AN INVESTIGATION INTO THE ELECTRICAL PROPERTIES
OF GALLIUM PHOSPHIDE BEFORE AND AFTER IMPLANTATION
WITH ELECTRICALLY ACTIVE IONS.

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Slices of single crystal gallium phosphide were subjected to a number of methods of surface polishing and etching. These were evaluated and the most effective used to prepare samples for ion implantation. The electrical properties were investigated, before and after implantation, using Hall and Van de Pauw measurements and the capacitance–voltage, capacitance–time relationships for Schottky barriers. This enabled an explanation for the anomalous concentration of acceptor carriers in implanted, annealed material to be formulated.

Unannealed, implanted specimens were investigated and it was shown that a crude approximation to an MIS device could give an indication of the depth of implantation.

The barrier height of tin on p-type gallium phosphide was established, experimentally, as 1.52±0.18eV.
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1.1. Why Gallium Phosphide?

Two recent developments lay behind the reason for starting this investigation into ion-implantation of gallium phosphide. Firstly, the ability to grow single-crystal gallium phosphide by a simple method, and secondly the realisation of ion-implantation as a tool for the fabrication of devices. Implantation became a reproducible and accepted research tool in the early '60's, and the combination of these two relatively new techniques meant that little reported work had been published at the start of this project.

Gallium phosphide was chosen as a semiconductor with potential in commercial terms of electroluminescent devices. Silicon, germanium and gallium arsenide had been used mainly because of the ability to produce good electrical devices with them. Gallium phosphide on the other hand has one major advantage over the others - it is electroluminescent in the visible spectrum. Most reported work has been concentrated on the electroluminescent aspect of the material - specifically in producing light emitting diodes (LEDs). Rapid advances in electronic technology in recent years, particularly in micro-electronics, computers and control, has led to a demand for information displays more compatible in terms of size, ruggedness, reliability and operating voltage than provided by the CRT, although a number of other display media exist, e.g. gaseous discharge matrices and liquid crystals.

Solids can generate visible light in several ways: by chemical reaction (chemiluminescence), by bombardment with light (photoluminescence) or electrons (cathodoluminescence) or by the passage of electrons through the material (electroluminescence).
In the latter case the emission characteristics depend on the chemical composition of the host crystal and the incorporation of small amounts of special impurities. These impurities can give rise to centres which generate either useful, visible light or non-useful, infra-red or ultra violet light, and heat; these centres are referred to as radiative or non-radiative centres respectively. Most reported work has been concentrated on the radiative centres and the location of the impurities in the host lattice. During the development of the project, reported here, it became clear that with the type of crystal and expertise available, the location of recombination centres by non-radiative techniques was desirable. Consequently, the treatment and examination of radiative recombination will be fairly brief, and that of non-radiative recombination longer.

1.2. Historical background.

With the development of semiconductor devices in the 1950's, the basic principles of carrier injection across junctions was postulated by Lehovec et al. in 1951 and 1953. Historically, electroluminescence was first observed by Round in 1907 when working with SiC crystals for the detection of radio waves. Lossev was the first to investigate the phenomenon in 1923, and then in a series of systematic studies up to 1940.

Meanwhile Destriau had demonstrated a.c. electroluminescence in ZnS. Polycrystalline ZnS was used for a commercial solid-state light source in 1959 by Westinghouse, but the low brightness which decayed rapidly during operational life resulted in few applications.
About this time the III-V single crystal semiconductors were beginning to be more fully investigated, with the main objective of increasing the upper temperature limit of germanium device operation. It became increasingly apparent that these materials had other applications, one of which was electroluminescence. In 1955 reports concerning GaP (Wolff et al), InSb (Allen et al), and InP, GaAs, and GaSb (Braunstein) were published. Work was concentrated on GaAs due to its applications in microwaves, but efficient infra-red devices were constructed by 1962 (Koyes et al). In 1964 SERL produced the first single crystal LED based on GaP technology. Since then the complex compound material GaAsP has been investigated and now LEDs using GaP, GaAsP and SiC are being marketed.

Other potential materials, such as InGaP (Harcoev et al), GaAlAs (Kressel et al) and GaN (Dingle et al) are currently under investigation.

1.3. Radiative recombination.

Since luminescence is produced by electronic energy changes, a luminescent material must have an energy gap. The size of this gap will determine the maximum energy of radiation which can be emitted with any reasonable efficiency. It is possible to draw up a chart of materials indicating the energy range up to which they will emit (Fig 1) and from this diagram it can be seen that only materials with an energy gap in excess of approximately 1.8 eV (700 nm) are capable of producing visible luminescence directly. Some materials can be intermixed to form solid solutions with a wide range of energy gaps.
Figure 1. Comparison of spectral colour, relative eye response and wavelength with various materials and their bandgaps. Known direct gap materials are indicated by cross-hatching. A material will only be able to emit radiation below that of its band-gap.
Figure 2. Simplified band structure diagrams plotted in momentum space of: a) direct gap semiconductor where the electrons predominantly occupy the minimum at \( k = 0 \) and can transfer between bands without changing momentum and b) an indirect gap material where electrons mainly lie in the indirect minimum and lattice phonons are required to conserve momentum on exchange between bands.
For practical applications, however, features other than the energy gap play an important part and further restrict the choice of material. As can be seen from the diagram, GaP is placed directly in the middle of the visible spectrum.

GaP also possesses satisfactory electrical and crystal-growth properties as well as a large enough energy gap (2.26 eV at 300°K). However it is an indirect band-gap semiconductor. In a direct band-gap material (e.g. GaAs), the minimum energy of the conduction band and the maximum energy of the valence band lie at the same position in momentum k space. In an indirect-gap semiconductor (e.g. GaP), the minimum of the conduction band does not have the same value of k as the maximum of the valence band. For comparison a simplified band structure for the two cases is shown in Fig 2.

For an electron in the conduction band to recombine with a hole in the valence band in an indirect-gap semiconductor, momentum must therefore be absorbed or emitted in the form of phonons from the lattice. Because of the restriction on the crystal momentum, the intrinsic recombination probability of the electrons and holes is low. The recombination of electrons and holes can be greatly enhanced by addition of impurities which interact strongly with free carriers, thus enabling crystal momentum to be conserved through an impurity-carrier interaction. Therefore, it is possible to think of the impurity inducing an efficient luminescence. In fact, it is just such an impurity-induced emission which produces efficient light generation in GaP.

Many possible impurity-induced transitions can be postulated. The more simple ones are: a) recombination of an electron trapped on a donor site with a hole trapped on an acceptor site, b) a trapped electron at a deep donor recombining with a free hole c) excitonic (an electron and hole bound together as a pair) recombination at isoelectronic and other neutral traps.
Figure 3. Schematic representation of three types of Auger processes. In these processes, energy released due to an electron-hole recombination is transferred as kinetic energy to a nearby third particle (electron or hole). a) Auger process associated with the excitonic transition at a neutral sulphur donor. b) Auger process associated with the bound excitonic transition at Zn-O complex utilizing a free hole in the valence band as the third particle. An alternative process is when electron at Zn-O complex combines with the free hole and energy is transferred to the hole at Zn-O complex. c) Auger recombination process at a doubly ionized donor. The energy released in electron-hole recombination is transferred to the second bound electron at the donor.
An isoelectronic trap refers to a bound state produced by an isoelectronic substituent (e.g. N replacing P in GaP). These isoelectronic traps, which are electrically neutral, could either be a point defect or a molecule in the GaP lattice. A good example of a point defect is a nitrogen isoelectronic centre which replaces phosphorus in GaP (green) LEDs. A well known molecule-type isoelectronic trap is the zinc acceptor on a gallium site with an oxygen donor on a phosphorus site nearest-neighbour complex which is responsible for visible-red emission in GaP. Such isoelectronic traps provide the greatest impurity induced luminescence efficiencies at room temperature in GaP.

In addition to the radiative recombination at these impurity centres, there are competing non-radiative recombination mechanisms. Most of the energy released in exciton recombination at a neutral donor or acceptor goes into non-radiative processes. Non-radiative recombination mechanisms are more difficult to study than radiative since direct observation of this process is impossible.

The most relevant non-radiative process in GaP is the Auger process. In the Auger process, energy released due to electron-hole recombination, instead of being carried away by a photon, is transferred as kinetic energy to a nearby third particle (electron or hole). This third particle could be bound or free. Several cases have been studied and the three most relevant are shown in Fig 3.

The first case relates to S-doped GaP in which S acts as a shallow donor. In this Auger process, the bound electron at the sulphur atom takes the energy released in the exciton annihilation (3a), this non-radiative process being 500 times more rapid than the radiative decay.
It is known that all neutral acceptors and donors bind excitons at low temperatures and that the resulting emission is primarily non-radiative. However, these centres do not act as non-radiative centres at room temperature, because the excitons are already dissociated at this temperature.

The second type of Auger process is related to neutral centres, such as the Zn-O complex (3b). In efficient p-type (Zn-O) doped material, free holes are in abundance at room temperature (5x10^17 cm^-3). Whenever the bound hole of the exciton recombines with the deep bound electron, energy can be transferred as kinetic energy to one of the free holes, resulting in an Auger process. To get a large number of Zn-O complexes, the concentration of Zn doping is required to be high. However, at these high concentrations, the non-radiative process due to Auger recombination dominates. For the most efficient electroluminescent diodes an optimum Zn concentration of approximately 3x10^17 cm^-3 has been found.

An alternative approach to achieve higher efficiencies is to create a large number of Zn-O complexes, without doping with a large number of Zn atoms. One method could be the use of ion implantation, and this was the initial impetus behind the implanting of p-type GaP with O and Zn, and will be discussed later. Other methods are reported to be the basis of experiments now in progress.

Finally, there are a group of non-radiative centres which are deep centres and could act as non-radiative centres at room temperature. These are doubly ionized centres, which are capable of binding two particles of the same type. For example Cl, a Group VII element, will replace P to generate doubly ionized donors. Normally, Cl atoms can capture two electrons. If free holes are available, hole and electron combination take place.
However, this energy does not result in photon generation, but instead can be transferred to the second bound electron at the chlorine atom (3c). Doubly ionised centres have a large capture cross-section, i.e. they can control the recombination kinetics in GaP, and impurities like Si and Cl are present in most GaP crystals.

1.4. Material fabrication.

If the three methods of fabricating GaP single crystals are compared, it is found that the diodes fabricated using vapour-phase epitaxy and liquid-phase epitaxy have similar concentrations of non-radiative impurities, whereas the Czochralski technique tends to give higher concentrations. Thus it is easier to make electroluminescent devices from epitaxial material. Most epitaxial material is grown on Czochralski materials produced by the liquid-encapsulation technique. As $\text{B}_2\text{O}_3$ is used in the process most material has a concentration of oxygen. It was considered necessary to investigate bulk grown material, not only because an understanding of its behaviour would aid those interested in epitaxial material, (and thus provide information for the time when bulk-grown material has a lower dislocation density and therefore useful for electroluminescent applications) but also because of the availability of the material. This latter reason (availability) became the prime one after several unsuccessful attempts at crystal growth. Bulk grown material was donated by Services Electronic Research Laboratories, Baldock and purchased from Metals Research Limited when price limitations had been overcome. Consequently, the research reported concentrated on the non-radiative behaviour of the material.
1.5. Rectifying junctions.

The fabrication of a rectifying junction provides a mechanism by which the carriers or centres may be excited above their state at thermal equilibrium. To achieve this excitation, a potential barrier must be present at the surface or in the bulk of the semiconductor material, so that on traversing this barrier the carriers will gain energy from the applied field. This excess energy may be achieved by carrier injection, tunnelling or avalanching. Although the most efficient mechanism developed to date is injection at a forward-biased p-n junction, the work presented here used junctions between a metal and the semiconductor. When a metal is deposited on a semiconductor surface, it will either be ohmic or rectifying. The latter is useful as carrier injection is high. Such a rectifying junction is the Schottky Barrier. The fabrication of Schottky barriers and their theoretical behaviour will be referred to later.

1.6. Ion Implantation.

It has previously been mentioned that impurities in the crystal lattice affect the electroluminescent response of the material. They also affect the electrical properties, and this fact was used to study the changes caused by introducing different species of impurities into the host lattice. Normal doping requires high temperatures, as this is accomplished either in the melt or during epitaxial layer growth. During ion implantation, at the low dose rates used, the substrate temperature does not rise above 100°C. A difficulty arises, though, because the host lattice becomes disordered during the bombardment and heat is required to anneal out the damage.
GaP is difficult to work with, as it dissociates at around 450°C at atmospheric pressure, and surface passivation is necessary to anneal at temperatures above this. It has been reported, however, that implantation at elevated temperatures could prevent damage without the need for post-implantation annealing.

1.7. Linear accelerators.

Although J. J. Thomson first produced a beam of positive ions in 1910, it was some years before use was made of the fact that the deflection produced by a uniform magnetic field was inversely proportional to the square root of the ion mass. Thus it became possible to separate ions of different masses and led to mass spectrometry. The forerunner of ion implantation was the Manhattan Project for producing the first atomic bomb, by enriching uranium 238 with uranium 235. Not only is it possible to separate ions and isotopes of different elements, but also recent developments have led to them being accelerated to high energies. The bombardment of solids by ion beams, introducing foreign atoms, has become a precise tool for investigating host crystals and for the manufacture of semiconductor devices.

The first essential is a simple and versatile source of ions, one capable of producing ions from gases or metals. The apparatus used in this work is described in Chapter 2. The second essential is a means of accelerating the ion beam and then focussing it. Both are achieved electrostatically, although a certain amount of focussing is carried out magnetically in the source. The beam then needs to be separated, and this is achieved using an electromagnetic separator. The resulting pure ion beam, is then directed onto the target.
Figure 5. Distribution of implanted ions following the normal statistical distribution about the statistical range (a) and the statistical distribution about a new channelled range due to channelling (b).
20.
The transfer of charge from source to target results in a charge increase, and this can be monitored by transferring the charge to earth via an external integrating circuit. Thus the beam current can be monitored externally. Fig 4 shows a schematic diagram of an accelerating system.

1.8. Ranges of implanted ions.

It is necessary to be able to control and measure the depth of penetration of the bombarding ions, i.e., the "range." Energetic ions, travelling through a solid, lose energy by collisions with both the electrons and atoms of the solid. For ions with atomic numbers greater than 10, for example, in the energy range of 150 keV, the energy lost in atomic collisions predominates and the energy lost by electron collisions can be ignored. Thus the penetration depth depends on the rate of energy loss in a series of statistically independent atomic collisions. Consequently it is unlikely that successive ions will come to rest at the same range, and the statistical range is defined as the mean or average penetration. Lindhart et al. have calculated the theoretical distribution and have demonstrated that the distribution of implanted ions follows a normal statistical distribution about the statistical range (Fig 5c). Since the atoms of a crystalline solid are arranged in a regular lattice, any ion which happens to pass between rows and planes of atoms without having major collisions will not experience a high rate of energy loss. This phenomenon is called channelling and results in ions being implanted into single crystals to a depth far greater than their statistical range (Fig 5b).
For example, if a finely collimated beam is directed accurately along a channelling direction, the channelled range can be greater than ten times the statistical range, and over 90% of the ions will be channelled. To achieve a statistical distribution, therefore, it is necessary to have the incident ion beam at such an angle that the channelled fraction is negligible. Calculations of this critical angle are made in Chapter 2.

1.9. Annealing.

As the incident ion is slowed down by a succession of collisions with the lattice atoms in its path, some of these atoms will be displaced from their normal sites, and will recoil with sufficient energy to initiate a chain reaction of collisions. If this occurs near the surface, atoms which receive energy greater than the surface binding energy will be ejected. Thus sputtering occurs.

Inside the lattice the result is a heavily disordered region of radiation damage where the atoms have been displaced. This damage can be minimised by channelling. In general there are two types of lattice defect produced: atoms forced into unusual positions between the lattice sites (interstitials) and those causing "holes" in the lattice (vacancies). Both can occur as single defects or as clusters.

As the temperature of the crystal is raised the lattice will emit thermal energy to the defects and they become mobile, migrating randomly through the solid. Therefore, if the damaged crystal is heated to a sufficiently high temperature it will return to its normal ordered state as the interstitials and vacancies recombine or are ejected at the surface. This process, annealing, is used to remove the radiation damage.
The accurate experimental measurement of ion ranges in solids is desirable, but not straightforward. Most methods are reliable to within 50\% \textsuperscript{+}, with the electrical methods probably more accurate than those using sectioning techniques. The use of capacitance-voltage measurements, described in the following chapters, can indicate not only the profile, but also the number of atoms in their disordered state.

1.10. Objectives.

Having considered the material and the method of doping the overall object of the work must be defined.

Gallium phosphide was taken in its "raw" state, in slices from the ingot, and a method was found for polishing the surface so that damage due to sawing, etc. was removed. The electrical properties of the material were then investigated and values for mobility, concentration and energy levels of donors and acceptors, calculated. The material was then implanted with active ions of different doses and energies and some annealing experiments carried out. The changes in the electrical properties were investigated. During this programme, various techniques for measuring the electrical properties were developed and since the work was completed these methods have been developed further by other workers. Results were compared with those published or communicated.
2.1 Implantation.

2.1.1 Introduction to implantation apparatus.

The basic requirements of an implantation facility have been described in the previous chapter. An easily accessible source of ions is required, and a fairly simple method of accelerating them. Two sources were used in this work. Firstly, a source using elements with gaseous compounds, and secondly, one using elements and compounds in a metallic form.

2.1.2 R.F. ion source.

This source consisted of a glass bottle into which a low pressure gaseous mixture, containing the required element, was passed. An r.f. discharge was then induced in the gas and ions extracted from the plasma through a small hole by the application of an electrostatic field. A schematic diagram is shown in Fig 6. This source is described in detail by Thonemann et al. and was developed at AEHE and AWRE. The one developed by AWRE was used in this project. Typical ion currents achieved are in the order of 5-10 mA. The r.f. field is supplied by an oscillator and 200-300 W of r.f. power is usually required.

2.1.3 Sputtering ion source.

A more versatile ion source was the one fitted to the 180 keV ion accelerator which was the machine used in these experiments. This source is of the Hill-Nelson design and constructed by C & N (Electrical) Ltd., Gosport, Hants.
Figure 6. R.F. ion source

Diagram showing a R.F. ion source with labels indicating:
- 0-30 kV
- r.f. field
- gas inlet
- glass sheath
- Al canal
- Al base
- plasma compression coils
- ion beam
Although this source can be operated in a gaseous mode it was more frequently used in the sputtering mode. In the sputtering mode, argon, (or another gas), is fed into the arc chamber gas inlet. The filament is held at 100V negative with respect to the arc chamber and the gas ionised by an electron beam originating at the tungsten filament. This filament usually required 50 A at 5V a.c. The ions are attracted to the sputtering electrode by the application of a 2kV negative potential. It is possible to constrain the plasma by energising an axial magnetic field. The gas ions striking the negative electrode sputter neutral metallic ions from the electrode tip. The tip can be changed to provide ions of most elements that are metallic in form. These sputtered metallic ions form a gas-metal plasma in the chamber. The source is represented schematically in Fig 7. The ion beam is extracted from the plasma, via the extractor cup, into the accelerating system by a 180keV (max) three element electrostatic lens system. The accelerating system is described by P. J. Cracknell et al and G. Brown and M. L. Renton in greater detail and shown in photo 1. The analysing magnet is used to deflect the beam by 20°.

2.1.4 Target chamber.

The target chamber is typically at a pressure of $10^{-7}$ torr with the gas inlet valve, at the source, closed. The samples to be implanted were placed in a six-position holder. This was linked to the chamber casing and enabled the samples to be rotated, and allowed a number of implantations with the same ion, but different doses or energy to be completed under the same conditions. One position was occupied by a piece of printed-circuit board. This enabled the incident beam current to be measured fairly accurately. As the incident beam was scanned across the samples, mounting them on conducting material enabled monitoring of the beam during implantation.
Photo 1. 150 keV accelerator showing bun, magnet and flight tube.

Photo 2. Six-position rotatable target holder.
Figure 7. Cross-section of Hill-Nelson sputter ion source.
Date: 16/9/70
Oxygen gas in sputtering source
100 keV accelerating voltage
Source pressure: 0.1 torr
Filament voltage: 4.5 V
Filament current: 31 A
Helium Gas in Sputtering Source
Date: 11/3/71

Extractor voltage: 16 keV  Extractor current: 1.5 mA
Filament voltage: 3 V  Filament current: 40A
Arc voltage: 87 V  Arc current: 0.4 A
Source pressure: 0.1 torr  Target pressure: $10^{-6}$ torr
Generator voltage: 110 keV  Generator current: 0.7 mA
Photo 2 shows the rotatable holder. The cylindrical section was at a potential of -90V to reduce any secondary emission from the target. It was possible to accurately align the samples, as ten turns of the external knob rotated the holder through 60°, so that channelling did not occur. The critical half angles for different ions and energies was calculated (Appendix A) and it was assumed that implantations at 6° to the beam would avoid significant channelling. All samples used were <111> orientation.

2.1.5. Analysis of ion beam.

If the current through the magnet is varied then the amount of deflection of the beam is dependent on the mass of the ion. Thus a scan of magnet current will give an analysis of the plasma extracted from the arc chamber. A typical scan is shown in Fig 8. Oxygen was the gas being fed into the chamber, and it was accelerated to 100keV. The argon peak is due to residual gas left from previous experiments with the sputtering source where argon was the plasma gas. Fig 9 shows the source operating in the gaseous mode, with helium as the source gas. All the other peaks are due to residual gases in the source. In this case the magnet current was selected to separate ions of mass 16, i.e. singly charged oxygen ions.

2.1.6. Ion beam current.

Typical values of current for oxygen, at 100keV, were 2 - 5μA. When a metallic ion was needed, the sputtering mode was used. For zinc, a small pellet was machined from a zinc rod. Due to the spectrometer action of
the separator magnet, the purity of the sputtering electrode is not critical. It was noticed that to stop the pellet melting the temperature of the electrode had to be controlled using the Freon cooling system. The relationship between mass and magnet current enabled the approximate value of current to be calculated, so that locating a particular ion was fairly simple. Typical values for a 70 keV zinc implantation gave a zinc ion beam current of 1.5 µA, the argon beam current being 20 µA. The source pressure was 0.1 torr and the target chamber pressure 10^{-5} torr with a beam present.

2.2 Surface Preparation.

2.2.1 Chemical preparation.

Before implantation could begin, the surface of the specimen had to be flat and free from mechanical damage. All the samples used were grown in ingots using the Czochralski technique. Consequently, they had considerable surface damage due to the saw that cut the ingot into slices. This damage had to be removed mechanically, and the resulting surface chemically etched to provide a surface that was free from pitting and contamination. Previously reported work indicated that the usual method of preparing GaP was by cleaving the single crystal, and most chemical etches were preferential in their etching, giving a surface that was predominantly Ga or P. It was necessary to develop a method of polishing and etching that was repeatable and fairly simple.

A programme of experiments using different abrasives, polishing cloths, times and pressures was carried out. The two main forms of abrasive for polishing semiconductors are based on diamond or alumina. The former

\[ \frac{B_2}{B_1} = \sqrt{\frac{E_2M_2}{E_1M_1}} \]

\( B = \text{Magnet Field} \)
\( E = \text{Energy of keV beam} \)
\( M = \text{Mass of Ion} \)
usually come in colour coded paste form and the latter as powder that needs a liquid to create a slurry. Three types of abrasive were chosen. Lustrox and Linde A were of the alumina variety, and Dialap a diamond paste. Two types of polishing surfaces are usually available: a. smooth surface, usually a silk or nylon cloth, providing little adhesion for the abrasive whilst keeping it moist; and a more furry surface that will hold the abrasive and keep the polishing surface clean, as loosened material will not be free. It was noticed that the latter type of surface gave a cleaner finish. All specimens were examined under the microscope at up to 400x magnification.

With GaAs it is possible to achieve a good polished surface with a Bromine : Methanol, 1:10 solution. This was not possible with GaP as the resulting surface was spongy. Whilst this programme was being conducted, G.R. Wronski gave a method of preparation combining the two techniques. It was found that a mixture of Linde A (0.3 μ alumina) in a solution of 20:1 Methanol-Bromine at 250 lb/in² pressure using a Metron B polishing cloth erased all visible damage and gave a good, optically flat, scratch free surface at 400x magnification. Photos 3-6 show the surface after different treatments, and it can be seen that the Linde A/Bromine : Methanol is superior.

The amount of residual damage due to the mechanical polishing was established by A. Tinsley using Rutherford Backscattering techniques. He found that surface damage was present up to 150 μ below the surface, but that this annealed out at 250°C, 1 hr. It was considered easier to chemically etch this damage, as annealing might have affected other properties of the material. Aqua Regia is used to etch single crystal GaP, but on pulled single crystals this introduces a large number of etch pits, and is relatively fast (6-8 μ/min.). Recent work by E. Hájková et al proposes an etch for epitaxial GaP based on a Nitric/Hydrochloric acid etch. The etches containing HCl seem to be fairly dependent on time and doping level.
Photo 3. Lustrox 3lb/in² pressure
50x    Lapmaster 10 mins.

Photo 4. Linde A 1%Br/Methanol
400x   Metaserv 5 mins.

Photo 5. Lustrox 1½lb/in² pressure
50x    Lapmaster 2 mins. etch
       H₂SO₄:HNO₃:HF
Figure 10. Graph showing amount of material removed with time for samples 73/49 and 150/35, using $\text{H}_2\text{SO}_4$:$\text{HNO}_3$:$\text{HF}$ (30:60:10) at 50°C.

Figure 11. Talystep trace for one step etched into material with the etch of Fig. 10.
An etch that proved to be fairly independent of these variables consisted of $\text{H}_2\text{SO}_4 : \text{HNO}_3 : \text{HF}$ (30:60:10) with a few drops of bromine per litre. Used at 50°C this gave an etch rate of 2-3 μ/min. The rotating beaker technique was used to maintain an even flow of etch across the sample. This involved mounting a sample on a Teflon disc, using wax, and placing it in a rotating Teflon beaker, so that the sample rotated whilst the etch flowed over the surface. The shortness of the etching time (∼1 min) obviated the need for any heating apparatus. Photo 7 shows a typical surface, the visible pattern being a spiral dislocation within the material.

The rate of etching was found using a Talystep, and measuring the step between an etched and unetched area, the unetched area being covered with wax. Fig 10 shows the results obtained, from these measurements. Fig 11 shows a typical Talystep trace.

2.2.2. Electrochemical polishing - introduction.

For purposes other than cleaning up the material prior to implantation or metallic deposition this etch was too fast. A controllable form of polishing was necessary that had a slow etch rate. During work on silicon and germanium, electrochemical etching was used. It was decided to investigate the electrochemical polishing of GaP. A slow etch would allow controlled layers of the surface to be taken off, so that the thickness of the implanted layer could be reduced. This would allow the doping profile to be studied. Unfortunately, the only reference or work previously attempted in this area was classified and unavailable. Pankove states that this etch consisted of 1% HF in a solution of 100% Ethanol, and that low current densities were necessary.
Photo 6. Aqua Regia  5 mins.  
200x

Photo 7. Metaserv polisher  
50x  5 mins. etch  
\( \text{H}_2\text{SO}_4 : \text{HNO}_3 : \text{HF} \)

Photo 8. 1mA/cm\(^2\)  30 mins.  
100x
Figure 12. Current density-voltage characteristics of perchloric acid-acetic acid polishing GaAs samples, low resistivity, n-type. 
Figure 13. Schematic diagram of the Shandon 6500 Electropolisher as converted for use as an electrochemical etcher of GaP.

Figure 14. Control circuit for Shandon 6500 Electropolisher
2.2.3. Electrochemical polishing - practical considerations.

The removal of material by electrolytic means, as opposed to chemical means, presents advantages of cleanliness and flexibility of control. The cleanliness results from the fact that electrolytic etching usually forms soluble products and therefore no residue is left on the surface after the treatment. The common method with silicon and germanium is to form an oxide, using the sample as the anode. This oxide is removed when it has reached the desired thickness. Unfortunately, anodic oxidation cannot be applied, easily, to compound semiconductors and electropolishing is used instead.

The removal mechanism is dependent on current density. At low current densities, twin boundaries and other grain boundaries are attacked preferentially. As the current density is increased etching takes place, and etch pits become visible. These pits are usually better defined than those produced by chemical etching. Polishing occurs at higher densities and at even higher current densities, etch pit formation is very rapid, followed by a certain amount of polishing. A graph of current density against voltage shows a dip where polishing occurs, (Fig 12). This was found to be true for GaP, and each sample had its own definable current density for polishing - depending on type, concentration and dislocation density. Photos 8-11 show the four regions when p-type material was used.

For electrochemical polishing, a Shandon 6500 polishing apparatus was used. Photos 12 and 13 show the apparatus. Fig 13 shows a diagrammatic representation of the Shandon polisher. The pump speed is adjusted to give a reasonable approximation to laminar electrolyte flow. This can be determined by inspection of a test sample - Fig 14 shows the control circuit used.
Photo 9. 4mA/cm² 5 mins.
100x

Photo 10. 20mA/cm² 5 mins.
200x

Photo 11. 50mA/cm² 10 mins.
100x
Photo 14. Capacitance-voltage measuring apparatus

Photo 12. Electro-chemical polishing apparatus

Photo 13. Close-up of Shandon Electrolytic Polisher 6500
A constant current is passed through the electrolyte, the sample being held onto the polythene/perspex holder by wax, exposing a known area of the sample to be polished. Fig 15 shows the curve of current density against voltage for a particular sample. The flat portion of the curve corresponds to the polishing section, as shown in Photo 9.

The etch pit count, using this method, gave values of dislocations to be $10^5/\text{cm}^2$, which agrees well with those obtained by chemical etching at SERL on similar material and also with those published by Laister and Jenkins. Harper and Astar used this method to investigate the crystal orientation of GaAs. Laister and Jenkins also investigated crystal orientation. From the results obtained all the material used in these experiments were in the $<111>$ plane. The process proved very reproducible and controllable.

Unfortunately, a yellowish deposit appeared with n-type material (S-doped). This deposit proved difficult to analyse. It was resistant to all chemical analysis and mass spectrometry. Recently, Chase and Holt found the same deposit, using a Chlorine/Methanol electrolyte. Transmission electron microscopy showed that high density networks of tunnels about 300Å in diameter were being formed. They were also unrelated to any of the pre-existing defects in the material and ran in the $<111>$ directions. As this film could not be removed, it was not possible to use this method on n-type material. Chase and Holt recommend that a 15 second etch with no current flowing will remove the film. Future work will, no doubt, take this into account.

2.3 Contacts.

To make electrical measurements, contacts must be easily fabricated, and their characteristics reproducible. Three methods were used for putting
Figure 15. Graph of current density v. voltage for p-type GaP sample electrochemically etched in 1% HF/99% Ethanol.
contacts onto the samples; evaporation, alloying and thermo-compression bonding. Ohmic contacts can be defined as those having a contact resistance of less than $10^{-6}$ and exhibiting linear I-V characteristics over a range of voltages from -20V to +20V. Rectifying contacts are defined as those which cause the I-V characteristics to behave diodically without the contact resistance becoming a limiting factor to the forward characteristic.

Reproducible evaporated contacts need very clean, flat surfaces. This is achieved by washing the samples in warm trichlorethylene a few times, at least once ultrasonically. A rinse in high grade methanol and a wash in deionised water then complete the cleaning process. Two evaporators were used. For metals, except zinc, the Edwards E120 was used. Evaporations were carried out at $5 \times 10^{-6}$ torr, the substrate being at room temperature. Tungsten filaments were used for gold and a tantalum boat for tin. A small 6" evaporator was reconstructed to evaporate zinc, as this tends to contaminate the evaporation system used. The redesigned system enabled the rotary pump and diffusion pump oil to be changed easily. A closed tantalum boat was used for zinc, as zinc does not 'wet' easily and the a.c. heating tends to make the 'non-wetted' ball of molten zinc move. Masks of the appropriate area and size were made, but a standard was finally adopted. This used ready-drilled Lorchkit paxolin, as the holes were 1.25mm in diameter at 2.50mm spacings. This proved to be an ideal size for the samples used.

Once an evaporation had been carried out contact was made using a probe; for Schottky Barrier measurements a blob of Silver DAG or Ge-In eutectic gave good ohmic contact to any wire if the sample was firmly held e.g. on a transistor head.

A small rig was constructed out of glass to make alloyed contacts (Fig 16). The molecular sieve used was BDH 5A pellets and the lamp a Philips 100W 12V pre-focused projection lamp. This lamp was capable of producing a temperature of $500^\circ$C at the focus of the beam.
Figure 16. Schematic diagram of contacting apparatus.

Figure 17. Schematic diagram of thermo-compression bonder.
A 0-12V variable a.c. source was constructed to control the intensity and temperature of the lamp. Samples were placed on the graphite strip and small pellets of Zn or Sn placed on the sample. For Hall measurements, four pellets were placed equidistant from each other on the perimeter of the sample. The system was flushed by H:10% gas for approximately 5 mins. and then the lamp was switched on and the light output increased until the metal pellets melted. At this point the tap was turned to flush HCl vapour through the system. This has been found to aid the 'wetting' of the molten pellet. Experiments were carried out at Mullard Research Labs. using GaAs as the substrate and various metals for contacts. Using normal sectioning techniques the depth of alloying, variation of contact resistance and mechanical bonding was investigated as a function of alloy time. The optimum time was found to be 2 mins. at 300°C for Sn onto n-type and 4 mins. for H:Pt:Sn - 50:5:55 onto either p or n-type. For GaP it has been found that the same time for Sn onto n-type gave good ohmic contacts but a temperature of 500°C for 5 mins. was needed to obtain good Zn contacts to p-type material.

Thermo-compression bonding involves heating the sample until it reaches the eutectic temperature for the 3-phase system concerned and then lowering a wire of the metal to be used for the contact onto the substrate under pressure. A single piece of apparatus was constructed for this purpose. A block heater, with variable (0-600°C) controlled temperature was constructed. A micro-manipulator having a glass guide made from capillary tubing shaped to a point was used to position the wire. A hydrogen flame was used to form a small ball on the end of the wire (H was used to prevent oxidation) and with pressure applied this was lowered onto the sample. (Fig 17). Using a stereo microscope, the ball was observed and when it had melted - without cracking - the guide was removed leaving the contact on the substrate. For GaAs, a temperature of 350°C was sufficient but for GaP, a temperature of 540°C was found to be necessary. Good ohmic and rectifying contacts have been formed using this method on p and n-type material respectively.
To make an electrical connection to an alloyed contact Pt, wire of 0.002" diameter was used. This was soldered to either the Sn or the Zn contact using normal Pb.Sn solder with a 'pink' acid flux (Appendix B).

2.4 Capacitance Measurements.

2.4.1 Capacitance measuring apparatus.

To measure the change in capacitance with voltage, it was necessary to construct a circuit that would measure capacitance accurately over a wide range of voltages and frequencies. This was achieved by using a transformer ratio arm bridge with an external source and detector. The bridge used for the majority of the measurements was a Wayne Kerr B221 Mk. III with a Wayne Kerr Signal Generator SR1 and STC Null detector Type 96016. (Photo 14)

The bridge consists, basically, of the circuit in Fig 18. At balance, with $Z_s$ adjusted to give a null indication in the detector, the voltages across the unknown and the standard are $E_u$ and $E_s$. The usual balance conditions exist and it can be shown that

$$Z_x = \frac{E_x}{E_s} \frac{n_s}{n_s} Z_s$$

Thus it is possible, by means of suitable combination of tappings, to produce a wide range of measurements. In practice the impedances are divided into their respective resistive and reactive components. This allows the conductance, $G$, and the reactance, $X$, to be measured separately. A full account of the operation of the bridge can be found in ref. 56.

As the bridge measures the parallel combination of the reactive and resistive components, the devices measured must be assumed to be of a parallel nature. As the value of conductance measured was small, the value of parallel capacitance was nearly equal to that of an equivalent series capacitance.
Figure 18. Circuit diagram of a transformer ratio-arm bridge.

\[ Z_x = \text{unknown impedance} \]
\[ Z_s = \text{standard impedance} \]

Figure 19. d.c. bias circuit for capacitance-voltage measurements.
The source gave a signal of 0 - 30V over the frequency range 10Hz - 100kHz. All measurements were made with a source voltage of 150mV rms.

The d.c. applied bias was obtained from the circuit in Fig 19. A Solartron DVM was used to measure the voltage and the current monitored across a 100Ω 1% standard resistor.

2.4.2. Capacitance - voltage measuring procedure.

To make a series of measurements it was initially necessary to forward bias the device to neutralise all the deep traps. If a time-dependance measurement was being made, the stop-watch was started immediately the bias voltage was reversed. In these cases, this forward bias was applied before an initial reading was taken and was applied for as long as the capacitance shown by the bridge was changing. The device was then disconnected, reverse bias reset and the former procedure followed. It was usually unnecessary to retrim the bridge for a series of readings, unless either the frequency was changed, or the time between readings was long.

2.5. Current - voltage measurements.

Current - voltage characteristics were also measured for each barrier. To facilitate measurements, the control box-sample holder used for C-V measurements was used, but connected to a General Electric Model 12130A valve voltmeter, with a Keithley Model 602 Electrometer measuring the current. With this system it was possible to read currents as low as 5 x 10^{-8}A. This gave a current density of 4 x 10^{-14}A/m^2. A Tektronix Model 575 Transistor curve tracer was used to initially check each device. This showed whether the evaporated contact was behaving diodically or ohmically. If results were being taken over a long period of time, (e.g. two days with capacitance - time measurements,) the I-V characteristics would occasionally be checked to see if 'punch-through', by the probe, of the evaporated contact had occurred.
All the above measurements, C-V and I-V, were taken in a screened room. The leads for I-V characteristics, at low currents, were taped to the bench and screened to minimise stray currents.

2.6. Hall and Van de Pauw measurements.

To measure the carrier concentration, mobility, defect levels and effective mass, Van de Pauw and Hall measurements were taken. The theory behind these measurements is in Chap.3.

Measurements were taken using a vacuum cryostat. This allowed measurements to be made from room temperature down to liquid nitrogen temperature. In conjunction, a heated specimen holder was available. This allowed measurements to be taken up to 500°C, or 250°C with Sn contacts. All contacts used were of the alloyed type. Tests for resistive contact characteristics were made at a range of temperatures to ensure accuracy. Readings of voltage and current were taken for various combinations of connection. A Solartron DVM was used to measure voltage and a Keithley 602 Electrometer to measure current. The magnetic field was provided by a Newport Instruments 2" diameter electromagnet. For the initial Hall measurements, a field of 1.6kG was used, although later measurements were made using 4.7kG when a more powerful supply became available.
CHAPTER 3

Theoretical Considerations

3.1. Metal-Semiconductor Rectifying Barriers

3.1.1. The Schottky Effect.

The Schottky barrier lowering (also referred to as image-force lowering), $\Delta \phi$, and the location of the lowering, $x_m$, (as shown in Fig 20) are given by the condition $d \{PE(x)\}/dx = 0$

$$x_m = \sqrt{\frac{q}{16\pi\varepsilon_0 E}}$$

or

$$\Delta \phi = \sqrt{\frac{qE}{4\pi\varepsilon_0}} = 2Ex_m$$

where $PE(x)$ is the total potential energy at a distance $x$ from the surface. The lowering of the metal work function by an amount $\Delta \phi$ as a result of the image-force and the electric field is called the Schottky effect.

From eqns. (1) and (2) we obtain $\Delta \phi = 0.12V$ and $x_m = 60\AA$ for $E = 10^5$ V/cm; and $\Delta \phi = 1.2V$ and $x_m = 10\AA$ for $E = 10^7$ V/cm. Thus at high fields there is considerable Schottky barrier lowering, and the effective metal work-function for thermionic emission ($q \phi_B$) is reduced.

The above results can also be applied to metal-semiconductor systems. However, the field should be replaced by the maximum field at the interface, and the free-space permittivity $\varepsilon_0$ should be replaced by an appropriate permittivity $\varepsilon_s$ characterizing the semiconductor medium. This value may be different from the semiconductor static permittivity.

This is because, during the emission process, if the electron transit time from the metal-semiconductor interface to the barrier maximum $x_m$ is shorter than the dielectric relaxation time, the semiconductor medium does not have enough time to be polarized, and a smaller permittivity
Figure 20. Energy band diagram between a metal surface and a vacuum. The metal work function is $q_{\Phi m}$. The effective work function (or barrier) is lowered when an electric field is applied to the surface. The lowering is due to the combined effects of the field and the image force.
Figure 21. Detailed energy band diagram of a metal n-type semiconductor contact with an interfacial layer of the order of atomic distance.
than the static value is expected. Usually though, for Ge, Si, GaAs and GaP the appropriate permittivities are about the same as their corresponding static values.

3.1.2. Energy Band Relation at Metal-semiconductor Contact.

The barrier height is the difference between the metal work function (Fig. 21) and the electron affinity of the semiconductor. For an ideal contact between a metal and a p-type semiconductor, the barrier height, \( q \phi_{bp} \), is given by

\[
q \phi_{bp} = E_g - q(\phi_m - \chi) = E_g - q(V_{bi} + E_t - \Delta E)
\]

(3)

For a given semiconductor and for any metals, the sum of the barrier heights on n-type and p-type substrates is thus expected to be equal to the band gap, or

\[
q(\phi_{bn} + \phi_{bp}) = E_g
\]

(4)

From the above discussion it can be seen that when a metal is brought into intimate contact with a semiconductor, the conduction and valence bands of the semiconductor are brought into a definite energy relationship with the Fermi level in the metal. Once this relationship is known, it serves as a boundary condition on the solution of the Poisson equation in the semiconductor, which proceeds in exactly the same manner as in the p-n junction. The energy band diagrams for metals on both n-type and p-type materials are shown, under different biasing conditions, in Fig. 22.

Under the abrupt approximation that \( p \approx qN_D \) for \( w < W \), and \( p = 0 \), \( \frac{dV}{dx} = 0 \) for \( x > W \), where \( W \) is the depletion width, the results for the metal-semiconductor barrier are identical to those of the one-sided abrupt p-n junction, and we obtain

\[
W = \sqrt{\frac{2e}{qN_D} (V_{bi} - V - kT)}
\]

(5)
Figure 22. Energy band diagram of metal n-type and metal p-type semiconductors under different biasing conditions.

a) thermal equilibrium

b) forward bias

c) reverse bias
\[ |E(x)| = \frac{qN_D}{\varepsilon_s} (W - x) = E_m - \frac{qN_D}{\varepsilon_s} x \]  
\[ V(x) = \frac{qN_D}{\varepsilon_s} (Wx - \frac{1}{2}x^2) - \frac{qE_m}{\varepsilon_s} x \]

where the term \( \frac{kT}{q} \) arises from the contribution of the mobile carriers to the electric field. \( E_m \) is the maximum field strength which occurs at \( x = 0 \):

\[ E_m = E(x=0) = \sqrt{\frac{2qN_D}{\varepsilon_s} (V_{bi} - V - \frac{kT}{q})} \]

\[ = 2 \left( \frac{V_{bi} - V - \frac{kT}{q}}{W} \right) \]

The space charge \( Q_{sc} \) per unit area of the semiconductor and the depletion layer capacitance \( C_a \) per unit area are given by:

\[ Q_{sc} = qN_D W = \sqrt{2q\varepsilon_s N_D (V_{bi} - V - \frac{kT}{q})} \]

\[ C_a = \frac{dQ_{sc}}{dV} = \sqrt{\frac{q\varepsilon_s N_D}{2(V_{bi} - V - \frac{kT}{q})}} = \frac{\varepsilon_s}{W} \]

Eqn. (10) can be written in the form

\[ \frac{1}{C_a^2} = \left( \frac{2(V_{bi} - V - \frac{kT}{q})}{q\varepsilon_s N_D} \right) \]

\[ \frac{d}{(-dV)} = \frac{2}{q\varepsilon_s N_D} \]
or \[ \frac{W_D}{q} = \frac{2}{q} \left( \frac{-dV}{d(1/Q)} \right) \]  

If \( W_D \) is constant throughout the depletion region, one should obtain a straight line by plotting \( 1/Q \) against \( V \). If \( W_D \) is not constant, one can use the differential capacitance method to determine the doping profile from eqn. (11c).

It is possible to obtain an expression for the barrier height for the case where surface states affect the result. This will not be considered in detail, but referred to when necessary. Fig 21 shows the detailed energy band diagram.


The current transport in metal-semiconductor barriers is mainly due to majority carriers, in contrast to p-n junctions where the minority carriers are responsible. Three different approaches can be made to this problem: 1) the simple isothermal thermionic emission theory by Bethe, 2) the simple isothermal diffusion theory by Schottky and 3) the more general theory which incorporates the above two theories into a single thermionic emission - diffusion theory by Crowell and Sze.

The thermionic emission theory is derived from the assumptions that 1) the barrier height \( q\phi_{BM} \) is much larger than \( kT \), 2) electron collisions within the depletion region are neglected, and 3) the effect of image-force is also neglected. Because of the above assumptions the shape of the barrier profile is immaterial and the current flow depends solely on the barrier height. The current density \( J_{BM} \) from the semiconductor to the metal is then given by the standard thermionic emission equation.
The velocity $v_{ox}$ is the minimum velocity required in the $x$-direction to surmount the barrier and is given by the relation

$$J_{sm} = qn \left( \frac{kT}{2\pi m^*} \right)^{3/2} \exp \left( -\frac{m^* v_{ox}^2}{2kT} \right)$$  \hspace{1cm} \text{(12)}$$

where $v_{ox}$ is the minimum velocity in the $x$-direction required to surmount the barrier.

$$\frac{1}{2}m^* v_{ox}^2 = q(V_{bi} - V)$$  \hspace{1cm} \text{(13)}$$

where $V_{bi}$ and $V$ are the built-in potential and the applied voltage, respectively. ($V$ is positive for forward bias). The electron concentration $n$ is given by

$$n = N_c \exp \left( -\frac{E_p - E_F}{kT} \right) = \frac{N_c}{2} \left( \frac{2m^* kT}{\hbar^2} \right)^{3/2} \exp \left( -\frac{qV}{kT} \right)$$  \hspace{1cm} \text{(14)}$$

Substitution of eqn. (13) and (14) into (12) gives

$$J_{sm} = A^* T^2 \exp \left( -\frac{qV}{kT} \right) \exp \left( \frac{qV}{kT} \right)$$  \hspace{1cm} \text{(15)}$$

where $A^* = \frac{4\pi m^* k^2}{\hbar^3}$

For free electrons, $A^* = 120 \text{ A/cm}^2/\text{oK}^2 = A$, which is the Richardson constant for thermionic emission into a vacuum. For semiconductors with isotropic effective mass in the lowest minimum of the conduction band such as $n$-type GaAs, $A^* / A = m^*/m_0$, where $m^*$ and $m_0$ are the effective mass and free-electron mass respectively. For multiple-valley semiconductors the appropriate Richardson constant $A^*$ has to be modified, taking the direction cosines of the normal to the emitting plane into account. For GaP this is difficult as the effective masses in the different directions are not accurately known. Recent reported work indicates that in the $<111>$ direction, the transverse effective mass $m_t = 0.19m_0$ and the longitudinal effective mass $m_l = 1.7m_0$. As the
actual model of the conduction band is a matter of dispute it will be
assumed, for theoretical purposes, that $m_e^* = 0.35m_o$ and that $m_n^* = 0.47m_o$. Experimental results will show that this assumption is
justified. Since the barrier height for electrons moving from the metal
into the semiconductor remains the same, the current flowing into the
semiconductor is thus unaffected by the applied voltage. It must
therefore be equal to the current flowing from the semiconductor into
the metal when thermal equilibrium prevails, i.e., when $V = 0$.

The corresponding current density is obtained from eqn. (15) by setting
$V = 0$.

$$J_{ns} = -A*T^2 \exp \left( -\frac{q\phi_{bn}}{kT} \right)$$  \hspace{1cm} \text{(16)}

The total current density is given by the sum of eqns. (15) and (16).

$$J_n = (A*T^2 \exp \left( -\frac{q\phi_{bn}}{kT} \right)) (\exp \left( \frac{qV}{kT} \right) - 1)$$  \hspace{1cm} \text{(17)}

$$= J_{ST} (\exp \left( \frac{qV}{kT} \right) - 1)$$

where $J_{ST} \sim A*T^2 \exp \left( -\frac{q\phi_{bn}}{kT} \right)$  \hspace{1cm} \text{(18)}

Eqn. (17) is similar to the Shockley equation for p-n junctions. However
the expressions for the saturation current densities are different.

The diffusion theory is derived from the assumptions that: 1) the
barrier height is much larger than $kT$, 2) the effect of electron
collisions within the depletion region is included, 3) the carrier
concentrations at $x = 0$ and $x = W$ are unaffected by the current flow,
i.e., they have their equilibrium values, and 4) the impurity concen­
tration of the semiconductor is nondegenerate.
Since the current in the depletion region depends on the local field and the concentration gradient, we must use the current density equation

\[ J_x = J_n = q(n(x))_n \mu E + D_n \frac{dn}{dx} \]  

-(19)

where \( D_n \) is the diffusion coefficient of the electrons. The solution of this equation for the boundary conditions stated above i.e.,

\[ qV(0) = -q(V_n + V_{bi}) = -q\phi_{Bn} \]

\[ qV(W) = -qV_n - qV \]

\[ n(0) = N_c \exp \left( -\frac{E_0(0) - E_F}{kT} \right) = N_c \exp \left( -\frac{\phi_{Bn}}{kT} \right) \]  

-(20)

\[ n(W) = n = N_c \exp \left( -\frac{qV_n}{kT} \right) \]

gives

\[ J_n = qN_c \frac{D_n}{e_s} \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) / \int_0^W \exp \left( -\frac{qV(x)}{kT} \right) dx \]  

-(21)

For Schottky barriers, neglecting image-force effects, the potential distribution is given by eqn. (21).

or \( qV(x) = \frac{q^2 N_0}{\varepsilon_s} (Wx - \frac{x^2}{2}) - q\phi_{Bn} \)

Substituting into eqn. (21), and expressing \( W \) in terms of \( V_{bi} + V \) gives

\[ J_n = \frac{2D_n \varepsilon_s}{kT} \left( \frac{q(V_{bi} - V)2\varepsilon_s}{\varepsilon_s} \right)^{1/2} \exp \left( -\frac{\phi_{Bn}}{kT} \right) \left( \frac{\exp(\frac{qV}{kT}) - 1}{1 - \exp(-\frac{2q(V_{bi} - V)}{kT})} \right) \]  

-(22)

where \( V \) is positive for forward bias. Since \( qV_{bi} >> kT \) is one of the basic conditions, for all reverse and small forward voltages the exponential term in the denominator can be neglected. Hence eqn. (22) reduces to
\[ J_n = \left( \frac{q^2 D_n N_c}{kT} \right) \left( \frac{q (V_{bi} - V) 2 N_c}{e} \right)^{\frac{1}{2}} \exp \left( -\frac{q \Phi_{bn}}{kT} \right) \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) \]

\[ = J_{SD} \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) \]

The "saturation current density" \( J_{SD} \) for the diffusion theory varies more rapidly with the voltage but is less sensitive to temperature in comparison with the "saturation current density" \( J_{ST} \) of the thermionic emission theory.

A synthesis of the two approaches above can be considered. This approach is derived from the boundary conditions of a thermionic recombination velocity, \( v_R \), near the metal-semiconductor interface. In addition, effects of electron optical-phonon scattering and quantum-mechanical reflection at the metal-semiconductor interface are incorporated. Crowell and Sze show that if the barrier acts as a sink for electrons the current flow can be described in terms of an effective recombination velocity at the potential energy maximum. An effective diffusion velocity, \( v_d \), associated with the transport of electrons from the edge of the depletion layer at \( W \) to the potential energy maximum can also be postulated. If \( v_d \gg v_R \), the thermionic emission theory is applicable, and if \( v_R \gg v_d \) the diffusion process is dominant. If image-force effects were neglected and the electron mobility were independent of the electric field \( v_d = \mu E \), and the standard Schottky diffusion equation (23) would be obtained and

\[ J = q N_c \mu E \exp \left( -\frac{q \Phi_{bn}}{kT} \right) \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) \]

If optical-phonon scattering and quantum-mechanical reflection of electrons is considered, then the Richardson constant has to be modified. Crowell and Sze conclude that at room temperature, and for electric fields in the range of \( 10^4 \) V/cm, the current transport mechanism in Schottky barrier diodes is due to thermionic emission of majority carriers.
3.1.4. Measurement of Schottky Barrier Height.

From eqn. (19) and assuming the Crowell and Sze relationships previously postulated, it is possible to predict the ideal forward and reverse I - V characteristics of a Schottky barrier diode. In the forward direction with V > 3kT/q the equations can be rewritten as

$$J = A^* T^2 \exp \left(-\frac{q\phi_{Bo}^c}{kT} \right) \exp \left(\frac{A\phi + V}{kT} \right)$$  \hspace{1cm} -(25)

where $\phi_{Bo}^c$ is the zero-field asymptotic barrier height as shown in Fig 21. $A^*$ is the effective Richardson constant, and $A\phi$ is the Schottky barrier lowering. Since both $A^*$ and $A\phi$ are functions of the applied voltage, the forward $J - V$ characteristic (for $V > \frac{3kT}{q}$) is not represented by $J = \exp \left(\frac{qV}{kT} \right)$ but by

$$J = \exp \left(\frac{qV}{nkT} \right)$$ \hspace{1cm} -(25a)

The extrapolated value of current density to zero voltage gives the saturation current $J_S$, and the barrier height can be obtained from the following equation

$$\phi_{Bo} = \frac{kT}{q} \ln \left(\frac{A^* T^2}{J_S} \right)$$ \hspace{1cm} -(26)

The value of $\phi_{Bo}$ is not very sensitive to the choice of $A^*$. Consequently, the value of $A^*$, which is known, will be adequate.

In the reverse direction the dominant effect is due to the Schottky barrier lowering, or

$$J_R \approx J_S \text{ (for } V_R > \frac{3kT}{q} \text{)}$$
If the barrier height $q_{Bi,n}$ is reasonably smaller than the band gap such that the depletion layer generation-recombination current is small in comparison with the Schottky emission current, then the reverse current will increase gradually with reverse bias, as given by eqn. (27)

$$J_R \propto (V + V_{bi} - \frac{kT}{q})^{1/2}$$

Hence at fixed $T$, $\log J \propto V^{1/2}$ permits a determination of $\phi_{Bi,n}$.

The barrier height can also be determined by the capacitance measurement. When a small a.c. voltage is superimposed upon the d.c. bias, charges of one sign are induced on the metal surface and charges of the opposite sign in the semiconductor. The relationship between $C$ and $V$ is given in eqn (14). If $\frac{1}{C^2}$ is plotted against $V$, a straight line is predicted, for homogeneous doping. From the intercept on the voltage axis the barrier height can be determined

$$\phi_{Bi,n} = V_i + V_n - \frac{kT}{q} - \Delta \phi$$

where $V_i$ is the voltage intercept, and $V_n$ the depth of the Fermi level below the conduction band which can be determined if the doping concentration is known.

### 3.1.5 Determination of Impurity Energy Levels, using Schottky Barriers.

If a deep energy level is present in the depletion region of a reverse biased barrier, it will take a finite time to ionize. It can be shown that when a bias is applied to a S.B. on a semiconductor having both shallow and deep centres, the measured capacitance will change with time.
Due to thermal ionization of the defect levels the capacitance will show a characteristic behaviour with varying frequency\(^{68}\) and time\(^{69}\).

Bleicher and Large use a model based on an abrupt space charge distribution to calculate the important parameters of a monoenergetic defect centre. Their approach is used to evaluate the results of this project.

If the shallow level doping concentration is \(N_s\) the number of deep levels of energy \(E_t\) will be \(N_t\). In the steady-state the charge state of the traps above the Fermi level is positive compared to their charge state below the Fermi level. Fig 23 shows the resulting band diagram, with the charge distribution similar to that described by Senechal et al.\(^{71,72}\)

A change of bias applied to the junction will change the width of the space charge layer \(l\) and the region \(1 - \lambda\). As soon as \(1 - \lambda\) increases, the space charge within the depletion region will depend on time, since additional deep centres will be ionized. Both these effects will cause a change in the junction capacitance.

The following assumptions are made: all voltages applied to the junction are reverse biases; the diode is in darkness; the space charge region is abrupt.

A double integration of Poisson's equation over the depletion region gives

\[ V_g = V_{bi} - V = \frac{\alpha}{2e} \left( (N_g + N_t^d) (l^2 + N_t^d (\lambda^2 - 2l)) \right) \]

where \(V_{bi}\) is the built-in voltage, \(V\) the applied voltage, \(l\) the total length of the depletion region, and \(\lambda\) that part where the charge density is \(N_s\).
Figure 23. Energy band diagram and space charge distribution of Schottky Barrier, with shallow and deep levels.
If the frequency is high, so that there is no contribution from a change in occupancy of the deep levels, the junction capacitance is

$$C = \frac{\varepsilon A}{t}$$  \hspace{1cm} -(31)$$

From eqn. (30), I can be substituted into eqn. (31)

$$C = \frac{N^+ A e \lambda}{2eV - e \lambda^2 N^+} + \frac{N^+ A e \lambda}{2eV - e \lambda^2 N^+} + \frac{(N^+ + N^0)ce^2 \lambda^2}{2eV - e \lambda^2 N^+}$$  \hspace{1cm} -(32)$$

This equation is not limited by any values of time, bias or deep level density. If the time dependence of the ionized deep centre $N^+_t$ is considered, ionization can occur either by thermally influenced hole or electron emission. Only one of these is considered, for simplicity. Electron emission will be assumed to govern the ionization process, i.e. the emission rate of electrons $e_n$ is much larger than the emission rate for holes $e_p$. Sah has derived an expression for this emission rate

$$e_n = \sigma_n v_{th} N^+ \exp\left(-\frac{E_c - E_k}{kT}\right)$$  \hspace{1cm} -(33)$$

where $\sigma_n$ is the capture cross section of electrons, $v_{th}$ the thermal velocity, $N^+_c$ the conduction band density of states and $E_c$ the energy level of the conduction band.

Therefore the time dependence of the increase of space charge density in the region $0 < x < 1 - \lambda$ due to the thermal ionization of deep levels is

$$N^+_t = N^+_t (1 - \exp (-e_n t))$$  \hspace{1cm} -(34)$$

Bleicher and Large show that a plot of $C_o^{-2}$ ($C_o$ being the capacitance at time $t = 0$) vs $V$ will yield a straight line graph, the slope of which
is directly proportional to $N_s$. The ratio of $C_\infty / C_0$ ($C_\infty$ being the capacitance at $t = \infty$) can be found and the relationship

$$\frac{N_s}{N_t} = \frac{\left( \frac{E_p}{eV} \right) (C_\infty / C_0 - 1)^2}{(C_\infty / C_0)^2 - 1}$$

is derived. This equation is shown to be accurate over larger ranges of $V$ and $N_s/N_t$ than the simpler equations of Senechal et al. It is possible to calculate $\sigma$ if $N_s/N_t$ and $eV/E_s$ are known. $E_s = E_p - E_t$.

Two methods can now be used to determine the deep energy level and capture cross section. The first makes use of temperature variation, and will not be considered as all the measurements were made at room temperature. The second method is to find the value of capacitance, $C_\lambda$, where the time variation of capacitance ceases. At this point the total length of the space charge layer will be $\lambda$. Using

$$C_\lambda = \frac{eA}{\lambda}$$

$\lambda$ can be obtained, using the equation derived from doubly integrating through the region $1 - \lambda < x < 1$, ie

$$\lambda = \sqrt{\frac{2E(E_p - E_t)}{e^\frac{(X^2 - 1)}{N_s}}}$$

Thus the value of $E_p - E_t$ can be derived, and hence $E_C - E_t$. As all variables in eqn. (33) are now known, $\sigma$, the capture cross-section can be calculated.

It is possible to show that the frequency dependence of the Schottky barrier capacitance is a function of the number of deep centres. Although measurements were taken at different frequencies, a rigorous analysis of these results will not be attempted.

This analysis assumes n-type material. The analysis for p-type is similar.
3.1.6. Schottky Barriers on Implanted Semiconductors.

After implantation, the surface of the semiconductor is damaged, to approximately the depth of implantation. If a barrier is deposited on such a surface, it will obviously behave differently to that of a normal surface. It was found that these barriers exhibited a form of m.o.s. characteristic. It should therefore be possible to postulate the behaviour of unannealed specimens, and to estimate the depth of damage and the number of defects produced by implantation. If this is then followed by progressive annealing, two things should happen: the damage anneals out from the undamaged material, i.e., the depth of damage reduces; and at the same time the number of defects in the damaged layer will decrease, due to the thermal excitation restoring the lattice to its original form. Consequently a study was made, and a simplified form of theory developed to explain the behaviour.

Fig 24 shows a schematic diagram of an implanted, unannealed device. As the voltage is varied the depletion capacitance, $C_d$, will vary. It is assumed that the number of charges in the "insulator" layer remains constant i.e. the "insulator" capacitance is constant. Fig 25 shows the energy band diagram for such a system.

When an ideal MIS system is biased with positive or negative voltages, there are basically three cases which may exist at the semiconductor surface. When a positive voltage is applied to the metal, the top of the conduction band bends downwards and is closer to the Fermi level. For an ideal MIS diode there is no current flow in the structure, so the Fermi level remains constant in the semiconductor. Since the carrier density depends exponentially upon the energy difference ($E_c - E_F$), this band bending causes an accumulation of majority carriers near the semiconductor surface.
Figure 24. Schematic diagram of an MIS diode.

Figure 25. Energy band diagram for an ideal MIS structure at $V = 0$. (p-type semiconductor).

d = insulator depth
$C_d$ = depletion capacitance
$C_i$ = insulator capacitance
When a small negative voltage is applied, the bands bend downwards and the majority carriers are depleted. When a larger negative voltage is applied, the bands bend downward so much that the intrinsic level $E_i$ at the surface crosses the Fermi level $E_F$. At this point the number of minority carriers at the surface is larger than the number of the majority carriers and inversion takes place.

If an a.c. signal is applied and the capacitance of the MIS structure measured, assuming that the minority carriers follow the a.c. signal, the resulting $C - V$ curve will be as shown in Fig 26. The insulator capacitance is therefore constant. If the area of the diode is known:

$$C_i = \frac{\varepsilon_A}{d} \quad \text{where } d \text{ is the insulator thickness, } \varepsilon_i \text{ the permittivity}$$

The increase in capacitance is dependent upon the ability of the minority carrier concentration to follow the applied a.c. signal. This is only possible at low frequencies where the recombination-generation rates of minority carriers can keep up with the small signal variation and lead to charge exchange with the inversion layer in step with the measurement signal. The non-equilibrium case applies if the minority carriers cannot accumulate at the surface. The high-frequency curve is caused by the minority carriers following the d.c. but not the a.c. signal. (Fig 27).

In a practical MIS diode there exist many other states. Fig 28 shows the basic classification of the states and charges; for our analysis, the two most important are mobile ions and ionized traps. Although an abrupt system is considered, it is possible to ignore surface effects, as there will be no clearly defined boundary between the "insulator" and the semiconductor.
Figure 26. C–V curve for an ideal MIS diode (low frequency applied signal).

Figure 27. C–V curves for an MIS structure, showing the effect of varying the frequency of the applied signal. a) low frequency, b) high frequency c) non-equilibrium.
Figure 28. Basic classification of states and charges in a non-ideal MIS diode.
Two methods have been proposed to calculate the density of these ions and traps. Bias-temperature tests allow the polarity and origin of the mobile ion to be determined. The number of ionized traps can be calculated using the voltage shift in the C - V characteristics.

3.2. Electrical Properties of Semiconductors

3.2.1. Resistivity and Hall Effect

The two most common methods of measuring resistivity are the four-point probe and the method developed by Van de Pauw. The former uses four probes pushed onto the surface of the material. The pressure needed to make good contact to GaP was such that surface damage occurred, and therefore this method was not used.

Van de Pauw's method involves putting 4 ohmic contacts onto the material and measuring the voltage between two of the contacts whilst maintaining a constant current through the other two. It is possible to do this with a non-symmetrical configuration of contacts.

It can be shown that if the resistances between pairs of contacts are $R_1$ and $R_2$ $\Omega$ respectively, and that $R_1 : R_2 < 5$

$$\rho = \frac{\pi d}{\log 2} \frac{R_1 + R_2}{2} \sqrt{F} \text{ cm}$$

- (39)

where $F = 1 - 0.347 \left( \frac{R_1 - R_2}{R_1 + R_2} \right)^2 - 0.09235 \left( \frac{R_1 - R_2}{R_1 + R_2} \right)^4$

and $d$ is the thickness of the sample in cm.

To measure the carrier concentration directly the most common method is the Hall effect.
The Hall mobility is given by
\[ \mu_H = \frac{|R_H \sigma|}{q} \]
where \( \sigma \) is the conductivity
\[ -(40) \]
This mobility is different from the drift mobility \( \mu_n \) (or \( \mu_p \))
\[ R_H \]
is defined as
\[ R_H = r \frac{1}{q} \frac{b n^2}{(p + b n)^2} \]
\[ b = \frac{\mu_n}{\mu_p} \]
\[ -(41) \]
and \( r = \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} \)
\[ -(42) \]
where \( \tau \) is the mean free time between carrier collisions, which depends on the carrier energy. For semiconductors with spherical constant-energy surfaces, \( \tau = \frac{E}{B} \) for phonon-scattering, \( \tau = B^\frac{1}{2} \) for ionized impurity scattering, but in general \( \tau = aE^{-s} \) where \( a \) and \( s \) are constants. \( r \) can be calculated to be \( \frac{2m}{\hbar} = 1.18 \) for phonon scattering and \( \frac{315\pi}{512} = 1.93 \) for ionized impurity scattering.
\[ -(43) \]
From eqn (41) if \( n \gg p \)
\[ R_H = r \frac{1}{qn} \]
\[ -(42) \]
and if \( p \gg n \)
\[ R_H = r \frac{1}{qp} \]
\[ -(43) \]
Thus the carrier concentration and carrier type can be obtained directly from the Hall Measurements, provided that one type of carrier predominates.

Assignment of the proper scattering mechanism is difficult, and it has become customary to assume \( r = 1 \), and thus values which represent the donor and acceptor concentrations, the thermal ionization energy, and density of states effective mass can be found. Other techniques may then be used to evaluate these quantities.
The temperature dependence of the majority carrier concentration allows the calculation of the minority carrier concentration, and the majority carrier ionization energy. For conditions of classical statistics, the quantities are determined by the condition of electrical neutrality which may be written as

$$\frac{n(n + N_A)}{N_D - N_A - n} = N^* \frac{m^*_n}{g} \exp\left(-\frac{E_D}{kT}\right)$$

for n-type, where $N_A$ denotes the acceptor concentration, $N_D$ the donor concentration, $m^*_n$ the effective density-of-states electron mass, $N^*_o$ the effective density-of-states in the conduction band, $g$ the spin degeneracy factor associated with the donor level, and $E_D$ the ionization level of the donors.

For p-type the relationship is

$$\frac{p(p + N_D)}{N_A - N_D - p} = N^*_v \frac{m^*_p}{g} \exp\left(-\frac{E_A}{kT}\right)$$

where $N^*_v$ is the effective density-of-states in the valence band, $m^*_p$ the effective density-of-states hole mass, and $E_A$ the ionization energy of the acceptor.

$$N^*_v = N^*_o = 2\left(\frac{m^*_o}{h^2}\right)^2 \text{ where } m^*_o \text{ is the electron mass}$$

$g$ has been given a value of 2 for n-type GaP, and 4 for p-type.

The logarithm of the left side of eqn. (45) when plotted as a function of the reciprocal of the temperature $1/T$ will give a straight line only for correct values of $N_A - N_D$. The slope of the resulting straight line plot permits determination of $E_A$ and the time intercept at $1/T = 0$ gives $m^*_n^2/2g$.

Graphs of mobility against temperature permit the dominant carrier scattering mechanisms to be analysed. Toyama et al. give a full treatment of this analysis, and this will be referred to later.
CHAPTER 4

RESULTS

4.1 Introduction.

In Chapter 1 the broad objectives are outlined. During the course of experimentation many different ideas were presented as offering useful and interesting areas of study. An initial programme of measurements yielded information that was useful in a different context to that originally envisaged. Also some measurements could not be explained at the time that they were made, and a year or so later the theory was evaluated. Consequently some of the calculations presented in this section are retrospective. Unfortunately this rather 'unscientific' approach showed that certain measurements had not been taken, and consequently the analysis eventually made was not as conclusive as would be desirable.

The Hall and Van de Pauw measurements allowed the material to be evaluated with reasonable accuracy, thus some information on the effects of implantation was obtained. The major work was centred on capacitance - time measurements and the information obtained from these proved difficult to evaluate. A certain correlation with the electrical measurements was obtained from the capacitance - voltage results.

The heights of the Schottky barriers were measured, and some original results are presented. Unannealed specimens were used to prove the validity of the assumption that a disordered layer approximated to the insulating layer in an MIS - type structure.

4.2 Electrical measurements.

Hall and Van de Pauw measurements were made on n and p-type material
before and after implantation. The nominal doping of the samples covered
the range $7 \times 10^{15} \text{ cm}^{-3}$ to $1 \times 10^{18} \text{ cm}^{-3}$. For $n$-type material, two ranges
were available and were classified as high and low concentration.
For $p$-type material high, medium and low concentration was used.

Graphs 1 and 2 show the variation of carrier concentration for unimplanted
$n$ and $p$-type material respectively. As values of resistivity and Hall coefficient
were measured for the temperature rising and falling, the points indicate
averaged values. The experimental points are indicated, and the solid line was
obtained from the parameters $N_A$, $N_D$, $F_A$, or $F_D$ and $m^*$, calculated from a least-
squares curve fitting technique, being substituted into the theoretical equations
(Eqns. 45 and 46). The calculated values are given in Table 1. It can be seen
that for most of the curves the solid line is a close fit to the experimental
points. Two of the curves indicated some of the difficulties encountered in
determining the parameters. From the theory (Sec.3.2.1.) it was shown that the
carrier concentration is calculated from the resistivity and the mobility.
Neither of these are obtained by direct measurement, hence there will be a
significant error in the calculated concentrations, (approx. 10-15%). Therefore
any difficulty in measuring either resistivity or mobility will cause the
carrier concentration curve to have a large error. In the lower curve in Graph 1
it can be seen that the log. concentration varies linearly with inverse
temperature. In this case the resistivity became very high and difficult to
calculate. Thus there may have been some curving but it could not be measured.
In the $m^*$ curve in Graph 2, the curve folds over at high temperatures. This
is not possible theoretically, as the curving indicates the approach of the
saturation range. This can only be explained as experimental error in the
Graph 1. Plot of carrier concentration as a function of reciprocal temperature for n-type GaP for samples of different nominal doping.

- High
- Low
- High
Graph 2. Plot of carrier concentration as a function of reciprocal temperature for p-type GaP for samples of different nominal doping.

Nominal doping
- ▲ High
- □ High
- × Medium
- ○ Low
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>(N_A \text{ cm}^{-3})</th>
<th>(N_D \text{ cm}^{-3})</th>
<th>(E \text{ meV})</th>
<th>(\frac{m^*}{m_0})</th>
<th>DOPANT</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>high doped</td>
<td>(3 \times 10^{16})</td>
<td>(8.5 \times 10^{17})</td>
<td>52</td>
<td>2.41</td>
<td>S</td>
</tr>
<tr>
<td>high doped</td>
<td>(4 \times 10^{17})</td>
<td>(2.7 \times 10^{18})</td>
<td>49.6</td>
<td>1.44</td>
<td>S</td>
</tr>
<tr>
<td>low doped</td>
<td>(-)</td>
<td>(2.5 \times 10^{16})</td>
<td>250</td>
<td>0.21</td>
<td>?</td>
</tr>
<tr>
<td>p-type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>high doped</td>
<td>(2 \times 10^{17})</td>
<td>(7 \times 10^{16})</td>
<td>40</td>
<td>0.44</td>
<td>Zn</td>
</tr>
<tr>
<td>high doped</td>
<td>(4.7 \times 10^{17})</td>
<td>(4 \times 10^{16})</td>
<td>49.2</td>
<td>1.26</td>
<td>Zn</td>
</tr>
<tr>
<td>low doped</td>
<td>(1.5 \times 10^{14})</td>
<td>(5 \times 10^{12})</td>
<td>278</td>
<td>0.2</td>
<td>?</td>
</tr>
<tr>
<td>medium doped</td>
<td>(7.6 \times 10^{15})</td>
<td>(5 \times 10^{14})</td>
<td>58.6</td>
<td>0.35</td>
<td>?</td>
</tr>
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</table>

Table 1. Values obtained from the analysis of Hall Data, unimplanted GaP.

<table>
<thead>
<tr>
<th>n-type</th>
<th>(\text{cm}^{-3})</th>
<th>(\text{cm}^{-3})</th>
<th>(E \text{ meV})</th>
<th>(\frac{m^*}{m_0})</th>
<th>DOPANT</th>
</tr>
</thead>
<tbody>
<tr>
<td>before</td>
<td>(3 \times 10^{16})</td>
<td>(8.5 \times 10^{17})</td>
<td>52</td>
<td>2.41</td>
<td>S</td>
</tr>
<tr>
<td>after</td>
<td>(2 \times 10^{17})</td>
<td>(2.5 \times 10^{18})</td>
<td>61</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>p-type</td>
<td>(4.7 \times 10^{17})</td>
<td>(4 \times 10^{16})</td>
<td>49.2</td>
<td>1.26</td>
<td>Zn</td>
</tr>
<tr>
<td>before</td>
<td>(7 \times 10^{17})</td>
<td>(4 \times 10^{16})</td>
<td>71.3</td>
<td>0.36</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Values obtained from the analysis of Hall Data, implanted GaP.
measurement of resistivity, as the mobility behaved reasonably (Graph 4, lower curve).

The mobilities of each sample were plotted in Graphs 3 and 4. The temperature and mobility of the peak is dependent on the interrelationship between the predominant scattering processes, and an analysis of these results, with those from implanted samples, is discussed later. It can be seen that the peak mobility was highest for low concentration material in n-type material, but there was a greater discrepancy with p-type material. In the case of the 'L' curve in Graph 4, it proved impossible to accurately determine the mobility for temperatures below 200°K, for the reason stated before, is the resistivity became too high.

Resistivity and Hall coefficient measurements were then made to material that had been implanted with oxygen. These results are shown in Graphs 5 – 8. The changes in concentration and mobility show an anomaly, as oxygen is a donor. It would be expected that the donor concentration would rise and the acceptor concentration remain fairly constant. It can be seen from Table 2 (obtained in a similar way to Table 1) that the acceptor concentration has risen by a greater amount than the donor concentration. A possible explanation can be deduced from the capacitance – time measurements and will be discussed later.

4.3 Capacitance – voltage measurements.

Tin was evaporated onto unimplanted p-type material, and gold onto unimplanted n-type material to form Schottky barriers. Measurements of capacitance were made. From the slope of the \( C^2 - V \) curve the carrier concentration was calculated. The capacitance was measured as soon as possible after the required bias was applied, and this gave the value \( C_0 \). The capacitance was again measured when the rate of change, over at least 100 sec., was so small that it could be considered constant. This gave the value of \( C_\infty \). The curves labelled \( C_0 \) are therefore the curves produced by the shallow carriers only, and those labelled \( C_\infty \) produced by both the deep and shallow levels. Tables 3
Graph 3. Plot of the variation of mobility with temperature for n-type GaP for samples of different nominal doping.

Nominal doping
- High
- Low
- High
Graph 4. Plot of the variation of mobility with temperature for p-type GaP for samples of different nominal doping.
Graph 5. Variation of carrier concentration with reciprocal temperature for n-type GaP, before and after implantation with a dose of $10^{13}/\text{cm}^2$ oxygen at 100 keV and a 1 hour anneal at 700°C.
Graph 6. Variation of mobility with temperature for n-type GaP, before and after implantation a dose of $10^{13} \text{cm}^{-2}$ oxygen at 100 keV and a 1 hour anneal at 700°C.
Graph 7. Variation of carrier concentration with reciprocal temperature for p-type GaP, before and after implantation with a dose of $10^{13}$ cm$^{-2}$ of oxygen at 100 keV and a 1 hour anneal at 700°C.
Graph 8. Variation of mobility with temperature, before and after implantation with a dose of $10^{13}$ cm$^{-2}$ oxygen at 100 keV and 1 hour anneal at 700°C. p-type GaP.
and 4 give the measured values of carrier concentration obtained from the results shown in Graphs 9 and 10.

Graph 11 shows a p-type sample, with two barriers and measurements made at different frequencies. The intercept voltage can be seen to vary only slightly for changes in frequency, even though the carrier concentration changes. This value of intercept voltage, $V_i$, was taken to be $1.42 \pm 0.06$ eV. Using eqn. 29 the barrier height, $\Phi_{bp}$, was calculated to be $1.44 \pm 0.06$ eV. Measurements were made to other p-type material and the results are shown in Table 5. Sze gives a generalised formula for the barrier height, and this theoretical value, for tin barrier on p-type material, is $1.20 \pm 0.26$ eV. Thus the experimental results are within the rather wide limits of the theoretical values.

For n-type material the barrier height for gold is shown in Table 6. The value of $1.54 \pm 0.16$ eV, for the experimental results, is in reasonable agreement with the theoretical value of $1.30 \pm 0.27$ eV.

4.4 Capacitance - time measurements.

With the p-type GaP, doped as grown with zinc and oxygen, there was a distinct time dependence of the capacitance. This variation was measured and using the theory in Sec. 3.1.5, an attempt was made to analyse the processes involved. Two samples are used here to demonstrate the method used. Tin was evaporated onto nominally medium and nominally highly doped material. At least four good diodes were manufactured on each sample. The medium doped was implanted with oxygen at 120 keV, dose $10^{13}$ cm$^{-2}$, and annealed at 600°C for 1 hour. 1000 Å had been etched from the surface to remove the layer caused by dissociation, as the surface had not been passivated prior to annealing.
Graph 9. Variation of reciprocal capacitance squared with applied voltage for Schottky barrier diodes, Sn on p-type GaP, for samples of different nominal doping.
Graph 10. Variation of reciprocal capacitance squared with applied voltage, Au on n-type GaP Schottky Barrier diodes.
Table 3. Values of carrier concentration obtained from C - V measurements, p-type GaP.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>CONCENTRATION cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly doped</td>
<td>$4.7 \times 10^{17}$</td>
</tr>
<tr>
<td>Medium doped</td>
<td>$1.4 \times 10^{17}$</td>
</tr>
<tr>
<td>Lowly doped</td>
<td>$1.2 \times 10^{16}$</td>
</tr>
</tbody>
</table>

Table 4. Values of carrier concentration obtained from C - V measurements, n-type GaP.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>CONCENTRATION cm$^{-3}$</th>
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<tbody>
<tr>
<td>Lowly doped</td>
<td>$1.0 \times 10^{17}$</td>
</tr>
<tr>
<td>Highly doped</td>
<td>$2.1 \times 10^{17}$</td>
</tr>
<tr>
<td>Highly doped</td>
<td>$7.5 \times 10^{17}$</td>
</tr>
<tr>
<td>Highly doped</td>
<td>$2.7 \times 10^{17}$</td>
</tr>
</tbody>
</table>

Table 5. Barrier heights of Sn on p-type GaP, C - V measurements.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$V_i$ volts</th>
<th>$kT/q$ volts</th>
<th>$V_n$ volts</th>
<th>$\Delta\phi$</th>
<th>$\phi_{BP}$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowly doped</td>
<td>1.52±0.02</td>
<td>0.026</td>
<td>0.198</td>
<td>0.023</td>
<td>1.67±0.02</td>
</tr>
<tr>
<td>Medium doped</td>
<td>1.30±0.02</td>
<td>0.026</td>
<td>0.135</td>
<td>0.048</td>
<td>1.36±0.02</td>
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<tr>
<td>Highly doped</td>
<td>1.60±0.02</td>
<td>0.026</td>
<td>0.107</td>
<td>0.055</td>
<td>1.63±0.02</td>
</tr>
<tr>
<td>Highly doped</td>
<td>1.42±0.06</td>
<td>0.026</td>
<td>0.107</td>
<td>0.060</td>
<td>1.44±0.06</td>
</tr>
</tbody>
</table>

Mean value $1.52±0.18$

Theoretical value $1.20±0.26$
Graph 11. Variation of $\frac{1}{c^2}$ with applied voltage for two tin barriers on p-type GaP showing the effect of varying frequency.
Graph 12 shows the unimplanted highly doped sample and Graph 13 the measurements from the medium doped sample. They both illustrate the time dependence of the capacitance. From Graph 12 the concentration of the shallow centres can be calculated from the slope of the upper curve, and the total concentration from the lower. From Graph 13 the effects of implantation can be seen, and it is possible to calculate the concentration profile from this curve. (This was attempted using a relatively simple computer program. Unfortunately the large errors produced made the result meaningless). The value of capacitance in Graph 12 where the two curves meet is the value required in eqns. 36 and 37. Using the values from the graph \( C = 1290 \, \text{pF}, \lambda = 1.13 \times 10^{-7} \, \text{m}, \Delta E_g = 1.08 \, \text{eV} \) the value of \( E_g \) was calculated to be 1.17 eV. (The analysis has been modified to account for p-type material). An average value for this level of 1.20 ± 0.04 eV was determined when other diodes were measured. For the medium doped sample a value of 954 meV was calculated. The average value of this centre, over a number of samples, was calculated to be 960 ± 90 meV.

Using these values, and the values of emission rates calculated from the initial rate of rise of the capacitance-time curves (Graphs 14 and 15), the capture cross section for the centres was calculated to be in the order of \( 10^{-7} \, \text{cm}^2 \). This is exceptionally large. (The values of the parameters needed in equation 33 to calculate the capture cross section were: \( N_v = 8.1 \times 10^{18} \, \text{cm}^{-3} \), \( T = 300^\circ \text{K} \), \( v_{th} = 1.7 \times 10^3 \, \text{cm/sec} \).

The energy level associated with substitutional oxygen is 900 meV, which is approximately 1.3 eV above the valence band, oxygen being a donor. If oxygen were providing the deep level, the value of the capacitance should have dropped with time, as the net charge in the depletion layer would be reduced. As the capacitance is seen to increase with time there must be an acceptor trap present, with a binding energy greater than \( E_g / 2 \). The emission rate of this trap is small and the emission rate found from Graphs 14 and 15 must be associated with another, intermediate, level.
Graph 12. Variation of $\frac{1}{C^2}$ with $V$, showing capacitance at $t=0$ and $t=\infty$.

$N_0 = 1.4 \times 10^{17}$ cm$^{-3}$

$N_\infty = 2.02 \times 10^{17}$ cm$^{-3}$
Graph 13. Variation of $\frac{1}{C^2}$ with $V$ after implantation with a dose of $10^{13} \text{cm}^{-2}$ oxygen at 100 keV. 1000A stripped. Capacitance at $t = 0$ and $t = \infty$. 1 hour anneal at 700°C.
Graph 14. Variation of capacitance with time. Highly doped sample, implanted with $10^{13}$ cm$^{-2}$ oxygen at 100 keV. 1000 Å stripped. Tin barrier on p-type GaP. -2.5V bias. 700°C anneal, 1 hour.

$e_n = 1.75 \times 10^{-2}$ sec$^{-1}$
Graph 15. Variation of capacitance with time for a highly doped sample, p-type GaP, tin barrier. -2.5V bias.
If the function \( \log_\epsilon \left( \frac{C_0^2 - C(t)^2}{C_0^2 - C^2} \right) \) is plotted against time then a straight line should be obtained, the gradient giving the emission rate. When this was plotted for a highly doped p-type sample, Graph 16 was obtained, and an emission rate of \( 2.5 \times 10^{-4} \ \text{sec}^{-1} \) was found. This analysis was applied to a highly doped p-type sample and it can be seen (Graph 17) that two straight lines can be drawn. The first uses the points at high time to obtain a gradient of \( 9.1 \times 10^{-4} \ \text{sec}^{-1} \). If these points are extrapolated back to zero a second straight line can be drawn using the emission rate equation for two levels. This gives a time constant of \( 4.2 \times 10^{-2} \ \text{sec}^{-1} \). This gradient is rather inaccurate as the extrapolation needed was large.

Within the limits of accuracy the emission rate for the upper line is consistent with that obtained from the previous capacitance-time results, and the other with that from Graph 16.

To eliminate any changes in the sample due to the annealing process alone, an unimplanted highly doped sample was annealed at 600 \(^\circ\)C for one hour. This enabled the effect of the annealing process to be investigated. Graphs 18-20 show the results obtained. The energy level given by Graph 18 was calculated to be 1.22 eV. Graphs 19 and 20 gave emission rates that were similar to those obtained from previous samples.

The results obtained from these calculations are difficult to explain, as many different recombination processes are taking place in the material. An attempt will be made in the next chapter to provide a model that may be consistent with the results obtained.

4.5 Current-voltage measurements.

To confirm the barrier height obtained from the capacitance-voltage measurements, some current-voltage measurements were made. Graph 21 shows
Graph 16. Variation of $F(x)$ with time for a highly doped sample, tin barrier on n-type GaP.

$$e_{n} = 2.54 \times 10^{-4} \, \text{sec}^{-1}$$
Graph 17. Variation of $F(C)$ with time for a highly doped sample after implantation with $10^{13}$ cm$^{-2}$ oxygen at 100 keV. 1000$^2$ stripped. Sn barrier on p-type GaP. -2.5V applied bias. 700$^0$C anneal, 1 hour.

$e_{h} = 4.2 \times 10^{-2}$ sec$^{-1}$

$e_{h} = 9.1 \times 10^{-4}$ sec$^{-1}$
Graph 18. Variation of $\frac{1}{C^2}$ with applied voltage for a highly doped sample, tin barrier on p-type GaP. 1 hour anneal.

$N_o = 2.34 \times 10^{17} \text{cm}^{-3}$

$N_o = 2.46 \times 10^{17} \text{cm}^{-3}$
Graph 19. Variation of capacitance with time for a highly doped sample
1 hour anneal. Tin barrier on p-type GeP. -2.5V bias.
Graph 20. Variation of F(C) with time for a highly doped sample
Tin barrier on p-type GaP. 1 hour anneal.
TABLE 6

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$V_i$ volts</th>
<th>$kT/q$ volts</th>
<th>$V_n$ volts</th>
<th>$A$ volts</th>
<th>$\phi_Bn$ volts</th>
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</thead>
<tbody>
<tr>
<td>Lowly doped</td>
<td>1.40±0.02</td>
<td>0.026</td>
<td>0.144</td>
<td>0.041</td>
<td>1.43±0.02</td>
</tr>
<tr>
<td>Highly doped</td>
<td>1.42±0.02</td>
<td>0.026</td>
<td>0.124</td>
<td>0.068</td>
<td>1.45±0.02</td>
</tr>
<tr>
<td>Highly doped</td>
<td>1.68±0.02</td>
<td>0.026</td>
<td>0.09</td>
<td>0.048</td>
<td>1.70±0.02</td>
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</tbody>
</table>

Mean value 
Theoretical value

Table 6. Barrier height of Au on n-type GaP, C - V measurements.

TABLE 7

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$J_o$ A/m²</th>
<th>$\Phi_{Bp}$ eV</th>
<th>$J_s$ A/m²</th>
<th>$\Phi_{Bp}$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly doped</td>
<td>5 $10^{-11}$</td>
<td>1.24</td>
<td>5.2 $10^{-14}$</td>
<td>2.61</td>
</tr>
<tr>
<td>Medium doped</td>
<td>2 $10^{-10}$</td>
<td>1.21</td>
<td>5.8 $10^{-16}$</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Table 7. Barrier height of Sn on p-type GaP, I - V measurements.

TABLE 8

Highly doped GaP implanted 70 keV Zn $4x10^{13}$cm$^{-2}$, no anneal. Au barrier, n-type material.

100 Hz. $C_i = 5.00$ nF $d = 2.6.10^{-8}$ m
1 kHz.  $C_i = 2.95$ nF $d = 4.4.10^{-8}$ m
10 kHz. $C_i = 2.25$ nF $d = 5.79.10^{-8}$ m
100 kHz. $C_i = 1.80$ nF $d = 7.24.10^{-8}$ m

Medium doped GaP implanted 100 keV O, $4x10^{13}$cm$^{-2}$, no anneal. Sn barrier, p-type material.

1 kHz.  $C_i = 662$ pF $d = 1.97.10^{-7}$ m
10 kHz. $C_i = 514$ pF $d = 2.53.10^{-7}$ m
100 kHz. $C_i = 430$ pF $d = 3.03.10^{-7}$ m

Table 8. Depth of implanted layer before annealling, effect of varying applied signal frequency.

(Statistical projected range. 70 keV Zn: 3.48±1.2 $10^{-8}$m. 100 keV O: 1.787±0.6 $10^{-7}$m.)
the forward and Graph 22 the reverse characteristics of two typical barriers of tin on p-type material. For the forward characteristics the gradient must give 1/n(2) (Eqn 23a), otherwise the current-voltage relationships in Sec. 3.1.3 break down. Most of the diodes measured were within this range, the two shown having n-factors of 1.08 and 1.23 respectively. The intercept currents are indicated on the graph and are fairly accurate in the forward direction as the extrapolation involved was small. In the reverse direction the extrapolation was large and some doubt must be cast on the accuracy involved.

The gallium-indium eutectic used for the back contact introduced a fairly high series resistance, and this is seen to cause the forward characteristic to curve in the higher voltage region. Table 7 gives the barrier heights obtained.

4.6 Capacitance-voltage measurements on implanted, unannealed samples.

Graphs 23 and 24 show the capacitance-voltage curves for gold barriers on n-type material and tin barriers on p-type material. The samples had been implanted but not annealed. It can be seen from Graph 23 that the shape of the curve is similar to that predicted for an ideal MIS structure in Sec. 3.3.6. The frequency variation shows that more carriers were ionised at the low frequencies, as predicted. Graph 24 shows normalised capacitance against voltage and it can be seen that there is a limiting value of capacitance in each case. This value, $C_0$, was placed in eqn. 38 and the approximate depth of an equivalent insulating layer calculated. The depth of this layer was dependent on frequency and assuming a relative permittivity of 12 (the relative permittivity of unimplanted GaP) the calculated depths are tabulated in Table 8. The theoretical estimation of range for the conditions specified is also given. An attempt was made to investigate the annealing behaviour of GaP using this method, as it is possible to calculate the number of carriers in the damaged region, but the removal of the Schottky barrier proved too difficult and the surface was damaged. This is discussed further in the next chapter.
Graph 21. Variation of current with voltage. Sn barrier on p-type GaP.
Graph 22. Variation of current with $V^{1/4}$ for reverse biased Sn barrier on p-type GaP.
Graph 23. Variation of capacitance with applied voltage for Au barrier on n-type GaP. Implanted by 10^13 cm^-2 of zinc at 100 keV, no anneal.
Graph 24. Variation of normalised capacitance \( \left( \frac{C}{C_1} \right) \) with applied voltage for tin barrier on p-type GaP implanted with 100keV oxygen, \( 4 \times 10^{13} \text{cm}^{-2} \).
CHAPTER 5

Discussion of Results

5.1. Shallow Levels.

5.1.1. Effective Mass and Energy Levels

The values of energy level and effective masses obtained with the unimplanted samples (Table 1, Chap. 4) varied considerably between similar samples, the greatest variation in ionization energy level being associated with lowly doped samples, and the greatest variation of effective mass associated with highly doped samples. This variation has been reported by other workers, a complete analysis being given by Toyama et al\(^67\), in which GaP had been doped with Te. Toyama's analysis initially assumed a model of the band structure containing a single valley minimum in the conduction band. Reported variations of \(m^*\) were between 1.4\(m_e\) and 3.3\(m_e\), with the \(E_D\) of the tellurium varying by a 2:1 ratio. Toyama proposes a model containing six minima in the conduction band, and assumes a value of \(m^*\) of 1.22\(m_e\), this being obtained from optical measurements. The fact that the values of \(m^*\) measured by Hall and resistivity measurements are within close agreement with Toyama indicates that the six-valley system is a valid model. If the value 1.22\(m_e\) is used in the calculations, the value of \(E_D\) for the n-type material converges on 30 meV and for p-type converges on 56 meV.

The errors inherent in the calculation become large in assuming this value of \(m^*\). If the values of energy levels obtained are inserted into the theoretical equation (eqn. 44) the resultant error in the carrier concentration is much larger (50%) than the experimental error (typically 10%).
It has been reported that it is possible for carriers to occupy more than one level and transitions between these levels certainly contributed to the different values of energy level obtained. The donor level at 30 meV is too low for sulphur. This has been identified by many workers as having an energy of $90 \pm 10$ meV. There is no evidence for a donor level as shallow as the one reported here. The acceptor level at 56 meV, on the other hand does correspond to the identified level for zinc—this being 60 meV, (with a shallower level at 30 meV, associated with the zinc—oxygen complex).

5.1.2. Mobility.

The variation of mobility with temperature indicates the predominant interrelationships between the various scattering processes. The two predominant processes in perfect single element crystals are ionized impurity scattering at high temperatures, and acoustic phonon scattering at low temperatures. In crystals where inhomogeneity is high and concentration low, the space-charge regions associated with the inhomogeneity affect the low temperature mobility and for compounds, affect inter-valley scattering at higher temperatures. As the latter case applies to the crystals used in this report, the position of the mobility peak can be taken as an indication of the lattice state. Fig 29 shows a typical variation of mobility with its component scattering mechanisms.

The main scattering mechanisms are indicated, and from this the curves in Graphs 3 and 4 (Chap 4) can be explained. If we assume that the inter-valley scattering is constant for the material, then the relative degree of inhomogeneity can be deduced. It can be seen that for n-type material the temperature at which the mobility peaks is the same for the low doped sample as a highly doped one. For optimum electro—optical properties in GaP, an impurity concentration of $5 \times 10^{17}$ cm$^{-3}$ is necessary (Sec 1.3.).
Figure 29. Variation of mobility with temperature showing component scattering mechanisms.

- $\mu_I$: impurity scattering
- $\mu_{AC+IV}$: acoustic phonon and intervalley transitions
- $\mu_{SC}$: space charge
- $\mu_{PO}$: optical phonon
From Graph 1 it appears that if the concentration exceeds this, inhomogeneity increases. For p-type material the peak mobility of the low concentration material was impossible to measure, as the resistivity became too high as the temperature fell. It would seem that the temperature of peak mobility was constant with concentration, but the peak mobility became lower as concentration increased.

For implanted and annealed specimens, two anomalies are presented. Firstly, with the variation of carrier concentration with temperature, it seems that both donor and acceptor values increase, although only a donor was implanted. Secondly, for n-type material only, the peak mobility decreased, whereas with p-type material only, the peak temperature increased. It appears that for n-type, the annealing process has increased both the number of space-charge regions and the impurity centres, so that the curve shifts downwards. For p-type, on the other hand the peak moves to a higher temperature. This could indicate that the space-charge scattering is less after annealing. The results from capacitance measurements tend to confirm this.

5.2. Deep Levels.

5.2.1. Energy level of the deep trap.

C-V measurements indicate the presence of a deep acceptor level around 1.2eV, with a slow emission rate - 2.5 \times 10^{-4} \text{sec}^{-1}. (From Graph 16). This trap has similar characteristics to a nearby level attributed to a substitutional oxygen donor. Wronski found this oxygen donor to have a similar emission rate and a level of 900 meV below the conduction band, or 1.34 eV above the valence band at 300°K. Therefore any discussion must take account of the contribution of this deep donor. As this donor and the acceptor have similar characteristics compensation must be taking place.
although the overall effect is one of net acceptor concentration increasing with time. If the concentration had decreased, i.e. capacitance decreased, then a simple explanation would have been possible. Unfortunately this is not the case. It is therefore necessary to identify all the possible levels in the band gap and to attempt to explain the results obtained from this information.

Electroluminescent measurements have revealed most of the information concerning the band gap and an analysis of the literature gives the information shown in Fig. 30. As stated previously, substitutional oxygen has a donor energy level of 900 meV and zinc an acceptor level of 60 meV. The Zn-O bound exciton nearest neighbour complex has been assigned the values of 240 meV and 30 meV for the electron and hole respectively. The acceptor level at 1.2 eV has not been reported. The only previous report concerning anomalous electrical properties of p-type GaP was from Foster et al. who doped solution grown GaP with zinc. When measured, the acceptor concentration exceeded the zinc concentration. Foster et al. proposed that an acceptor defect was present and postulated a phosphorus vacancy. As the nature of vacancies in III-V compounds had not been unequivocally established, it was not accepted that anion vacancies would generally be donors. As the material used for the present work was also solution grown it is possible to postulate the deep acceptor trap as being due to a phosphorus vacancy. The presence of gallium vacancies has been indicated by Bhargava and found to be present in vapour grown material. These gallium vacancies behave as doubly charged acceptors in their charged state. Furthermore interstitial zinc acts as a donor, the attraction between $Zn_{int}^+$ and $(V_{Ga} - O_p)^-$ leading to the formation of a neutral Zn - O bound exciton. Although gallium vacancies are probably present in solution grown material they have only been reported in vapour grown material, and their presence is discounted in unimplanted material.
Figure 30. Energy band diagram showing energy levels in the band gap. \( E_g = 2.24 \text{ eV} \) at 300°K.
5.2.2 Annealing.

It must be assumed that there is a substantial amount of interstitial oxygen, as the defect density was high, approx. $10^5 \text{cm}^{-2}$ (Sec. 1.9). During annealing some of this interstitial oxygen will become substitutional thus filling some of the phosphorus vacancies. This would explain the small change in capacitance in the unimplanted annealed specimens (Graph 18). The cause of the two straight lines in the $P(0)$-t results must be explained by the presence of an intermediate level. Its concentration is small compared to the deep acceptor trap and its effect probably swamped in Graph 16. Its emission rate of $1.84 \times 10^{-1} \text{sec}^{-1}$ would indicate a level of 620 meV if the capture cross section for a hole is assumed $(2 \times 10^{-13} \text{cm}^2)$. This would correspond with a level found to be copper$^{95}$. Copper is an impurity which is found in most III-V compounds, and it can be assumed that some is present in the material used.

5.2.3 Implantation.

The implantation of oxygen increased both the donor and acceptor concentration in n-type material, but only the acceptor concentration in p-type. If it is assumed that the implantation process destroyed the crystal homogeneity, it is possible that after annealing a number of changes had taken place. With the p-type material it is probable that the number of gallium and phosphorus vacancies increased. If these are assumed to be acceptor defects then the rise in acceptor concentration can be explained. It is probable that the number of Zn-O complexes had increased, and as these would not be measured by the Hall effect measurements the donor concentration would remain constant. For n-type material an explanation is more difficult. The donor increase is probably due to the implanted oxygen, and the acceptor increase to defects.
5.2.4. Defect Level Concentration.

It is possible to estimate the number of deep levels using the capacitance measurements. Using eqn. 35 (Sec. 3.1.5) gives the concentrations of the shallow and deep levels, and that in Ref. 90 (for the case where two levels are present) the concentrations of the deep and intermediate levels. These calculations give the results shown in Table 9. It can be seen that the shallow level increases with annealing, indicating that some interstitial zinc has become substitutional. The intermediate level is in fact swamped by the effect of the deep trap until the sample has been annealed. Then the number of deep levels decreases. This supports the assumption that the deep level is associated with a vacancy. After implantation the intermediate level is of the same concentration but the deep level has increased. Therefore it seems that the annealing has not eliminated all the defects due to the implantation.

5.3. Barrier Measurements.

The agreement between the C-V and J-V values of barrier heights indicate that the Schottky Barriers were fabricated without the presence of an interfacial layer. This indicates that the values of concentration found using barriers were accurate. The value obtained for tin on p-type, $1.52 \pm 0.18 \text{ eV}$ from C-V and $1.22 \pm 0.20 \text{ eV}$ from J-V measurements, cannot be compared with other workers results as there are no previously reported values. The extrapolation required in the reverse direction was so great that the variation in these values is understandable. For gold on n-type the value of $1.54 \pm 0.16 \text{ eV}$ is slightly higher than the accepted value of $1.36 \text{ eV}$, although within experimental error.
Table 9. Energy levels and concentrations obtained from C - V - t measurements on p-type GaP, Sn barriers, before and after implantation and annealing.

<table>
<thead>
<tr>
<th></th>
<th>$N_s\text{ cm}^{-3}$</th>
<th>$E_{t1}\text{ meV}$</th>
<th>$E_{t2}\text{ meV}$</th>
<th>$N_{t1}\text{ cm}^{-3}$</th>
<th>$N_{t2}\text{ cm}^{-3}$</th>
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</thead>
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<td>unimplanted</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>unannealed</td>
<td>$1.4 \times 10^{17}$</td>
<td>1230</td>
<td>600</td>
<td>$6.2 \times 10^{16}$</td>
<td>-</td>
</tr>
<tr>
<td>implanted</td>
<td></td>
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<td>annealed</td>
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<td>1210</td>
<td>620</td>
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<td>$6.6 \times 10^{15}$</td>
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<tr>
<td></td>
<td>$2.1 \times 10^{17}$</td>
<td>1130</td>
<td>580</td>
<td>$4 \times 10^{16}$</td>
<td>$6.5 \times 10^{15}$</td>
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</tbody>
</table>
5.4. "M.I.S." Results.

The results obtained indicate that the behaviour of unannealed specimens followed an MIS form. The results for both p and n-type material are similar, although shown in different ways (Graphs 23 & 24).

If the structure of the implanted layer is assumed to be represented by Fig 28, the surface states and traps can be ignored. This leaves mobile ions and ionised traps to be considered. The C-V results show that these are present even in annealed specimens. If temperature had been varied it would have been possible to calculate the relative concentrations of these. (Sec. 3.1.6.) The variation of frequency indicated that the ionised traps had different emission rates and were probably associated with defects throughout the energy gap. If the depth of the implanted layer is calculated, a variation of depth with frequency is expected. Empirically it seems that a frequency of 800 Hz gives a value of implantation depth similar to that given by theoretical means. It was hoped that annealing studies could have been made, as the number of traps would vary with annealing temperature and time. This might have given some insight into the annealing behaviour. It has been shown, however, that barriers to unannealed specimens could be used to investigate the anneal process in a simple experimental way.

5.5. Conclusions.

The bulk material was analysed to a degree making possible the investigation of the effects of implantation and annealing. The preparation of the material was successfully completed and the initial experiments in determining the techniques necessary justified the time spent in that area. As the material was an unknown quantity at the beginning of the research reported here, a method has been found that produces reproducible surfaces free from damage and suitable for implantation. Most material used in
industrial applications is grown by liquid phase epitaxy and the preparation techniques reported here will be useful when liquid encapsulated material is used in devices and not as a starting material for epitaxial layers. The chemical and electrochemical methods used showed that the number of defects in the material was high and similar to those reported elsewhere. Similar difficulty was experienced by other workers with the electrochemical preparation of the surfaces, and recent work has shown a way of overcoming these difficulties (Sec. 2.2.3). It should now be possible to use the electrochemical stripping on both n and p-type material and so provide a means of accurately sectioning the material for range studies. It would have been useful if some range measurements had been carried out in this work, but the difficulties encountered made it impossible.

The study of mobility indicated that a lattice reordering took place during annealing, and this was further shown by the capacitance-time results. It has been possible to locate and possibly identify a deep acceptor level in the material. This has an energy level of 1.3 ± 0.1 eV. Thus the anomalous results reported for solution grown material have been corroborated.

Hall and Van de Pauw measurements allowed the material to be precisely analysed and the energy levels of the impurities introduced at the growth stage were found. For zinc these were similar to reported levels found by other workers, but for sulphur a level was found that was far too shallow. It has not been possible to explain this discrepancy.

It has also been shown that there is a possibility that MIS theory could be used to investigate the behaviour of an implanted layer during annealing. It was found that the behaviour of a Schottky barrier applied to an unannealed implanted sample was similar to that of a classical MIS sample. It is possible therefore that the change in this characteristic during annealing could yield information about the annealing pattern of the material.
Finally, the barrier height of gold on n-type and tin on p-type gallium phosphide has been established. For gold barriers on n-type material this was found to agree with previously published results. For tin on p-type, the barrier height has been established experimentally for the first time as $1.52 \pm 0.18$ eV.
APPENDIX A

CRITICAL CHANNELLING ($\psi_{\frac{1}{2}}$) ANGLES FOR GaP

The value of $\psi_{\frac{1}{2}}$ has been treated in Lindhard's theory on directional effects. The critical angle for axial channelling is predicted to be

$$\psi_{\frac{1}{2}} = \alpha \psi_1$$

where $\psi_1$ is a characteristic angle expressing the functional dependence on energy, atomic number and lattice spacing, and $\alpha$ is a constant depending only on the vibrational amplitude of the lattice atoms. Calculations by J. V. Andersen show that typical values of $\alpha$ range from 0.8 to 1.6.

In Lindhard's treatment, the axial rows of atoms that steer the channelled particles are treated in terms of the average potential of the row of atoms, and the characteristic angle is determined from the maximum transverse energy for which a particle may still be steered. For a monatomic row of atoms with uniform spacing the result obtained is:

$$\psi_1 = \left( \frac{2Z_1^2 e^2}{Ed} \right)^{\frac{1}{2}}$$

provided $\psi_1 < \frac{a}{d}$

where $Z_1$ and $Z_2$ are the atomic numbers of the projectile and target atoms respectively, $e$ the electronic charge, $a$ the Thomas-Fermi screening distance, $d$ the lattice spacing along the row and $E$ the projectile energy.

For the case of more than one type of atom along the rows, or for a non-uniform spacing of atoms, use of an averaged potential calculation gives

$$\psi_1 = \left( \frac{2\bar{Z}^2 e^2}{E \bar{d}_{\text{avg}}} \right)^{\frac{1}{2}}$$

again provided $\psi_1 < \frac{a}{\bar{d}_{\text{avg}}}$ where $\bar{Z}$ is the average atomic number of the atoms along the row and $\bar{d}_{\text{avg}}$ is their average spacing.

For mixed rows of atoms (e.g. $\langle 111 \rangle$) in the axial direction, the steering of channelled particles is due to the average effect of both types of atoms in the lattice, i.e. the critical angle is obtained using the average atomic number $\bar{Z} = \frac{Z_A + Z_B}{2}$ and the average spacing $\bar{d}_{\text{avg}}$ along the $\langle 111 \rangle$ row.
For GaP in the <111> axial direction (all the implantation was in this direction) $d_{avg} = 0.87d$ where $d = 5.45 \times 10^{-6}$ and $\alpha = 1.12$.

Using the formulae $\psi = \frac{\alpha \psi_1}{d_{avg}}$ and using $Z = 23$:

For 70 keV Zn $\psi = 5.4^\circ$

and 120 keV O $\psi = 3.73^\circ$

therefore implantations at $6^\circ$ to the <111> axial direction would avoid channelling. (Error in axial calculations is around $\pm 0.5^\circ$)
APPENDIX B

Pink acid flux - for soldering Pt wire to Sn and Zn contacts.

Dissolve and filter

21 H₂O
200gm ZnCl
20gm NH₄Cl

Add 20ml tertiary butanol to filtrate

Add enough methyl orange to give a red solution

Add ammonia until solution turns pink.
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