however, \(N_{\text{exp}}\) is greater than \(N_{\text{theo}}\), then although annealing is occurring as the energy increases, the amount of damage at the low energies is greater than the \(K\) and \(P\) model estimates.

To establish whether the annealing is connected with either the charge exchange or electron production processes, \(N_{\text{theo}} - N_{\text{exp}}\) and \(N_{\text{exp}} - N_{\text{theo}}\) were plotted as functions of \(E^{-2}\), \(\log E\) and \(E^\frac{1}{2}\) figure (6, 3). Any correlation which exists should result in a straight line graph. As the absolute value of \(N_{\text{theo}}\) is not known section (6.3.2.1.), a theoretical introduction rate of 0.01 centres/displaced atom
was used in the case where \( N_{\text{exp}} > N_{\text{theo}} \) and a theoretical introduction rate of 1 centre/displaced atom in the case where \( N_{\text{theo}} > N_{\text{exp}} \). \( N_{\text{exp}} \) values were obtained from the data of figure (5.20). Figure (6.3) shows that for the centres producing the 0.61 eV level, the best fit is obtained when \( N_{\text{exp}} - N_{\text{theo}} \) is plotted against \( E^{-2} \). This was found to be independent of the value chosen for \( N_{\text{theo}} \) provided \( N_{\text{exp}} > N_{\text{theo}} \). This indicates that at low energies more centres are introduced than the K and P model predicts and that the charge exchange mechanism is responsible for the increase in annealing as the proton energy increases. A similar result was obtained for the centres producing the 0.19 eV level, whilst the trapping concentration/energy relationship for the 0.75 eV level did not correlate with any of the energy functions.

6.3.2.3. Types of trapping centre

Table (6.7) lists the mean recoil energy, the primary cross-section \( (\sigma_p) \) and the number of secondary displacements (rounded down) as a function of proton energy for both gallium and phosphorus atoms. The values were calculated from equations (9, 10, 11) of section (4.5.10)

The primary cross-section, mean recoil energy, and number of secondary displacements for both gallium and phosphorus atoms as a function of incident proton energy

<table>
<thead>
<tr>
<th>Proton Energy (keV)</th>
<th>Gallium</th>
<th>Phosphorus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean recoil energy (eV)</td>
<td>( \sigma_p ) (cm(^2))</td>
</tr>
<tr>
<td>50</td>
<td>50.69</td>
<td>( 1.92 \times 10^{-18} )</td>
</tr>
<tr>
<td>100</td>
<td>56.72</td>
<td>( 9.62 \times 10^{-19} )</td>
</tr>
<tr>
<td>150</td>
<td>60.26</td>
<td>( 6.41 \times 10^{-19} )</td>
</tr>
<tr>
<td>200</td>
<td>62.78</td>
<td>( 4.81 \times 10^{-19} )</td>
</tr>
<tr>
<td>250</td>
<td>64.73</td>
<td>( 3.85 \times 10^{-19} )</td>
</tr>
<tr>
<td>300</td>
<td>66.33</td>
<td>( 3.2 \times 10^{-19} )</td>
</tr>
</tbody>
</table>

Table (6.7)
The ratio of the primary cross-sections \( \frac{\sigma_p (\text{Ga})}{\sigma_p (\text{P})} \) is approximately 1.9. Gallium atoms, therefore, have a greater probability of being displaced in a primary collision. The number of secondary displacements, however, is slightly higher for a recoiling phosphorus atom (assuming that both elements have the same effective energy). On average a proton in the energy range 50 - 300 keV will produce four vacancies, with the corresponding interstitials. The vacancies can

a) remain as separate single vacancies
b) cluster into a group
c) associate to form stable complexes
d) recombine with their self-interstitial
e) associate to form complexes which anneal out at the temperature at which the implantation takes place.

Similarly the interstitials can

a) diffuse through the lattice
b) anneal out or combine to form complexes which anneal out at the implantation temperature
c) associate to form stable complexes or cluster
d) combine with the self-vacancy

discussing the annealing behaviour of GaAs, Weisenberger et al.\textsuperscript{147} suggest that interstitials, vacancy-interstitial pairs and AB divacancies anneal out below room temperature, whilst mono-vacancy annealing takes place above room temperature. If the interstitials in GaP behave in the same way, then for room temperature implantation it is the vacancies which will predominate as stable damage centres.

A simple model can then be proposed. Assume that there is equal probability that the primary displacement will be a gallium or a phosphorus atom. Then the probability of producing a \( V_{\text{Ga}} \) or \( V_{\text{P}} \) is a half. Similarly the first secondary
displacement may be either a gallium or a phosphorus atom, so that the
probability of producing \(2 V_{Ga}\) or \(2 V_p\) is then a quarter, and of one \(V_{Ga}\) and
one \(V_p\) a half. This treatment can be extended to any number of displacements
but as the average number (for 50 - 300 keV protons in GaP) is four, only four will
be considered here. If it is also assumed that complexes such as \(V_{Ga} - V_{Ga}\)
and \(V_{Ga} - V_{Ga} - V_{Ga}\) (but not \(V_{Ga} - V_p\) or other mixed divancies which
anneal out of low temperatures) can exist and are stable, then the probability that
a particular grouping will occur can be calculated from the total number of
combinations. Further, if recombination is treated as yet another possibility
then the probability, for example, that one vacancy will recombine and the remainder
stay in a certain combination can also be calculated. Table (6.8) lists the
probability that single vacancies and other groups will be produced, firstly
assuming no recombination, then that one vacancy-interstitial pair recombine
and so on. The probability of obtaining a given type of centre is simply the
introduction rate for that centre, therefore, the experimentally determined damage
centre introduction rates are given for comparison.

It can be seen that at the lower proton energy of 75 keV (where the
total energy going into electronic processes is small),
the introduction rate for the centres responsible for the 0.61 eV level is 0.43.
Comparison with the calculated values suggests that these centres may be
connected with a \(V_{Ga}\) or \(V_p\). At the higher proton energy of 300 keV, where some
annealing is taking place, there is good agreement between the experimental
value of 0.11 and the calculated value of 0.17 which is the introduction rate
for \(V_{Ga}\) or \(V_p\) assuming that one vacancy recombines. The introduction
(at 300 keV) of the centres producing the 0.75 eV level suggests that they also
may be connected with $V_{Ga}$ or $V_p$. In the case of the centres responsible for the 0.19 eV level, the introduction rates, at 75 keV of 0.073 and at 300 keV of 0.021, match those for a divacancy (0.07 and 0.026) in which first one and then a second vacancy recombines. From other measurements made on these centres it is known that they have a capture cross-section of $1.08 \times 10^{-14} \text{ cm}^2$, which corresponds to a trap diameter of approximately 12 Å. As the lattice constant is 5.45 Å, this again suggests a divacancy or a complex consisting of a divacancy and one substitional atom. Further, the centres have been shown to be donors, indicating that the phosphorus vacancy may be involved.
### Theoretical Introduction Rates

<table>
<thead>
<tr>
<th>Type of centre</th>
<th>Introduction rate with no recombination</th>
<th>Intro. rate if one pair also recombines</th>
<th>Intro. rate if 2 pairs recombine</th>
<th>Intro. rate if 3 pairs recombine</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V \text{Ga} {V \text{Ga}$</td>
<td>0.5</td>
<td>0.17</td>
<td>0.053</td>
<td>0.05</td>
</tr>
<tr>
<td>$V \text{p}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V \text{Ga} - V \text{Ga}$</td>
<td>0.25</td>
<td>0.07</td>
<td>0.026</td>
<td>-</td>
</tr>
<tr>
<td>$V \text{p} - V \text{p}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V \text{Ga} - V \text{Ga} - V \text{Ga}$</td>
<td>0.1</td>
<td>0.035</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$V \text{p} - V \text{p} - V \text{p}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Proton energy

<table>
<thead>
<tr>
<th>75 keV</th>
<th>300 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centres (level 0.19)</td>
<td>0.073</td>
</tr>
<tr>
<td>(level 0.61)</td>
<td>0.43</td>
</tr>
<tr>
<td>(level 0.75)</td>
<td>10.00</td>
</tr>
</tbody>
</table>

Table (6.8)
6.3.3. Trapping centre concentrations as a function of annealing temperature ($T_A$)

6.3.3.1. Low Temperature Region ($T_A = 20 - 200^\circ C$)

A general feature of the low annealing temperature region, a region in which no encapsulant was used, is that the concentrations of the majority of the centres in the bulk unimplanted material increase with $T_A$. In the implanted material, however, the centres (0.19) and (0.61) decrease with increasing $T_A$. A possible explanation is that with increasing $T_A$ new centres are produced in both cases. In the unimplanted material traps of the same type are created, the concentrations of which although increasing are still relatively low; whilst on the implanted material, more complex traps, are generated, the number of centres (0.19) and (0.61) being reduced as they associate to form the new complexes. The dose dependence curves of figure (5.19) show that with increasing dose the number of centres of a particular type decrease.

In both cases (unimplanted and implanted material) the enhancement of the defects may be caused by surface related effects. As $T_A$ increases, should Ga or P atoms diffuse to the surface in sufficient numbers, large concentrations of defects may result. An alternative explanation is that the annealing characteristic of the surface region may be different to that of a region which is buried in the material.

The difference in annealing behaviour, therefore, may be either a dose dependence effect, or it may be a surface/buried layer effect. The results do show directly, however, that even at low annealing temperatures changes occur in the material close to the surface. Implantation of the surface region should therefore be avoided, although an encapsulant which can be applied without heating the substrate, such as evaporated SiO, may reduce surface effects. Normally encapsulants are employed for $T_A \geq 500^\circ C$. 148
6.3.3.2. High temperature region \((T_A = 430 - 650^\circ C)\)

In the bulk material the concentration of the centres (0.4) and (0.61) all increase in this temperature range, as do the centres (0.4) and (0.75) in the implanted material. All other trapping centres anneal out, except for the centres (0.48) whose concentration value stays fairly constant. Dishman\(^{149}\) et al have reported a complex of the form \(V_{Ga} - 2\, Te_P\) in Te-doped LEC grown GaP, having an energy level of \(\sim E_v + 0.7\, eV\). This compares favourably with the level at \(E_v + 0.75\, eV\) found in this work. Dishman proposed that as the temperature increases this complex can "pair" with a further tellurium atom to give a neutral complex with an energy level at \(\sim E_v + 0.4\, eV\).

\[
(V_{Ga} - 2Te_P)^- + Te^+ \rightleftharpoons (V_{Ga} - 3 Te_P)^0
\]

The annealing behaviour of the centres (0.4) suggest that they are produced by this neutral complex. The centres (0.75) and (0.4) are probably both, therefore, gallium vacancy and substitutional tellurium complexes.

The numbers of gallium vacancies can be increased by proton bombardment but other mechanisms, involving the tellurium atoms must also operate in order to create the \(V_{Ga} - 2Te_P\) centres. The numbers of gallium vacancies produced may be enhanced by ionization processes but sufficient tellurium atoms must also be available. In order that two tellurium atoms should occupy adjacent phosphorus sites, the tellurium must be displaced from its original position and diffuse through the lattice. The number of tellurium atoms displaced by atomic processes, however, will be negligible and it is probable that, like other donor impurities such as tin and sulphur, it has a low diffusion coefficient \(^{148}\) of less than \(10^{-15}\, cm^2\, sec^{-1}\).

Possible explanations are:
a) the primary collision cross-section of a Te atom is larger than that of a gallium atom (in the ratio 1.4 : 1 at 300 keV) and the energy needed to ionize an outer shell electron is similar to that of a phosphorus atom. 

Tellurium atoms, therefore, may become ionized during proton bombardment and so be more readily displaced. Subsequently they migrate through the lattice, their mobility being increased because of the radiation damage, until they are attracted by a \( V_{Ga} \). One such atom could then fill an adjacent phosphorus vacancy or replace an adjacent phosphorus atom to form the \( V_{Ga} - Te_p \) complex. This centre then attracts a second ionized tellurium atom.

b) A variation on the explanation above. The gallium vacancies diffuse through the lattice because of their enhanced mobility caused by the radiation damage. A \( V_{Ga} \) is captured by an ionized tellurium atom which has not been displaced from its lattice site. Then as before, a second tellurium atom is attracted to the group.

c) Large numbers of interstitial tellurium atoms are present in the as manufactured material. These replace phosphorus atoms during bombardment and combine with \( V_{Ga} \).

It is not possible to deduce from any of the experiments carried out which, if any, of these explanations is correct. The features they have in common however, are

1) the tellurium atoms and gallium vacancies are mobile. This is supported by the dose dependence results, figure (5.19) which shows that the \( V_{Ga} - 2 Te_p \) centres are primarily produced in the range \( 10^{-13} - 10^{-14}/\text{cm}^2 \). This is the region in which the material is starting to become amorphous and overlapping of the individual displacement tracks is beginning to occur, therefore promoting diffusion.
2) an intermediate centre, namely \( V_{Ga}^{ Te_p} \), exists which has the following properties:

i) is connected with the gallium vacancy. It will be introduced, therefore by implantation.

ii) has a large capture cross-section.

and iii) has a high introduction rate at low proton doses.

A centre which fulfils these requirements is the one responsible for the \( (E^c - 0.61) \) ev level. A further indication that this band is connected with \( Te \) and \( V_{Ga} \) is that its annealing behaviour is similar to that of the \( V_{Ga} \) centres.

6.3.3.3. Encapsulation region \( (T_A = 200 - 430^0 C) \)

6.3.3.3.1. Annealing results

A possible explanation for the reverse annealing in this region is that as the temperature is raised from \( 20^0 C \) to \( 200^0 C \) new complexes etc are produced (section 6.3.3.1) whose component parts are made up of the centres already present. The number of centres at the levels in question, therefore, decrease with increasing temperature. At higher temperatures, however, these new complexes begin to break-up and the original centres are produced once more. The centres then anneal out at much higher temperatures \( 300^0 C - 650^0 C \).

Considering the unimplanted specimens, a \( 300^0 C \) anneal decreases the concentrations of the centres \( (0.19), (0.22), (0.24), (0.35) \) and probably the centre \( (0.61) \). Centres generated in the \( 20 - 200^0 C \) region, are either starting to anneal out, or the encapsulant has reduced any surface effects. It is possible that the increase in the numbers of centres in the implanted specimens, for \( T_A = 200 - 430^0 C \) is caused by the encapsulation preventing the migration and outdiffusion of centres.
If as has been suggested in the last section, section (6.3.3.2.) the energy levels are connected with $V_{Ga}$ and $Te_p$ then a more complex explanation of the annealing results in the region $200^\circ C - 430^\circ C$ is as follows.

Campbell et al.\(^{150}\) have implanted GaP, at elevated temperatures, with tellurium and have shown that as the implantation temperature increases in the range $20 - 350^\circ C$ the amount of tellurium which goes substitutional decreases; whilst above $350^\circ C$ it increases. The TSC results in the region $200-430^\circ C$ can be explained if it is assumed that the tellurium dopant behaves in the same way as the implanted tellurium. After a room temperature implantation, the lattice will contain some monovacancies, some interstitial tellurium and some complexes such as $V_{Ga} - 2 Te_p$. As the temperature of the subsequent anneal increases, the substitutional $Te$ atoms involved in the complexes will move into interstitial positions. The number of centres involving $Te$ sub will therefore decrease. As the movement is from substitutional to interstitial, $Te_i$ will remain in the channels. At higher temperatures $300 - 430^\circ C$ the $Te$ movement is in the opposite direction, so that any $Te_i$ which had not formed complexes will now do so and the numbers of centres will increase again. Picraux\(^{151}\) has suggested that $V_{Ga}$ anneals out at approximately $260^\circ C$; this does not mean, however, that a $V_{Ga}$ contained in a complex will anneal at the same temperature. The low temperature annealing stage could be explained in terms of a movement of the tellurium atoms.

The behaviour of all the centres produced by implantation (centres (0.19), centres (0.61) and centres (0.75)) is the same. As the centres (0.75) are thought to be $V_{Ga} - 2 Te_p$, the other centres could also be linked with the $Te$ dopant. It has already been suggested in the last section that the centres (0.61) are produced by $V_{Ga} - Te$; their annealing behaviour would confirm this. The centres (0.19) might also be connected with $Te$, possibly ($Te - 2 Vp$). A $Te-2Vp$ complex is associated with an $E_c - 0.15$ level in GaAs. Yet another explanation is that the energy levels
are connected with oxygen complexes and that the encapsulation process results in an increasing quantity of oxygen in the specimens. If, however, oxygen complexes are annealing out in the region 50-200°C, there is no reason why they should be stable at 300 - 400°C, particularly as the concentrations of centres are very similar after annealing at 300°C to the concentrations after implantation. Furthermore, levels associated with oxygen were not detected after encapsulation. There is little evidence therefore, to support this explanation. Regarding the other explanations there is no experimental indications of which, if any, is correct.

6.3.3.2. Energy levels introduced by the encapsulation process

The encapsulation process involves nitrogen, oxygen and silane (SiH₄). Nitrogen produces an isoelectronic centre with level \( (E_c - 0.008) \) eV whilst oxygen forms a level at \( (E_c - 0.9) \) eV. The oxygen may also combine with a nearest neighbour \( V_{Ga} \) to form \( (V_{Ga} - O) \) which binds an exciton at \( (E_c - 0.16) \) eV\(^43\). Silicon is amphoteric with levels \( (E_c - 0.08) \) eV and \( (E_v + 0.2) \) eV. In addition a silicon complex (Si, O) has been reported by R. Z. Bachrach et al\(^152\). They are not sure of the structure of the defect but suggest that it could be \( Si_{Ga} - O_{P} \) formed via the \( (V_{Ga} - O_{P}) \) complex. This defect binds an electron with energy 0.5 eV. Using the TSC technique the \( (E_v + 0.2) \) eV silicon level, the 0.5 eV \( (Si_{Ga} - O_{P}) \) level and possibly the oxygen \( (E_c - 0.9) \) eV level should be detectable. Comparison with the experimental results shows that the \( (E_v + 0.24) \) eV level is not due to silicon, as the centres producing it are introduced by the implantation, and that oxygen is not detected. The \( (E_v + 0.48) \) eV level, however, may be caused by the \( Si_{Ga} - O_{P} \) complex. The specimens, which were encapsulated in order to be annealed, did show an increase in the number of centres (0.48), the numbers remaining fairly constant up to \( T_A = 650°C \). In the case of implanted specimens the number of centres (0.48) actually decreased. This could be caused by the silicon and/or oxygen diffusing
into the surface region of specimen at a slower rate after it has been damaged.

6.3.3.4. C-V measurements

C-V measurements made on annealed material, figure (5.26), showed that there was a large increase in the majority carrier concentration after an anneal at 300°C for both unimplanted and implanted material, indicating the introduction of deep donors. As the temperature increases both types of material become semi-insulating. The unimplanted material has changed type after an anneal at 650°C, probably caused by the rapid increase, at this temperature, of the centres (0.4). The implanted material, however, remains n-type because of the larger number of deep donors.

6.3.3.5. Summary of annealing behaviour and comparison with other work from the literature

The annealing stages found in this work can be summarised as

1. a low temperature stage centred at about 323°C
2. a high temperature stage centred around 723-773°C
3. reverse annealing from 473 - 573°C.

Brailowskii et al. have made conductivity measurements on electron irradiated (1 MeV) n- and p-type GaP. After a room temperature implantation they found annealing stages, in the n-type material, at 433, 523-573 and 773°C. Eighty-eight per cent of the damage annealed out in the first stage. p-type GaP also had an annealing stage at 523 - 573°C.

S. T. Picraux has implanted GaP, GaAs, GaAs0.45P0.55 and GaSb with various ions at energies between 11 and 150 keV. The implantations and measurements were made at 90°C, the analysis being by RBS techniques using 1.5 MeV He⁺ and 450 keV H⁺ beams. For low fluence implants where the
initial disorder peak was \( \leq 30\% \) of the random, the annealing was independent of the ion type (Zn, O, Xe in GaAs, and Zn, Sb in GaP and GaSb) but was dependent on the target material. Changes in the dose provided the disorder was \( \leq 30\% \) of the random did not affect the annealing behaviour. Broad annealing stages centred on 320, 250 and 290°K were observed for GaP, GaAs and GaSb respectively. Picraux suggested that these annealing temperatures may be related to the bond energies of the materials, annealing occurring as a result of reforming bonds. He calculated the ratio \( kT_A/E_B \), that is the annealing temperature to band energy, and showed that this was similar for all three materials; the values being 3.9, 3.4 and 4.2 x 10^{-3} for GaP, GaAs and GaSb. In cases where a high dose was implanted the annealing behaviour was independent of the ion, and of the target material, there being a broad annealing stage centre at 530°K for all the compounds.

Thommen\(^{119}\) has investigated the annealing behaviour, using resistivity and Hall measurements, of n - GaAs bombarded with 0.5 MeV electrons at \( \sim 80°K \). Distinct annealing stages were found at 235, 280 and 520°K. All changes below 200°K were attributed to reversible electronic processes. Thommen's results therefore are similar to those of Picraux.\(^{151}\) In the latter case, however, the annealing stages are much broader. For example the broad stage centred at 250°K may well be Thommen's two stages at 235 and 280°K which are not resolved. This may be because the RBS technique is not very sensitive to small displacements close to the atomic rows or because the implantation of heavy ions create a large number of different types of damage each having a distinct annealing stage. If these annealing stages are close to one another then overlapping will produce a single broad annealing stage.
H. J. Stein\textsuperscript{155} has measured the optical absorption of proton bombarded GaAs and found that there is a broad annealing stage at 473\textdegree K.

Brailovskii\textsuperscript{153} observed reverse annealing in n-type GaP after electron irradiation at liquid nitrogen temperatures. The reverse annealing occurred at 200\textdegree K and was attributed to trapping effects. Haskell et al\textsuperscript{137} have also found a small amount of reverse annealing in the range 473 - 523\textdegree K in Te implanted p-type GaP. The recovery was approximately a 30\% increase upon the damage level at 473\textdegree K. As in section (6.3.3.3.1), an increase in substitutional Te would also explain this result.

The annealing stages found in this work with proton bombarded GaP are very similar to those found in electron and heavy ion irradiated GaAs. Similar types of damage may be annealing out, therefore at each stage.

6.3.4. Comparison of the trapping centre introduction rates in semi-insulating, medium and low resistivity GaP

Table (6.9) shows the introduction rates for each type of centre in the different materials. The values were obtained from thermally stimulated current measurements in the case of the semi-insulating and medium resistivity material, and from capacitance-time measurements (see section (4.4.2.)) in the case of the low resistivity material.
Comparison of the trapping centre introduction rate in semi-insulating, medium and low resistivity GaP

<table>
<thead>
<tr>
<th>Material Proton Energy</th>
<th>Semi-insulating 300 keV Level</th>
<th>Semi-insulating 300 keV Intro-rate</th>
<th>Medium Resistivity 400 keV Level</th>
<th>Medium Resistivity 400 keV Intro-rate</th>
<th>Low Resistivity 15 keV Level</th>
<th>Low Resistivity 15 keV Intro-rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.19</td>
<td>0.02</td>
<td>0.24</td>
<td>0.24</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>0.01</td>
<td>0.32</td>
<td>0.32</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.61</td>
<td>0.11</td>
<td>0.59</td>
<td>1.85</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.48</td>
<td>0.71</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.84</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.62</td>
<td>3.62</td>
<td></td>
<td></td>
<td>197</td>
<td></td>
</tr>
<tr>
<td>Equivalent semi-insulating introduction rate</td>
<td>0.5</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table(6.9)

The "total" is the introduction rate for all the measured centres. The "equivalent semi-insulating introduction rate" is the semi-insulating introduction rate at the same proton energies as were used for the other materials, i.e. (400 and 15 keV). These values were estimated from the energy dependence curves (figure(5.20)). In the case of the medium resistivity material there is a factor of between 7 and 8 in the "total" and "equivalent" values, whilst for the low resistivity specimens there is a factor of between 6 and 7. The "total" taking into account the energy dependence, is similar, for these two materials and so is not strongly doping concentration dependent. The table shows that there are differences in the introduction rates of the
various centres. The centre producing the 0.61 eV level is dominant in the medium resistivity material whilst there is little change in the introduction rates of the centre producing the 0.75 eV level in the semi-insulating and medium resistivity material, the rates being 0.48 centres/proton and 0.53 centres/proton respectively.

6.4 Remarks on sulphur implanted specimens

The 0.09 eV level present in both sulphur and proton implanted material is as a result of the tellurium dopant. The 0.19 eV level, again produced after both types of irradiation, was also found in the semi-insulating material where the results indicated that it may be associated with the dopant (Te) and phosphorus vacancies. Two levels, 0.44 eV and 1.2 eV, are unique to the sulphur ion damage.

The capture cross-section (\(\sigma_p\)) of the centres producing the 0.44 eV level is similar to that of the 0.4 eV level formed after the semi-insulating material was bombarded with a proton dose of greater than \(5 \times 10^{13}/\text{cm}^2\) i.e. \(\sigma_p = (1.0 \times 10^{-12} \text{ cm}^2)\). In the latter case, the level was attributed to a \(V_{Ga}^-3Te_p\) complex. This suggests that for heavy ion bombardment such a grouping of atoms can form directly. The intermediate stages of \(V_{Ga}^-3Te_p\) (associated level of 0.75 eV) and \(V_{Ga}^-Te_p\) (attributed to a level 0.61 eV section (6.3.3.2.)) were not created in sufficient numbers to be detected. The formation of the \(V_{Ga}^-3Te_p\) complex implies that a large number of tellurium atoms must be available, and that they are mobile.

There was no indication of the type of centre which was responsible for the 1.2 eV level.

The 0.26 eV level (after \(S^{32}\) irradiation) and the 0.22 eV level (after \(H^+\) irradiation) may be caused by the same centres as produce the 0.24 eV level in
proton bombarded semi-insulating material.

The band gap structure of the GaP after $^{32}$S bombardment is somewhat different from that obtained after proton bombardment. Although some of the same energy levels are produced, the deep level at 1.2 eV, approximately in the centre of the band gap, is dominant. The structure is similar, therefore, to the Mott-Davies model of the bandgap structure of amorphous semiconductors (figure (6.1(b)).

The annealing behaviour of the sulphur implanted material is similar to that of the proton implanted semi-insulating material, there being a broad annealing stage over the range 293 - 473°K.

6.5. Summary and conclusions

6.5.1. Semi-insulating material

1. Trapping centres producing discrete levels at $(E_c - 0.19)eV$, $(E_v - 0.24) eV$, $(E_v + 0.4) eV$, $(E_c - 0.61)eV$ and $(E_v + 0.75) eV$ are introduced by proton bombardment of LEC grown Te-doped GaP. Some of the properties of these centres are presented in table (6.10) Figure (6.4) shows their energy level position in the band gap.

2. With increasing proton dose the damage centres cluster causing the associated discrete energy levels to broaden, and in some cases e.g. shallow levels, to overlap.

3. The types of trapping centre produced are dose dependent. With increasing dose more complex centres are formed. For example for doses $\geq 5 \times 10^{13}/cm^2$ the 0.4 eV level possibly a $(V_{Ga}^-, 3 Te_{p})$ centre is created in sufficient numbers to be detectable.

4. The bandgap structure of GaP (after proton bombardment with proton doses in the range $10^{12} - 10^{15} cm^{-2}$) is a combination of the Mott-Davis and Cohen-Fitzsche-Ovshinsky models of amorphous semiconductors.
5. For low proton doses $\leq 10^{12}$/cm$^2$ there is an initial increase in the resistivity of the implanted layer by a factor of $10^7 - 10^8$ $\Omega$ cm. This may be connected with the introduction into the band gap of a deep energy level at $(E_g - 0.61)$ eV. There is evidence to suggest that the centre responsible is connected both with the gallium vacancy and with the tellurium dopant, possibly $V_{\text{Ga}} - Te_{\text{p}}$. The resistivity is increased further as more complex centres are formed at doses of greater than $5 \times 10^{13}$/cm$^2$.

6. More damage is created at low energies than the Kinchin and Pease model predicts. Ionization effects operating via a charge exchange mechanism results in a decrease in the number of centres with increasing proton energy.

7. At low anneal temperatures, $T_A = 100^\circ$C, atom re-arrangement and trapping centre formation takes place in the surface region for both implanted and unimplanted material.

8. The annealing behaviour of the trapping centres was found to be complex. Most of the centres have annealed out by $T_A = 650^\circ$C. However, over the range $T_A = 100 - 350^\circ$C the centres first decrease in numbers, up to $T_A = 200^\circ$C, and then increase again.

6.5.2. Medium and Low resistivity material

1. Trapping centres of large capture cross-section and with similar energy values to those found in proton bombarded semi-insulating material were found in Te-doped medium resistivity (50. $\Omega$cm.) gallium phosphide.

2. The proton implantation of low resistivity material (0.1 $\Omega$cm.) again results in the production of trapping centres with large capture cross-sections.

3. The total introduction rate for all the measured centres was approximately the same for both medium and low resistivity materials.
4. The type of centre(s) produced is dependent upon the doping concentration.

5. The carrier removal rate for proton bombarded GaP is similar to proton bombarded GaAs.

6.5.3. Sulphur implanted material

1. Several trapping centres with large capture cross-sections are produced by sulphur bombardment. Associated energy levels of 0.19 eV, 0.44 eV and 1.2 eV are introduced into the band gap.

2. Large numbers of complex centres (such as $V_{Ga} - 3 Te$) are created even by small doses of sulphur ions i.e. $3 \times 10^{12}/\text{cm}^2$. In comparison this type of trap resulted after proton doses of $5 \times 10^{13}/\text{cm}^2$ or more, and then only in small concentrations.

3. There is an annealing stage in the range 293 - 473$^\circ$K as for proton bombarded material.
The bandgap energy levels found to be present (using TSC methods) in proton bombarded semi-insulating GaP:

(all values in eV)

Fig (6.4)
Properties of the trapping centres

<table>
<thead>
<tr>
<th>Resulting Energy Level (eV)</th>
<th>Capture cross-section ($cm^2 S_T^2$), and temperature coefficient (A) of capture cross-section $S_T \alpha T^A$</th>
<th>Charge State</th>
<th>Centres present in unimplanted material</th>
<th>Centres introduced by proton implantation</th>
<th>Other Remarks</th>
</tr>
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<tr>
<td>$E_C - 0.19$</td>
<td>$1.0 \times 10^{-14}$, - 3.2</td>
<td>attractive singly charged</td>
<td>*</td>
<td>*</td>
<td>Associated with one or two Vp and Te. Possibly (Te - 2Vp)</td>
</tr>
<tr>
<td>$E_C - 0.22$</td>
<td>$5.0 \times 10^{-16}$, - 4.5</td>
<td>neutral</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>$E_V + 0.24$</td>
<td>$5.0 \times 10^{-16}$, - 3.2</td>
<td>neutral</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>$E_V + 0.35$</td>
<td>$1.0 \times 10^{-11}$, - 4.4</td>
<td>attractive single or doubly charged</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>$E_V + 0.4$</td>
<td>$1.0 \times 10^{-12}$, - 4.5</td>
<td>&quot;</td>
<td>*</td>
<td>*</td>
<td>Possibly $V_{Ga} - 3 Te_p$</td>
</tr>
<tr>
<td>$E_V + 0.48$</td>
<td>$5.0 \times 10^{-13}$, -</td>
<td>&quot;</td>
<td>*</td>
<td>*</td>
<td>Associated with $V_{Ga}$, and Te possibly $V_{Ga} - Te_p$</td>
</tr>
<tr>
<td>$E_C - 0.61$</td>
<td>$5.0 \times 10^{-12}$, -</td>
<td>&quot;</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>$E_V + 0.75$</td>
<td>$1.0 \times 10^{-15}$, - 2.9</td>
<td>attractive neutral or singly charged</td>
<td>*</td>
<td>*</td>
<td>Possibly $V_{Ga} - 2 Te_p$</td>
</tr>
</tbody>
</table>

Table (6.10)
Chapter 7

CONCLUSIONS

7.1 General summary of conclusions

The general aims of the work, as set out in chapter 1, section (1.3), have mostly been achieved. Certain areas, however, would have been examined in greater detail if time had been available. Sections (6.5.1.), (6.5.2) and (6.5.3) have already listed the detailed results and conclusions. In this section, therefore, the more general conclusions of the work are summarised. These are:

1. The proton bombardment of gallium phosphide produces defects which result in the introduction of deep energy levels into the bandgap. Some of the properties of these defects are summarised at the end of chapter 6. Certain of the damage centres introduced, were already present in the unimplanted material, whilst the remaining centres could also be created by annealing at fairly low temperatures (293 - 923°K). Proton irradiation does not produce, therefore, any defects which are unique (i.e. cannot be produced in any other way) but it does produce defects which would not normally be present in measurable concentrations at room temperature.

2. The energy level bandgap structure of GaP after proton bombardment, for doses between $10^{13} - 10^{15}/\text{cm}^2$, is a combination of the Mott-Davis and Cohen-Fritzsche-Ovshinsky models for amorphous semiconductors. With increasing dose shallow discrete levels broaden eventually overlapping and producing "band tails".

3. The type of defect(s) produced is dependent upon:

   i. the implanted ion.

   Irradiation with sulphur created defects which were more complex than those resulting from a similar dose of protons.
ii. the ion dose.

The more complex centres e.g. those thought to be associated with $V_{Ga - 2Te_p}$ and $V_{Ga - 3Te_p}$ were introduced in increasing numbers with increasing dose up to $10^{14}$/cm$^2$.

iii. the doping concentration of the starting material.

4. The total measured centre introduction rate was not significantly different for medium and highly doped Te GaP. The introduction rate for the different kinds of damage centre was found, however, to be both dose and energy dependent.

i. the dose dependence was complex. With increasing dose the introduction rate increased to a maximum at about $10^{14}$/cm$^2$.

ii. the number of damage centres produced at low proton energies was greater than that predicted by the Kinchin and Pease model. There are indications that ionization processes operating via a charge exchange mechanism are responsible for a decrease in the amount of damage with increasing ion energy.

5. Most of the damage centres are no longer present in measurable concentrations after an anneal at 923°C.

6. Considering the electrical behaviour of the material after proton implantation.

i. only a low dose ($<10^{12}$/cm$^2$) is necessary to increase the resistivity of the starting material by a factor of $10^7 - 10^8$ $\Omega$cm. This is independent of the dopant and doping concentration of the starting material.

ii. The carrier removal rate for proton implanted GaP is very similar to that of proton implanted GaAs, indicating that similar damage processes occur in both materials.
7.2 Suggestions for further work

A few suggestions for further work may include investigations of:

1. The dose rate dependence of the trapping centre introduction rates.
2. The spatial distribution of the damage. For this the C-t method would be the most suitable. By varying the bias across the Schottky barrier junction the type of centre and number of damage centres could be determined at different distances into the specimen.
3. The annealing behaviour of the centres using encapsulants such as Si$_3$N$_4$.

The same methods could be used on material with different dopants and material grown by different methods.

7.3 Applications

Two of the conclusions are important in this respect. Firstly, it has been confirmed that semi-insulating regions can be produced in GaP with only small proton doses (<$10^{12}$/cm$^2$); a dose of $10^{12}$/cm$^2$ giving an increase in the bulk material's resistivity of a factor of $\approx 10^7$ $\Omega$.cm. For higher doses ($10^{13}$-$10^{14}$/cm$^2$) the resistivity approaches that of intrinsic GaP. Comparison of the results obtained in this work with those of Spitzer and North suggests that the low dose resistivity increase (by a factor of $\approx 10^7$ $\Omega$.cm) is independent of the dopant and doping level of the starting material.

Secondly, it has been shown that the majority of the damage centres are no longer present in measurable concentrations after an anneal at $923^\circ$K (650°C). The damage produced by heavier electrically active ions which is more complex, would, therefore require an annealing temperature of at least 650°C. On the other hand proton isolated regions will be quite stable under normal operating conditions.
APPENDIX

It is interesting to calculate the Coulomb potential energy between unit charges at distances which correspond to the different lattice spacings within GaP. Fig. (A.1) shows the atomic spacing between atoms on the same and on the adjacent sub lattice.

The Coulomb potential between two charges \( Q_1, Q_2 \) a distance \( r \) apart is given by

\[
\int_{r}^{\infty} \frac{Q_1 Q_2}{4\pi\varepsilon_0 r^2} \, dr
\]

Table (A.1.) lists the potential between unit charges assuming these charges are different lattice spacings apart.
The potential energy between charges for different lattice spacings

<table>
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<th>Distance between charges</th>
<th>Coulomb Potential (eV)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r(\text{Å}) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.7</td>
<td>0.19</td>
<td>Same sub-lattice, atoms diagonally across face</td>
</tr>
<tr>
<td>9.3</td>
<td>0.15</td>
<td>From one sub-lattice to the other diagonally across face</td>
</tr>
<tr>
<td>5.45</td>
<td>0.27</td>
<td>Lattice spacing</td>
</tr>
<tr>
<td>7.13</td>
<td>0.21</td>
<td>From one sub-lattice to the other - one lattice spacing.</td>
</tr>
<tr>
<td>3.85</td>
<td>0.38</td>
<td>Same sub-lattice, - half diagonal distance across face.</td>
</tr>
<tr>
<td>5.25</td>
<td>0.26</td>
<td>From one sub-lattice to the other - half diagonal distance across face.</td>
</tr>
<tr>
<td>2.36</td>
<td>0.61</td>
<td>nearest neighbour distance</td>
</tr>
</tbody>
</table>

Table (A.1.,)

The table shows that for the distances experienced within a unit cell potentials in the range 0.15 \( \rightarrow \) 0.61 eV can be produced. Larger potentials i.e. \( > 0.6 \) eV would occur only if atoms were doubly charged, or if the distance between charges was less than the nearest neighbour distance (2.36Å) or if more than two atoms/simple defects were involved.
A 0.61 eV potential results from two nearest neighbours being charged whilst the potential between unit charges across the diagonal of the face is 0.19 eV. Two atoms at the half diagonal distance, or one doubly charged atom in such a position, would produce a 0.76 eV potential.

The similarity between the measured energy levels and the potential energy between unit charges at different distances does suggest the type of configuration which might produce the defect. If, as has been suggested in section (6.3.3.2.), the 0.61 eV level is caused by a V_Ga - Te_p complex, then the V_Ga and Te_p may be a nearest neighbour distance apart. Similarly, if the 0.19 eV level is associated with the Te - 2V_p (section (6.3.3.3.1)), then to produce a potential energy of 0.19 eV the two phosphorus atoms would each need to be twice the diagonal lattice distance away from the tellurium site.
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