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ELECTRICAL PROPERTIES OF IMPLANTED LAYERS IN GALLIUM ARSENIDE

A Thesis presented for the Degree of Master of Philosophy to the Department of Electrical and Electronic Engineering, University of Surrey.

by

John Ernest Tansey

May 1973
ABSTRACT

This thesis describes an experimental study of conducting layers formed in gallium arsenide (GaAs) substrates by the implantation of dopant atoms.

In particular p-type and n-type layers, formed by the implantation of cadmium (Cd) and tellurium (Te) respectively, have been studied in detail.

Hall effect and resistivity measurements, in conjunction with layer removal techniques, have been used to characterise the carrier concentration and mobility within the implanted layer.

The influence of various experimental conditions, in particular temperature of implant, total dose and post-implant annealing procedures, upon the electrical properties of the implanted layer is reported.

Some detailed measurements of the electrical characteristics of damaged layers formed by heavy ion bombardment are also reported.
ACKNOWLEDGEMENTS

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I am also indebted to Dr. K.G. Stephens, Reader at the University of Surrey, and Dr. P.L.F. Hemment, Research Fellow at the University of Surrey, for their unfailing encouragement and guidance.

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Finally, I wish to convey my thanks to my wife, Jan, for her patience and typing this Thesis.

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1.1 Aim of project

The purpose of this investigation was to examine the electrical properties of implanted layers in GaAs and to control these properties by the selection of implant and post-implant procedures. In particular it was hoped to form n and p-type device quality layers with carrier concentrations in the range $10^{15}$ to $10^{19}$ carriers cm$^{-3}$. The dopants chosen for implantation included the conventional dopants Cd, Zn, Te, S and Se although most of the detailed studies presented here refer to Cd and Te implanted layers.

Since the implantation of heavy ions can create a highly disordered layer, and the associated defects may be electrically active, some implants were carried out with the inert gas ion Ar$^+$, not a conventional dopant, in order to isolate and study the effects of radiation damage.

Bulk n and p-type and semi-insulating GaAs was used as substrates in order to characterise the implantation process in GaAs with the expectation that implants into high quality epitaxial layers could be designed and thereby minimise the influence of residual impurities in the substrate material upon the behaviour of the implanted dopants.

The electrical properties of a semiconductor are primarily influenced by the free carrier concentration and carrier mobility. Other properties, such as carrier lifetime, are also important, particularly in the design of semiconductor devices.

In this work it was intended to study the carrier concentration and mobility of implanted layers using well established Hall effect and resistivity measurement techniques.

An integral part of this work was also to relate the electrical properties of implanted layers to the position of the implanted atom.
within the crystal lattice. This atom site location and lattice damage study was undertaken by other members of the department using Rutherford back-scattering techniques.

A great number of experimental conditions can be expected to influence the observed properties of an implanted layer. Some of these can be listed as:

1. Ion species
2. Ion dose
3. Post implant anneal temperature
4. Temperature of implant
5. Ion beam density
6. Energy of implanted ions
7. Direction of ion beam relative to the crystal
8. Crystal growth method
9. Crystal orientation
10. Crystal resistivity

This work has been carried out under controlled conditions, setting most of the above parameters constant. The results reported in this thesis were obtained after changing one or more of these previously fixed parameters.

In particular the effects of the first four of the above parameters upon the electrical properties of implanted layers have been studied.

1.2 III - V Compounds

It is found that the compounds formed between the group III elements (Al, Ga, In) and the group V elements (P, As, Sb) crystallise in the zinc blende (ZnS) structure and possess semiconducting properties.

Several of these compounds are of technological importance. Comparison of these compounds with the group IV semiconductors (Si and Ge) reveals that the energy gaps and electron mobilities of the III - V's tend to be
larger although the hole mobilities are smaller (table 1). For these reasons the compounds have advantages over the elemental semiconductors as new device materials.

<table>
<thead>
<tr>
<th>Semi-conductor</th>
<th>Energy Gap (eV)</th>
<th>Mobility cm² V⁻¹ sec⁻¹</th>
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<tr>
<td>Si</td>
<td>1.2</td>
<td>1,300</td>
<td>500</td>
</tr>
<tr>
<td>Ge</td>
<td>0.785</td>
<td>4,500</td>
<td>3,500</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.58</td>
<td>8,500</td>
<td>420</td>
</tr>
<tr>
<td>InP</td>
<td>1.34</td>
<td>4,600</td>
<td>150</td>
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Table 1 Comparison of semiconductors

In particular materials with a large energy gap retain their semi-conducting properties to high temperatures. For example the maximum operating temperature for p-n junctions in Si is 250°C whereas it is 1,000°C for GaP and GaAs diodes can operate up to 350°C. This ability is also exploited in the power handling capacity of devices, for example GaAs diodes can be run continuously at a current density of 1,000 A cm⁻².

Furthermore, because of it's high electron mobility and low dielectric constant, GaAs is suitable for the production of high frequency devices. In fact variable capacitance diodes have amplified at 10¹¹ Hz.

Perhaps the most interesting and technologically significant effect observed in GaAs is that named after J.B. Gunn who, in 1963, discovered current instabilities when he applied electric fields larger than 3kV cm⁻¹. The effect can be explained by considering the energy contours of the GaAs conduction band which is found to consist of a central minima with three side valleys in the (100) directions. The energy difference between the central and the side valleys is 0.36 eV, the carrier properties
in the two types of valley are:

<table>
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<th>Effective Mass</th>
<th>Mobility cm$^2$ V$^{-1}$ sec$^{-1}$</th>
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<tr>
<td>Centre valley</td>
<td>0.07</td>
<td>5,000</td>
</tr>
<tr>
<td>Side valley</td>
<td>0.40</td>
<td>200</td>
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Under normal conditions the carriers are in the centre valley, however if they gain more than 0.36eV of energy they can be transferred to the side valley. Carriers in the side valley have a low mobility and electrons 'bunch-up' to form a high field 'domain' that travels along the length of the crystal and produces a pulse of current. The domain velocity, which is dependant upon the carrier mobility, is typically $10^7$ cm.sec$^{-1}$ so that a specimen 10 microns long will oscillate at $10^{10}$ Hz. The application of electric fields of greater than 3 kV.cm$^{-1}$ can transfer carriers from the central valley to the side valley and initiate oscillation.

The advantages of using solid state oscillators working at these frequencies has been demonstrated with the construction of portable, hand held radar transmitters.

1.3 Ion Implantation

The advent of nuclear technology and the building of nuclear reactors prompted the need to study the changes in physical properties of solid materials resulting from particle bombardment. One of the earliest observed effects of particle bombardment was the undesirable change in the physical dimensions of reactor grade graphite (Wigner growth). The advantageous uses of ion bombardment were limited at that time to sputtering and the cleaning of surfaces. In recent years however, the use of ion bombardment as a tool for altering the physical properties of a material has received increasing attention with the realisation that properties such as semiconductor
doping levels, mechanical hardness, catalytic processes, optical
transmission and magnetic properties can be usefully modified.

In particular, since 1963, the effects of ion bombardment upon the
electrical properties of semiconductors have been extensively studied
(ref.1) and used. The particular attractions of ion implantation,
as applied to the doping of semiconductors, are listed below:

1. The number of implanted ions and their depth distribution
can be adjusted by the external system (ion beam current and accel-
erating voltage) rather than the physical properties of the substrate.

2. Dopant atoms can be implanted at any temperature, if
so desired, which can be a significant advantage in the case of
compound semiconductors.

3. The dopant concentration is not limited by solubility
considerations and therefore dopants can be introduced by implantation
that cannot easily be introduced by diffusion.

4. The geometry of the implanted layer can be determined
by masks or beam writing techniques.

5. Devices might possibly be machined using sputtering
techniques.

For device applications the parameters of importance include
conductivity of the implanted layer and the depth distribution of
carrier concentration and mobility. In order to characterise the
layer usefully it is necessary to know the profile of carrier conc-
entration and mobility and also whether any scattering or trapping
centres have been introduced.

To date ion implantation has been used with some success to
construct shift registers, computer memories, amplifiers and multi-
plexers on silicon substrates (1). Ion implantation has also been
used to great advantage to form thin conducting windows on semi-
Applications to the compound semiconductors has not been so extensive although proton bombardment of GaAs has been used to isolate devices on a substrate (2).
The formation of conducting layers in semiconductors by the implantation of dopant atoms is greatly complicated by the introduction of radiation damage. It is an experimental fact that in most semiconductors studied, both donors and acceptors can be introduced as a result of bombardment.

Because of the wide range of intrinsic defects that can be created in a compound semiconductor the effects of radiation damage can be expected to be more pronounced than in the elemental semiconductors. Also, any attempt to remove, by heat treatment, the defects introduced into compound semiconductors can be expected to raise complications due to preferential loss of one of the semiconductor constituents at an elevated temperature.

As well as acting as electrically active centres themselves defects can interact with chemical dopant impurities present in the semiconductor and so influence the electrical properties.

This section therefore presents a survey of the experimental properties of heat treated GaAs followed by the properties of implanted GaAs, including radiation damage and implanted dopant effects.

2.1 Heat treatment of GaAs

Toyama et al (3) found that the heat treatment of GaAs created a double acceptor level in sufficient numbers to convert n-type GaAs to p-type. They attributed this acceptor level to gallium vacancies \(V_{Ga}^+\) with activation energies of 0.13 and 0.25 eV above the valence band.

Recent work by Munoz (4) on the heat treatment of liquid phase epitaxial GaAs in an arsenic overpressure revealed the presence of two types of electrically active vacancy depending upon the arsenic overpressure. At pressures of less than 50 torr the electrical behaviour was
governed by gallium vacancies with an activation energy of 0.01 and 0.18eV, while at pressures greater than 50 torr arsenic vacancies act as acceptors with an activation energy of 0.12eV.

Fuller et al (5) also observed an acceptor level at 0.01eV which they attributed to clusters of gallium vacancies; they found that the clusters could dissociate at temperatures in the range 500°C to 700°C to form stable donor – vacancy complexes in n-type GaAs. Vacancy – dopant complexes were also identified by Hwang (6,7) who observed \( V_{Ga} \) – Te and \( V_{As} \) – Zn complexes in n and p-type GaAs respectively. An analysis of Hwang's data by Logan (8) gave the binding energy of the \( V_{Ga} \) – Te complex as 0.3eV.

Chang (9) performed annealing experiments on GaAs in controlled arsenic atmospheres and identified electrically active levels associated with \( V_{Ga} \) and \( V_{As} \) as well as vacancy – dopant complexes. He found that the defects associated with gallium vacancies became increasingly important at high anneal temperatures.

Several authors have postulated the formation of \( V_{Ga} \) – donor complexes to explain the behaviour of n-type dopants in GaAs at high concentrations. Vieland (10) and Fane (11) for example, found that at concentrations greater than \( 4 \times 10^{17} \) atoms.cm\(^{-3} \) selenium could enter the lattice as an electrically inactive \( V_{Ga} \) – Se\(_3\) complex. As a consequence the electron concentration did not equal the impurity concentration at impurity concentrations in excess of \( 4 \times 10^{17} \) atoms.cm\(^{-3} \). Similar behaviour was also observed in the case of tellurium and sulphur by Fistul (12) and Young (13) respectively, both authors explaining their observations by postulating the formation of \( V_{Ga} \) – donor complexes.

The curves of Vieland and Fistul plus points extracted from Young's data are reproduced in fig.(1) and will be referred to in a later section.
Fig. 1  Carrier concentration versus atomic concentration for the n-type dopants Te and Se in GaAs

\[ \begin{align*}
\times & \quad \text{Te} \quad \text{Fistikul ref.12} \\
\circ & \quad \text{Se} \\
\circ & \quad \text{Se} \quad \text{Vieland ref.10}
\end{align*} \]
In contrast Black (14) reports 100% activity of the p-type dopants zinc and cadmium in GaAs for impurity concentrations of up to $10^{20}$ atoms cm$^{-3}$.

2.2 Radiation damage effects

Using Hall effect measurements Aukerman (15) found that the carrier concentration of both n and p-type GaAs was reduced as a result of irradiation with electrons or neutrons. Similarly Cleland (16) found that gamma irradiation of n-type GaAs resulted in a reduction in carrier concentration. Burkig (17) noted that the trapping rate of free carriers after neutron bombardment was greater from n-type than p-type GaAs and luminescence studies by Okenev (18) on proton irradiated GaAs revealed a reduction in carrier concentration that he attributed to the formation of a complicated defect associated with gallium vacancies, probably a $\text{Ga}_2\text{V}_{\text{Ga}}\text{Te}_3$ complex.

In fact the reduction in carrier concentration as a result of proton bombardment has been used by Foyt et al (2) to form insulating layers in GaAs for device isolation applications.

Harris and Eisen (19) found that a luminescence peak at 9,140 Å was introduced as a result of proton bombardment and that this same level could be created in GaAs by heat treatment at a temperature of 800°C. The intensity of this level could be reduced by heat treatment with a protective film of SiO$_2$ grown on the GaAs surface. They attributed this level to the formation of an acceptor level associated with arsenic vacancies.

Because of the heavy atomic masses of the dopant ions of interest in this thesis, the damage introduced by bombardment with such ions is much more extensive than that introduced by the elementary particles discussed above. As the heavy ion slows down it can transfer large amounts of energy to the lattice atoms and cause displacement of the
lattice atoms. The damaged region surrounding the particle track as it slows down can therefore be considered as a cylinder of highly disordered radiation damage. Crowder (20) uses such a model to explain the formation of amorphous layers in silicon as a result of heavy ion bombardment. He postulated that the diameter of the cylinder of damage was a function of implant temperature. An amorphous layer was thought to be created when a number of ions had been implanted such that cylinders of damage overlapped to create a disordered layer. If the bombardment was carried out at an elevated temperature then the diameter of the damage cylinders was reduced and a higher dose was required to form overlapping damage regions and therefore an amorphous layer.

Rutherford back-scattering measurements by Carter et al (21) show the formation of an amorphous layer in GaAs as a result of implantation of Cd and Te at an energy of 40 keV and doses of greater than $2 \times 10^{14}$ ions.cm$^{-2}$.

Scanning electron microscopy by Wolf and Hunsperger (22) on Cd implanted at 60 keV into GaAs shows a similar saturation of damage, associated with the formation of an amorphous layer, at a slightly lower dose of $6 \times 10^{13}$ ions.cm$^{-2}$. Furthermore they found that recovery of the lattice upon annealing for doses of less than $6 \times 10^{13}$ ions.cm$^{-2}$ was complete at 300°C whereas doses of greater than $6 \times 10^{13}$ ions.cm$^{-2}$ required annealing at temperatures of greater than 600°C to restore the lattice.

Zelivinskaya (23,24), Sansbury (25,26) and Littlejohn et al (32) found that the implantation of heavy ions (Zn, Si, Zn respectively) into semi-insulating GaAs created a low resistivity surface layer ($10^4$ to $10^5$ ohms.cm$^{-2}$), the properties of the layer being independent of implanted ion species and therefore thought to be associated with the creation of electrically active defects. Each author finds that the
resistivity of the damage layer is independent of dose at doses greater than about $2 \times 10^{13}$ ions/cm$^2$, suggesting a lower dose for the saturation of electrically active damage. These authors found that annealing at temperatures up to $400^\circ$C resulted in an increase in resistivity until eventually, at $400^\circ$C, resistivities characteristic of the starting material (greater than $10^8$ ohms/cm$^2$) were achieved. This increase in resistivity was associated with the annealing of radiation induced defects and appeared to follow a different pattern of recovery to lattice recovery as observed using Rutherford back-scattering measurements and discussed above.

2.3 Implanted Dopant Effects

Several authors have reported the formation of conducting layers in GaAs by the implantation of the conventional dopants from columns two and six of the periodic table. These include Zn, Cd, C, Se, Te, S and Si and will be discussed in two sections, namely p-type dopants and n-type dopants.

2.3.1 P-type Dopants

The conventional p-type dopants Cd and Zn have been implanted by several authors in attempts to form p-type layers and p-n junctions in GaAs. Hunsperger (27) implanted Zn and Cd at 20KeV into high resistivity n-type substrates held at $400^\circ$C. He found that a p-type layer was formed after implantation but annealing at temperatures in the range $500^\circ$C to $600^\circ$C resulted in a great improvement of mobility and an increase in carrier concentration. Furthermore he carried out detailed measurements of the effect of surface protection upon the anneal behaviour of the conducting layers. Prolonged annealing at $600^\circ$C without surface protection resulted in an increase in resistivity and a decrease in carrier concentration of the layer. He attributed this degradation of the layer to the loss of zinc by out diffusion. This
degradation could be inhibited by covering the specimen surface with a polished, un-implanted piece of GaAs, so reducing the concentration gradient at the specimen surface. Consequently Hunsperger carried out anneals with a grown layer of SiO₂ on the specimen surface to minimise out diffusion and surface degradation. The behaviour of sheet carrier concentration with anneal temperatures followed a peculiar pattern for Cd and Zn implants carried out at 400°C. Over the anneal temperature range 400°C to 700°C the carrier concentration first rose but then fell steadily; then at anneal temperatures of greater than 700°C, the carrier concentration again started to rise. The fall in carrier concentration was thought, by Hunsperger, to be due to either the release of compensating vacancies during annealing or to non-uniform variation of carrier mobility with depth. In a later publication (28) regarding room temperature implants of Cd and Zn this behaviour was not observed. Hunsperger (29) also observed an effect that he considered to be due to the formation and diffusion of defects during implantation: C-V measurements of implanted Zn diodes revealed the presence of a semi-insulating layer extending to depths of the order of 10 microns and resulting in a p-i-n diode structure. Electroluminescence studies on these diodes revealed an emission band that Hunsperger attributed to arsenic vacancies although he pointed out that a similar band was interpreted as due to gallium vacancies by other authors (Hwang et al. 6,7).

Roughan and Manchester (30) also observed p-i-n diode structures on Zn implanted diodes, particularly after long anneals. They attributed this to the spreading of the implanted zinc distribution into the substrate by diffusion so causing compensation to considerable depths.

The effects of radiation enhanced diffusion were also investigated by Arnold (31). He bombarded GaAs at room temperature with Xe ions then deposited a zinc doped SiO₂ film and annealed at 500°C. A nearly
uniform zinc luminescence profile was obtained extending to depths more than 10 times the expected Xe range indicating that defects created at room temperature can themselves diffuse to depths greater than the ion range.

Zelivinskaya (21) carried out experiments very similar to those of Hunsperger (27) by implanting Zn at 30Kev into semi-insulating and n-type substrates. He found that annealing at temperatures in the range 450-600°C resulted in the formation of high carrier concentration p-type layers and observed no significant difference in the anneal behaviour over a dose range of $3 \times 10^{13} - 4 \times 10^{15}$ ions/cm$^2$ or at implant temperatures of 20°C, 300°C and 500°C. Hall effect measurements in conjunction with layer removal experiments showed that the zinc diffused to a depth of 0.3 microns after annealing at temperatures greater than 600°C, but no significant diffusion was seen for anneal temperatures of 400°C and 500°C. After annealing at 750°C Zelivinskaya observed that the depths of the implanted layer was a function of dose, the higher doses penetrating to the greater depths. He also saw evidence for anomalous diffusion as a result of radiation induced defects: a zinc implant at 300°C, unannealed, penetrated further than the predicted range.

Littlejohn (32) implanted zinc ions into semi-insulating GaAs at 60Kev. In agreement with Hunsperger and Zelivinskaya he found that annealing between 450°C and 600°C resulted in the formation of a p-type layer with a resistivity of the order $10^3-10^4$ ohms/cm$^2$; however, he observed little change in the layer properties at anneal temperatures in the range 600-800°C. He also found that the electrical properties measured were independent of dose at doses greater than about $2 \times 10^{13}$ ions/cm$^2$ but at doses less than this the activity induced was compensated by residual impurities (mainly chromium) in the substrate and
consequently high resistivity, low mobility layers resulted. By measuring resistivity as a function of temperature he detected a deep acceptor level with an activation energy of +0.52 ev which he associated with (unspecified) vacancies.

Favennec (33) performed some interesting implantations of zinc at an energy of 1 Mev into n-type GaAs. He found that a p-type layer was formed after annealing at 600°C, the anneal behaviour being essentially independent of implant temperature (20°, 300° and 500°C). Profile measurements revealed that the peak in the carrier concentration coincided with the Lindhard, Scharff, and Schiott range (L.S.S.range); however, because of the unusually high energy of implant a buried p-type layer was formed confined to a region extending from 3,000Å to 7,000Å below the specimen surface.

2.3.2 N-type Dopants

Mayer et al (34) implanted Të at 20 keV into a high resistivity n-type substrate held at 400°C and upon annealing at 600°C found that a low resistivity n-type layer could be formed. C-V measurements on this layer showed a peak carrier concentration of about $10^{18}$ electrons/cm³ at a depth of 0.05 microns falling to the substrate doping level at a depth of 0.10 microns.

Foyt et al (35) attempted to form n-type layers in high resistivity n and p type GaAs by implanting Se at 400 keV. They found that efficient doping occurred only for implantations carried out at 500°C followed by a 2 minute anneal at 800°C. C-V measurements on n-type layers formed on high resistivity n-type substrates showed a peak carrier concentration of $2 \times 10^{17}$ electrons/cm³ at a depth of 750Å falling to the substrate doping level of $2 \times 10^{16}$ electrons/cm³ at a depth of 3,000Å. Hall effect measurements on similar implants into p-type substrates showed a minimum doping efficiency of 35% for doses up to $10^{14}$ ions/cm². At higher doses saturation of the carrier concentration occurred in a manner
similar to the observed behaviour of diffused Se in bulk GaAs at high Se concentrations. These Hall effect measurements revealed a significant improvement in doping efficiency as a result of implanting at 500°C rather than at room temperature.

Sansbury and Gibbons (26) reported that they could form n-type layers in semi-insulating GaAs by the implantation of silicon followed by annealing at temperatures of 600°C and greater. They implanted at 3 energies (10 + 30 + 50 keV) in order to form reasonably deep uniform profiles. In an extension of this work they later presented detailed measurements of anneal behaviour and depth distribution of carrier concentration and mobility following silicon and sulphur implants into semi-insulating GaAs. As before they found that n-type layers could be formed after annealing at 600°C with little improvement as a result of annealing at temperatures higher than 650°C. Using Hall effect measurements in conjunction with layer removal measurements to obtain carrier concentration and mobility profiles they found evidence for radiation enhanced diffusion of sulphur. They also found that incomplete annealing of radiation damage resulted in an increase in compensation at regions near to the surface.

A very interesting experiment was carried out by Itoh (36) in an investigation of radiation induced defects. He performed C-V measurements on an n-type layer formed after the implantation of Te into an n-type substrate and found that beyond the Te peak the carrier concentration fell below the substrate doping level before returning to this level. This implied that defects created during implantation diffused beyond the ion range causing compensation of the substrate. He repeated the experiment but before implanting the Te ions he pre-implanted one specimen with arsenic ions and another specimen with gallium ions. C-V measurements on these specimens after annealing revealed the same
dip in carrier concentration beyond the Te peak but the effect was much less pronounced in the specimen previously implanted with arsenic and much more pronounced in the gallium implanted specimen. These results suggest that the defects responsible for compensation are predominantly arsenic vacancies and that the pre-implant with arsenic created a supply of arsenic to fill the vacancies and therefore lessen their effect.
3.1 Collision and Range Theory

The mechanisms by which a charged particle loses its energy as it penetrates a solid are of importance to the understanding of ion implantation phenomena. The way in which an incident ion loses its energy can be characterised by considering the particle velocity. In this way the energy loss processes can be conveniently divided into two regimes corresponding to high and low velocities.

At high particle velocities the energy loss process is due mainly to interactions with the orbiting electrons of the target atoms, whilst at low velocities the particle loses energy mainly by collisions with the target atoms. These processes are known as electronic and nuclear stopping respectively and each can have a characteristic effect upon the scattering of an implanted ion, so that consequently a brief description of the characteristics of each mechanism is given below. The transition from the low velocity energy loss regime to the high velocity energy loss regime is of course a gradual one and other energy loss processes, such as charge exchange at intermediate velocities can also occur.

3.1.1 Electronic Stopping

When the particle velocity is of the same order as the velocity of the orbiting electrons of the target atom (about $10^7$ cms/sec.) there is a high probability that energy can be lost by excitation of the target electrons, this mechanism being an inelastic process. As the particle slows down, a point is reached when electrons can attach themselves to the ion, converting it into a neutral atom that cannot excite electrons. Energy loss due to electron excitation therefore diminishes. Electronic stopping is characterised by a small rate of energy loss and small deflections of the particle. The incident particle is therefore able to penetrate to considerable depths into the solid over the electronic
At low velocities electronic stopping diminishes and scattering of the particle by the screened Coulomb potential barrier around the target atom nucleus becomes responsible for energy loss. In this respect the nature of the atomic interaction potential is of the utmost importance for a full description of the scattering mechanism. The scattering of the incident particle may be characterised by a parameter known as the 'collision diameter' given by:

\[ b = \frac{2Z_1 Z_2 e^2}{M^* V^2} \]

where \( M^* = \frac{M_1 M_2}{M_1 + M_2} \)

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

\( Z_1, Z_2 = \) atomic number of projectile and target atoms respectively.

\( V = \) projectile velocity.

\( e = \) electronic charge.

Physically, \( b \) is the distance to which the two nuclei would approach in a head on collision. As can be seen, \( b \) is inversely proportional to the particle velocity squared. Nuclear stopping is an elastic process and can involve large fractional energy losses and large deflections of the particle. The energy transferred to the target atom can be sufficient to cause displacement. Nuclear stopping is therefore characterised by short ranges and the production of large amounts of damage.

3.1.3 Range-Energy Relations for Amorphous Targets

Lindhard, Scharff and Schiott (L.S.S. 37) developed a comprehensive
theory of atomic stopping for amorphous targets. They assumed a
Thomas-Fermi interatomic potential of the form:

\[ U(r) = \left[ \frac{Z_1 Z_2 e^2}{r} \right] \varphi_{TF}(r/a) \]

where \( r \) = distance from nucleus.

\( a = \) a factor involving the screening of the nucleus.

to arrive at the nuclear stopping term and also derived an electronic
stopping contribution proportional to the particle velocity.

The rate of energy loss due to nuclear stopping is then given in
terms of dimensionless length and energy parameters defined as:

\[ \rho = \pi R a^2 N \left[ \frac{M_1 M_2}{M_1 + M_2} \right] \]

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

This results in a general curve of \( \left( \frac{\partial \xi}{\partial \rho} \right)_n \).

The rate of energy loss due to electronic stopping is given by:

\[ \left( \frac{\partial \xi}{\partial \rho} \right)_e = k \xi^{M_2} \]

where \( R = \) particle range.

\( a = \) a function of \( Z_1 \) and \( Z_2 \).

\( N = \) number of atoms per unit volume.

\( E = \) particle energy.

\( k = \) a function of \( Z_1, Z_2, M_1 \) and \( M_2 \).

This produces a set of curves for \( \left( \frac{\partial \xi}{\partial \rho} \right)_e \), corresponding to
various values of the constant \( k \).
The form of the curves describing nuclear and electronic stopping are illustrated in fig. (2). From these curves it can be seen that nuclear stopping predominates in the reduced energy range up to $\varepsilon = 0.35$.

The energies of ions of interest in the context of this thesis corresponding to $\varepsilon = 0.35$ were calculated and are given in the table (2). It is apparent that within the range of energies and ions encountered in this work (mainly Te and Cd up to 300Kev) nuclear stopping processes predominate. It is therefore to be expected that phenomena characteristic of nuclear stopping will be observed over the entire particle range, i.e. the displacement of many lattice atoms and the creation of highly disordered regions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$Z$</th>
<th>$M$</th>
<th>$\varepsilon/E \times 10^{-3}$</th>
<th>$E$ in Kev for $\varepsilon = 0.35$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te</td>
<td>52</td>
<td>127</td>
<td>1.44</td>
<td>240</td>
<td>0.133</td>
</tr>
<tr>
<td>Cd</td>
<td>48</td>
<td>112</td>
<td>1.72</td>
<td>203</td>
<td>0.138</td>
</tr>
<tr>
<td>Se</td>
<td>34</td>
<td>79</td>
<td>3.16</td>
<td>110</td>
<td>0.152</td>
</tr>
<tr>
<td>Zn</td>
<td>30</td>
<td>65</td>
<td>4.01</td>
<td>87</td>
<td>0.166</td>
</tr>
<tr>
<td>S</td>
<td>16</td>
<td>32</td>
<td>10.8</td>
<td>32</td>
<td>0.240</td>
</tr>
</tbody>
</table>

Table (2)

3.1.4 Crystalline Targets

It must be emphasised that the range energy relationships outlined above refer to amorphous targets. Here however, the targets of interest are semi-conductor single crystals and the ordered arrangement of atoms in the very open diamond type lattice plays an important role in determining the range and distribution of implanted ions. In fact computer calculations by Robinson and Oen (38) as early as 1963 predicted that charged particles could penetrate to large depths along major crystallographic directions and indeed such effects were subsequently observed experimentally (Ref. 39, 40 and 41).
Fig. 2 Nuclear and electronic stopping contributions as a function of the reduced energy.
(reproduced from data in ref. 1)
If a charged particle enters a crystal within a small angle of an atomic row or plane it will be confined to the region between the atomic rows (or planes) by successive gentle collisions. This steering of the particle away from atomic rows prevents close encounters with the target nuclei and consequently nuclear processes will be attenuated. In particular, the particle will lose energy by electronic stopping processes within the region between atomic rows (or planes) and will therefore travel to a considerable depth. The region between atomic rows and planes can be considered as 'channels' along which particles can easily travel. The phenomena has therefore been given the name of 'channelling'.

The channelling process can be characterised by the angle within which the particle must approach the atomic rows or planes to undergo a steering collision. This is known as the critical angle and is a function of particle energy \( E \) given by:

\[
\theta = \sqrt[3]{\frac{2Z_1Z_2e^2}{Ed}}
\]

where \( d \) = atomic spacing along aligned direction.

For the ions of interest in this thesis (Te and Cd at about 150Kev) this expression yields a critical angle of about 4° to 5°.

A particle can be deflected out of a channel as a result of thermal vibrations of the lattice atoms or by collisions with atoms located within the channel. Such atoms can be present within a channel as a result of damage to the crystal lattice or the presence of impurity atoms. Also as the particle slows down within the channel the cross section for nuclear collisions increases and the particle will eventually be deflected out of the channel as a result of collisions with the target atoms. Once out of the channel the particle will have a random trajectory and the range will be that predicted by L.S.S. theory. Therefore, even for a channelled
particle, the end of the particle range will be characterised by nuclear stopping and associated phenomena.

3.1.5 Projected Range

The range referred to in the L.S.S. theory is the total path length traversed by the particle until it comes to rest. In practice it is more convenient to refer to the projected range onto the direction of incidence of the particle as shown below:

![Projected Range Diagram]

In amorphous targets the distance between collisions and the energy loss per collision are random variables. Therefore all particles will not come to rest at the same depth but will have a distribution about a mean range. The distribution of implanted ions can therefore be characterised by a mean projected range $R_p$ and a deviation from this range $\Delta R_p$.

Using L.S.S. theory, Johnson and Gibbons (42) have computed and tabulated values of $R_p$ and $\Delta R_p$ for a wide selection of substrates, ions and energies.

NOTE:

Recently, in a discussion between Crowder and Johnson Ref.(43), an anomaly in the computer calculations of Johnson was brought to light. In these calculations Johnson ignored second order terms with the result that the calculated $\Delta R_p$ was too small for heavy ions in light substrates. This is the situation of interest in this thesis and it was found by Crowder...
that a better approximation to $\Delta R_p$ was $\Delta R$. This anomaly does not effect the projected range, only the deviation from this range and was therefore not considered to be of critical importance in this thesis.

### 3.2 Rutherford Back-Scattering (R.B.S.)

In section 3.1.4 it was mentioned that the crystalline structure of a solid could influence the range distribution of an incident ion beam. This phenomena is known as channelling and is characterised by the critical angle for channelling.

The process of channelling, in conjunction with the back-scattering of incident ions, is used as a powerful tool for the study of crystal structure.

When a beam of ions strikes a solid surface a proportion of the beam will be scattered from the surface as a result of elastic collisions with the atoms of the solid. The number versus energy spectrum of the back-scattered ions will be a function of:

1. The number of scattering centres per unit area
2. The angle of scattering
3. The mass of the incident and scattering particles
4. The particle velocity

If the solid is amorphous (i.e. the incident ion beam 'sees' a random array of scattering centres) then the back-scattered spectrum consists of a sharp edge, corresponding to scattering from the surface region, followed by a smooth slowly changing yield at lower energies. This is illustrated by curve A, fig. (3). If the ion beam strikes a crystal in a low index direction it will be faced with a reduction in the number of scattering centres and consequently there will be a reduction in the back-scattered yield. This is illustrated by curve B, fig. (3).
Any crystalline defects, such as surface damage, interstitial atoms etc. that tend to increase the number of scattered centres will influence the back-scattered yield. Of particular interest to this thesis is the application of the R.B.S. technique to the study of radiation induced crystal disorder and the location of impurity atoms within the lattice structure. These aspects will be discussed briefly below:

3.2.1 Radiation Damage

The implantation of heavy ions is likely to result in the displacement of lattice atoms and therefore, the formation of a damage layer. In practice this damage layer will be near to the crystal surface.

This surface damage will present an increase in the number of scattering centres to the analysing beam directed along a major crystal direction and will cause an increase in back-scattered yield. If the damage is confined to the crystal surface it will be revealed as a peak in the back-scattered yield as shown by curve C in fig. (3).

If the damage layer extends to a considerable depth, such as that caused by abrasive polishing, then the back-scattered yield may show a general increase rather than a peak. This is illustrated by curve D in fig. (3).

The peak height can be used as a measure of the damage by comparing it to the back-scattered yield when the ion beam is in a random direction to the crystal i.e. completely unaligned. The ratio of damage peak height to random height is denoted by $X$ and was used by the author as a 'damage parameter' in some measurements of crystal damage introduced by abrasive polishing. These measurements are reported in section 4.1.

3.2.2 Atom Site Location

If an incident particle is scattered from an impurity atom of heavier
Fig. (3) Illustration of Rutherford Back Scattering Spectra
atomic mass than the substrate then it will be scattered with a higher energy than from the lattice atoms. Consequently a peak will be observed outside the back-scatter spectrum corresponding to the crystalline lattice. Lighter atoms will also give rise to peaks but these will be inside the crystalline spectrum and may be difficult to observe in practice except at very high atomic concentrations.

The presence of such peaks is illustrated in fig. (3). In this manner R.B.S. can be used to detect the presence of impurities within the crystal lattice. Furthermore, spectra obtained after aligning with various crystal directions can give very precise data concerning the lattice site occupied by the impurity atoms. Such studies are being made by other members of the department, particularly for Te and Cd implanted atoms in GaAs.
3.3. Electrical Properties of Semiconductors

The electrical properties of a semiconductor are primarily determined by the free carrier concentration and associated parameters such as carrier mobility and lifetime. This thesis is concerned with the determination of carrier concentrations and mobilities resulting from the implantation of electrically active impurities. Consequently this section outlines the important aspects of theory concerning the distribution of carriers amongst the available energy levels within the semiconductor as a function of temperature and a consideration of the factors limiting the carrier mobility, also as a function of temperature.

The theory of conductivity and Hall effect measurement techniques is then discussed including the application of these techniques to the determination of carrier concentration and mobility profiles.

3.3.1 Carrier Statistics

For simplicity we will consider electrons in the conduction band: the description of holes in the valence band however, is exactly analogous. Under all conditions the carrier concentration in the conduction band is given by:

\[ n = \int_{-\infty}^{\infty} f(E) g(E) \, dE. \]

where \( f(E) \) is the Fermi-Dirac probability of occupancy for a state at energy \( E \) given by:

\[ f(E) = \frac{1}{1 + \exp \left( \frac{E - E_F}{kT} \right)} \]

\( E_F \) is a normalising parameter, characterised by the number of electrons per unit volume and the density of states.
and \( g(E) \) is the density of available electron states at an energy \( E \) which, for a parabolic energy band, is given by:

\[
g(E) = 4\pi^2 \frac{2m^*}{\hbar^2} \left( E - E_C \right)^{3/2}
\]

Substitution of the expressions for \( f(E) \) and \( g(E) \) gives the carrier concentration as:

\[
n = N_C \int \left[ \frac{E_F}{kT} \right] \frac{1}{1 + \exp \left( \frac{E - E_F}{kT} \right)}
\]

where

\[
N_C = 4\pi^2 \frac{2m^*kT}{\hbar^2}^{3/2}
\]

where \( m^* \) = effective mass of electrons

\( h \) = Planck's constant

\( E_C \) = energy of conduction band edge

\( k \) = Boltzmann's constant

\( T \) = absolute temperature

\[ \int \left[ \frac{E_F}{kT} \right] \frac{1}{1 + \exp \left( \frac{E - E_F}{kT} \right)} \] is known as the Fermi integral. These integrals cannot be solved analytically but have been calculated numerically and tabulated by McDougall and Stoner (42). Over most of the range of carrier concentrations and temperatures encountered in practical situations, equation 1 can be satisfied for values of \( E_F \) much less than \( E_C \); under these conditions \( f(E) \) can be approximated by:

\[
f(E) = \frac{1}{1 + \exp \left( \frac{E - E_F}{kT} \right)} \approx \exp \left[ \frac{E - E_F}{kT} \right] \quad \text{for} \quad E_F \ll E \quad \ldots \quad 3.
\]
and the carrier concentration is then given by:

\[ n = N \sqrt{\frac{m_e}{2\pi k T}} \exp\left(\frac{E - E_F}{k T}\right) \]  

This is the well known classical or Boltzmann region and for carrier concentration calculations this classical approximation can be used as long as \( E_F \) is at least 2kT away from the band edge. If the carrier concentration or temperature is such that \( E_F \) approaches to within 2kT of the band edge then the full expression of equation 2 must be used to describe the carrier concentration.

3.3.2 Conduction mechanisms

Electrons can enter the conduction band by excitation from energy levels within the valence band or within the forbidden gap. The resulting electrical conduction is known as Intrinsic or Extrinsic conduction respectively.

Intrinsic conduction is so called because it is characteristic of the semiconductor in question. For the common semiconductors, with band gaps of the order of 1 to 2 eV, the intrinsic carrier concentration at room temperature is extremely small and can be ignored for practical purposes.

For practical applications the electrical properties of a semiconductor are controlled by the introduction of chemical impurities into the lattice. These impurities are responsible for extrinsic conduction and can be characterised by small activation energies of the order of 0.01 to 0.1 eV. At room temperature (kT = 0.03 eV) the majority of these impurities will be ionised and the carrier concentration of the semiconductor will depend primarily upon the concentration of impurities.

If the impurities in the lattice are such that electrons are
donated to the conduction band the impurity is known as a donor. Likewise if electrons are removed from the valence band to the impurity it is known as an acceptor.

In general a semi-conductor will contain both donors and acceptors and the electrical properties will be determined by the nett effect of both types of impurity.

Conditions of charge neutrality will determine the distribution of electrons over the available conduction and valence band states and the impurity levels within the band gap.

The condition of charge neutrality requires that:

\[ n + N_a^- = p + N_d^+ \]

where:
- \( n \) = number of electrons in conduction band
- \( p \) = number of holes in valence band
- \( N_a^- \) = number of ionised acceptors
- \( N_d^+ \) = number of ionised donors.

As we have seen \( n \) and \( p \) can be determined using Fermi-Dirac statistics, in a similar manner Fermi-Dirac statistics can be applied to the impurity states within the band gap to determine the number of ionised donors and acceptors. Equation 5 is a formidable equation to solve if conditions are such that the full Fermi integrals must be used (\( E_f \) closer than about 2kT to either band). However, for non-degenerate conditions the exponential approximation to equation 3. can be used to simplify the solution of equation 5.

### 3.3.3 High Doping Levels

As the number of impurities in the crystal lattice is increased the wave functions corresponding to individual impurity levels overlap and eventually an impurity band will be formed with a reduction in ionisation energy. This effect has been observed many times for impurities in Si and Ge. (Ref. 45, 46). Under these conditions the dopants will be fully
ionised at all temperatures and the semi-conductor will behave in the fashion of an 'impurity metal'. (Blakemore Ref. 47)

The concentrations of donors and acceptors in GaAs at which impurity banding leads to the merging of the impurity band with the conduction and valence band respectively have been calculated and experimentally determined by Hilsum (48) to be $4 \times 10^{16}$ donors/cm$^3$ and $6 \times 10^{18}$ acceptors/cm$^3$. These concentrations are well within the concentrations encountered in device material and expected to be achieved in this work. Effects associated with impurity banding should therefore be anticipated.

3.3.4 Carrier Mobility

The mobility of carriers in a semi-conductor will be limited by various scattering processes, the most important of these being scattering by lattice thermal vibrations and scattering by ionised impurities in the lattice.

Other processes such as scattering by neutral impurities, dislocations and carrier-carrier interactions can also influence the mobility but are usually of secondary importance. The two main processes mentioned above are discussed briefly below:

3.3.4.1 Lattice Scattering

At temperatures above absolute zero the thermal energy of the lattice gives rise to vibrations of the lattice. These vibrations can be considered as a perturbation of the regular lattice structure and can therefore act to scatter electrons. The scattering of electrons can be characterised by considering the frequencies at which the lattice can vibrate in two principal modes.

1) Acoustic Vibrations

These vibrations are vibrations of the lattice as a whole and are important in the elemental semi-conductors Si and Ge. The scattering of carriers by the acoustic modes is elastic and leads to a variation of
mobility with temperature of the form $T^{-3/2}$.

ii) Optical vibrations

These vibrations are the result of the relative movement of alternate atoms. Because of the presence of two different types of atom in the compound semiconductors these vibrations give rise to an electrical polarisation of the lattice. This polarisation results in a strong interaction with the free carriers and therefore pronounced scattering of the carriers by optical vibrations.

This scattering process is inelastic and therefore the analysis of mobility is complicated, however at high temperatures the carrier mobility has a $T^{-3/2}$ dependence on temperature while at intermediate temperatures the mobility variation is dominated by an $\exp(-T)$ term.

3.3.4.2 Impurity scattering

At low temperatures the mobility of the free carriers is limited by collisions with physical imperfections in the lattice such as impurity atoms, lattice defects, grain boundaries and dislocations.

In all but the purest semiconductors it is found that collisions with electrically charged impurity atoms limits the mobility of free carriers at low temperatures.

In the region of a charged impurity atom (ionised donor or acceptor) an electron will be scattered by the electrostatic field associated with the impurity. This scattering is similar to the scattering of alpha particles by atomic nuclei investigated by Rutherford.

It is found that the mobility of the carriers associated with this type of scattering varies as $T^{3/2}$. Thus, when this mechanism is dominant, the mobility falls as the temperature is lowered.

The mobility will also be a function of the total number of scattering centres i.e. the impurity concentration. The mobility therefore falls as the impurity concentration increases, this effect
Fig. (4) Mobility of electrons and holes in GaAs as a function of carrier concentration. (Data from ref. 48 and 67)
Fig. (5) Mobility of electrons in GaAs as a function of temperature due to scattering by ionised impurities and optical lattice vibrations. (Data from ref. 48 and 67)
is shown in fig.(4) where mobility is plotted against free carrier concentration (i.e. concentration of ionised impurity atoms) for n and p-type GaAs.

At very high carrier concentrations other mechanisms such as carrier-carrier scattering have a significant effect on the mobility but these mechanisms have not been studied to any great extent.

3.3.4.3 Combination of scattering processes

The carrier mobility at any temperature will be limited by the combined effect of the various scattering mechanisms.

When several scattering mechanisms must be combined the procedure is to calculate relaxation times \( \tau_1, \tau_2, \tau_3 \ldots \) for each process.

The resultant relaxation time \( \tau \) is obtained by writing

\[
\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} + \ldots
\]

\( \tau \) is then used in evaluating the integrals for calculating the transport properties.

This is often a tedious process and in practice the combination of mobilities can be approximated by writing:

\[
\frac{1}{\mu} = \frac{1}{\mu_1} + \frac{1}{\mu_2} + \frac{1}{\mu_3} + \ldots
\]

Fig.(5) shows the resulting variation of mobility with temperature for n-type GaAs when the mobilities due to ionised impurity scattering and optical vibrations are combined.

The data for fig.(4 and 5) were taken from a mass of experimental data summarised in ref.(48).
3.3.5 Hall effect and conductivity

The Hall effect was discovered in 1879 by E.H. Hall and since then has been used extensively in the study of conduction processes to determine carrier concentration and mobility.

A general derivation of the relevant expressions is given below where it is assumed that the carrier concentration and velocity (mobility) are functions of position. These conditions are of particular interest in the case of implanted layers.

With reference to the diagram above, a current density \( J_x \) flows through the specimen in the x direction. When placed in a magnetic field \( B_z \), in the z direction, the electrons will experience the Lorentz force and be deflected in the y direction. This will give rise to an electric field in the y direction of \( E_y \).

If \( n \) = the carrier concentration

\( \mu \) = the carrier mobility = carrier velocity per unit electric field

then the current density in the y direction is given by:

\[
J_y = e E_y n \mu .
\]
If the specimen is not uniformly doped and/or the carrier velocity is a function of position then the contributions from the various groups of carriers must be included and:

\[ J_y = e E_y \int n(x) \mu(x) \, dx \]

also the mobility \( \mu(x) = v_x / E_x \)

and the Lorentz force \( E_y = v_x B_z \) where \( v_x \) is the velocity of the carriers in the \( x \) direction.

therefore \[ J_y = e B_z \int v_x n(x) \mu(x) \, dx \]

i.e. \[ J_y = e B_z E_x \int n(x) \mu^2(x) \, dx \]

This \( y \) component of the specimen current will give rise to an electric field, in the \( y \) direction, of:

\[ E_y = J_y / \sigma \]

where \( \sigma = e \int n(x) \mu(x) \, dx \) and is known as the conductivity

therefore \[ E_y = \frac{e B_z E_x \int n(x) \mu^2(x) \, dx}{e \int n(x) \mu(x) \, dx} \]

but \[ E_x = J_x / \sigma \]

therefore \[ E_y = \frac{B_z J_x}{e \left[ \int n(x) \mu(x) \, dx \right]^2} \]
where $R_H$ is known as the Hall constant and is given by:

$$R_H = \frac{1}{e} \frac{\int n(x) \mu^2(x) \, dx}{\left[ \int n(x) \mu(x) \, dx \right]^2} = \frac{e \int n(x) \mu^2(x) \, dx}{[\sigma]^2}$$

Evidently, if $n$ and $\mu$ are constants, the expression for the Hall constant reduces to:

$$R_H = \frac{1}{n \cdot e}$$

This is a much quoted expression and shows the value of Hall constant determination for the calculation of carrier concentrations.

Also:

$$\sigma = n \cdot e \cdot \mu_c$$

where $\mu_c$ is known as the conductivity mobility. In the simple case of uniform doping, the product

$$R_H \cdot \sigma = \mu_c$$

In fact this simplification is only true if all the carriers have the same velocity, which is not true for the relatively low carrier concentrations met in semiconductors. (In metals the carriers which undergo scattering have only a small spread in velocity, about the Fermi level, and the above approximation is applicable.)

In general the right hand side of equation 2 should be multiplied by a numerical factor, known as the Hall scattering factor $r_H$, but this does not depart far from unity. The scattering factor $r_H$ is a function of the processes that influence the velocity of the carriers and therefore their scattering e.g. magnetic field, degeneracy and...
temperature. In the limit of high magnetic field and/or high degeneracy the scattering factor approaches unity.

Stillman et al (49) made some measurements of the Hall scattering factor for n-type GaAs and found that the error expected in calculating carrier concentrations by assuming $r_H = 1.0$ was at most $-15\%$ at room temperature.

The simple expression for the Hall constant (equation 3) was used by the author to characterise the carrier concentration and mobility of implanted layers although, from the derivation above, it can be seen that great caution must be used when using these expressions for non-uniform material.

For these reasons the complete description of the electrical properties of an implanted layer can only be obtained if the carrier concentration profile is known.

3.3.6 Application of Hall effect to profile measurement

Although L.S.S. theory can be used to predict the implanted profile, deviations from the predicted profile can be expected to occur as a result of channelling, radiation enhanced diffusion and diffusion during subsequent heat treatment. Also, due to interactions with radiation induced defects, the profile of electrically active atoms may differ from the atomic profile.

In this work Hall effect measurements in conjunction with layer removal were used to determine carrier concentration and mobility profiles.

The Hall effect expressions derived in section 3.3.5 will therefore be considered and applied to the case of layer removal.

Differentiation of equations 1 and 2 of section 3.3.5 for Hall constant and conductivity gives:

$$d(R_H r^2) = e_n(x) \mu^2(x) \, dx$$

48.
and \( \sigma = e. n(x). \mu(x). dx \)

Therefore \( \mu(x) = \frac{\frac{d}{dx}(R_H. \sigma^2)}{e.n(x). \mu(x)} = \frac{\frac{d}{dx}(R_H. \sigma^2)}{\sigma/\mu} \)

If thin layers are removed the derivatives can be approximated by:

\[
\frac{d\sigma}{dx} = \frac{\Delta \sigma}{\Delta x}
\]

and \( \frac{d}{dx}(R_H. \sigma^2) = \frac{\Delta(R_H. \sigma^2)}{\Delta x} \)

Therefore the mobility in the i'th layer is:

\[
\mu_i = \frac{\Delta(R_H. \sigma^2)_i}{\Delta \sigma_i}
\]

also \( n(x) = \frac{d\sigma}{dx} \)

Therefore the concentration in the i'th layer is given by:

\[
n_i = \frac{\Delta \sigma_i}{e.u_i \Delta x_i}
\]

where \( x_i \) is the thickness of the i'th layer

A computer program was developed by the author to calculate \( n_i \) and \( \mu_i \) from the above expressions.
4.1 Specimen preparation

Because of the limited depth of penetration of the ions of interest (up to about 1,000 Å) the process of ion implantation can be thought of as essentially a surface phenomenon and consequently calls for the use of careful surface preparation techniques. In particular a surface free from mechanical damage is required, although this need not necessarily imply a physically flat surface. In fact good optically flat surfaces can be produced by conventional mechanical polishing techniques but several reports (50, 51, 52) indicate that the damage created as a result of these preparation techniques can extend to depths of several microns. It was therefore decided, for this work, to rely on chemical polishing and etching methods to obtain the desired surface finish. In particular the use of a mixture of bromine in methanol is reported as a successful polish - etch for GaAs (53).

The specimens for implantation had to be prepared from GaAs supplied in ingot form, the first step in the preparation being the slicing of the ingot into wafers about 1mm thick using a diamond wheel saw. In order to estimate the depth to which lattice disorder was introduced by this sawing (and therefore estimate the amount of material to be removed from the surface to minimise residual damage) the author carried out a series of Rutherford back-scattering measurements on specimens progressively etched in bromine - methanol after sawing. The damage parameter (discussed in section 3.2.1) so obtained is shown plotted against the amount of material removed in fig. (6). From this figure it is evident that the removal of some 5 microns from the surface reduces the lattice disorder remaining to below the detection limit of the Rutherford back-scattering technique. Because this technique is only sensitive to
Fig. 6  Sawing damage remaining as a function of the amount of material removed.
gross lattice disorder it was planned to remove considerably more than
this 5 microns during subsequent preparation.

As mentioned above, specimens were to be prepared from GaAs ingots. The ingots used were of (110) orientation with end faces parallel to (110) planes. The ingots were first sliced parallel (judged by eye) into wafers 1mm thick on a rotary diamond wheel saw.

After degreasing in an ultrasonic bath with solvents the slices were mounted, using Apiezon-w wax, onto a quartz disc (usually 3 at a time). This assembly was then carefully degreased with solvents in an ultrasonic bath and after drying was ready for chemical polishing.

Polishing was carried out on Hyprocel - Pan-W pads, first of all with a 3% bromine methanol solution. This leaves the surface with an 'orange peel' appearance. A final polish in a 1% bromine methanol solution improves this surface finish. This polishing removes a total of about 250 microns which is considerably greater than the depth to which damage can be detected by R.B.S. (5 μ) and is therefore considered adequate to remove sawing damage.

The polished slices are then removed from the quartz disc and thoroughly cleaned in solvents in an ultrasonic bath. The majority of implants were into specimens 5mm x 5mm x 0.5mm, this size being found a convenient size to handle and enabling several specimens to be implanted at one time over the available implantation area (about 4 cms diameter).

Consequently after polishing, the slices were diced into 5mm squares using a wire saw to minimise wastage of material.

Before implantation the 5mm squares were etched in 1% bromine methanol to remove a further 10-20 microns and the last traces of preparation damage.
4.2 Annealing studies

It has been shown that the implantation of heavy ions creates a highly disordered region and the damage so produced may dominate the electrical properties of a semiconductor immediately after implant. The electrical activity associated with the implanted dopant will only be realised when such radiation damage effects are removed and, in most cases, when the dopant atoms occupy lattice sites. This re-ordering of the crystal lattice can be achieved by annealing the specimen at elevated temperatures after implantation or by implanting at elevated temperatures in order to minimise the introduction of radiation damage. It has also been reported (sec. 2.1) that heat treatment of GaAs at elevated temperatures can introduce electrically active defects, therefore some protection of the specimen surface may be necessary to inhibit surface degradation and contamination at elevated temperatures.

Since the mechanisms of re-ordering are likely to be temperature dependent rather than time dependent isochronal anneal stages were decided upon for this work. Isochronal annealing also yields the activation energy of the re-ordering process. The mathematics of analysis used in this thesis are given in appendix 1.

The annealing equipment consisted of a tube furnace that held a clear, synthetic quartz annealing tube. Before use any new tube was heated for several hours at 1,000°C to drive off water vapour from the quartz. The tube was also regularly cleaned by etching in Aqua Regia (3HCl + 1HNO₃) and then rinsing in distilled water. Annealing was carried out in a flowing atmosphere of nitrogen (O₂ free), the gas supply and exhaust being coupled to the quartz tube with brass connections: the inlet connector also held a push rod.

At anneal temperatures greater than 500°C the specimen surface was protected against deterioration with a film of SiO₂. This film was
Fig. 7  Schematic diagram of SiO₂ deposition apparatus.
grown using the technique described by Goldsmith and Kern (54) in which silane (SiH₄) reacts with oxygen at a temperature of 350°C - 400°C to form SiO₂. The films were grown in the apparatus shown diagrammatically in fig.(7). The specimens were placed on a hot plate inside a bell jar. The hot plate was warmed to 300°C and the silane, diluted with nitrogen, plus the oxygen were flushed through the bell jar. The films grown were generally about 5,000 Å thick, as judged by interference colours.

After annealing the SiO₂ film was removed by dissolving in 40% hydrofluoric acid (HF) for about 2 minutes then rinsing in distilled water.

To provide further surface protection the specimen was placed face down on a GaAs boat during annealing in the fashion of Hunsperger (27) to reduce concentration gradients at the specimen surface. The GaAs boat was regularly etched in 3% bromine - methanol before annealing.

4.3 Contacts

Ohmic contacts were required to both n and p-type GaAs over the resistivity range 50 - 1 x 10⁻³ ohm.cm. The contacting techniques used were:

1. Alloying
2. Evaporation
3. Painted Silver - Dag
4. Implantation

These techniques will be discussed separately.

4.3.1 Alloying

The contacting material is alloyed to the specimen in a suitable atmosphere. Various authors (55,56,57) have reported the use of metallic tin and an alloy of indium + zinc for contacts to n and p-type GaAs respectively. These contacting materials were therefore used mainly for measurements of bulk GaAs and found to give ohmic contact. The contacting material was alloyed to the specimen surface in an atmosphere of hydrogen bubbled through HCl. The HCl assists wetting.
of the surface and cleanliness of the alloy. Alloying was carried out at a temperature of 250°C for the tin contacts and 200°C for the indium + zinc contacts, alloying time being about 2-3 minutes.

Alloying is a simple method of contacting but has the disadvantage that the contact may penetrate through an implanted layer and destroy the electrical isolation of the layer from the substrate. Alloyed contacts were therefore only used for measurements of bulk material and a few measurements of layers implanted into semi-insulating GaAs.

4.3.2 Evaporation

In general evaporated metal semi-conductor contacts tend to be non-ohmic and require heat treatment to form a suitable contact. Evaporated contacts therefore suffer from the same electrical disadvantages as alloyed contacts i.e. they may diffuse through the implanted layer as a result of heat treatment. However, evaporated contacts have a significant advantage in that their position and size can be conveniently controlled by masks and they are also less bulky. Evaporated contacts were therefore used as an alternative to alloyed contacts for the measurement of layers implanted into semi-insulating GaAs, particularly in the more exacting circumstances of layer removal experiments where small accurately positioned contacts are required. Evaporated gold was found to give an ohmic contact to p-type layers without heat treatment and an alloy of 2% tin + gold gave an ohmic contact to n-type layers after heat treatment at 400°C for 3-4 minutes. All evaporations were carried out in a vacuum of about 10⁻⁶ torr, the specimens being held in the modules described in Section 4.6.2.

4.3.3 Silver-Dag Contacts

Silver-dag is a suspension of colloidal silver manufactured by the Acheson Colloids Company. The dag can be painted onto a surface to deposit a layer of metallic silver.
It was found that ohmic contacts could be made to p-type layers using dag. Usually the contact had to be formed by passing a current of a few milliamps through the contacts. In particular, dag was used as a contact to study the low temperature (less than 400°C) annealing behaviour of implanted layers. The electrical properties of such layers were invariably governed by the effects of radiation damage and tended to be p-type.

Silver-dag contacts had the great advantage that after a measurement and before the next anneal, they could be removed by thorough cleaning with acetone in an ultrasonic bath.

4.3.4 Implanted Contacts

The formation of low resistance ohmic contacts by the implantation of heavily doped regions on the semi-conductor surface offers significant advantages over conventional techniques. In common with evaporated contacts, the size and position of the contact area can be accurately controlled by suitable masks. Undoubtedly the most important aspect of implanted contacts is the fact that they can be formed before the layer itself is implanted, therefore minimising heat treatment and the risk of contamination.

The implanted contact regions must form a low resistance contact to the layer of interest and at the same time maintain the isolation of the implanted layer from the substrate i.e. form a p-n junction with the substrate.

The formation of implanted contact regions does, of course, imply some pre-knowledge of the behaviour of implanted ions. This knowledge can only be obtained after annealing studies etc. employing conventional techniques.

Contact regions of Te and Cd were implanted with the hope of forming 'semi-metallic' areas for use with the four point probe described in section 4.4.5.
Unfortunately time permitted measurements to be made only on Cd implanted contacts and therefore only these will be discussed.

Cd contact regions were formed by implanting a dose of $1 \times 10^{15}$ ions/cm$^2$ at an energy of 150Kev followed by an anneal at 600°C. The contacts were implanted at the temperatures proposed for the layer to ensure that any diffusion associated with implantation at elevated temperatures was common to the contact and layer.

The isolation properties of the contact regions were assessed by implanting contact regions only into n-type substrates and measuring the resulting p-n diode characteristics. Ohmic contact was made to the n-type substrate with an alloyed tin contact. Gold wire probes were used to probe the implanted contact areas.

The ability of implanted Cd contact regions to form low resistance contacts to implanted Cd layers was assessed by forming contact regions, as described above, and then implanting a layer. After annealing of the layer, at 600°C, the contact characteristics were measured.

A schematic diagram of the technique and resulting characteristics is shown in fig.(8 and 9).

A transistor curve tracer was used to obtain these characteristics.

The results can be summarised as follows :

i) From curve C-B of fig.(9) it can be seen that gold wire probes form a low resistance ohmic contact to implanted p-type regions. From this same curve it can also be seen that implanted p-type contact regions form low resistance ohmic contacts to implanted p-type layers.

ii) From fig.(8) it can be seen that implanted contact regions form p-n diodes on the n-type substrates. These diodes have a low reverse leakage current of about 1 micro-amp at 2 volts reverse bias.

iii) From curves A-B and A-C of fig.(9) it can be seen that implanted layers also form p-n junctions on the n-type substrates.
Fig. 8 Diode characteristics of implanted p-type contacts in n-type substrate
Fig. 9 Diode characteristics of implanted p-type layer and contacts in n-type substrate.
Because of the large area of the implanted layer (about 0.25 cm\(^2\)) the reverse leakage current is slightly higher i.e. 10 micro-amps at 2 volts reverse bias.

4.4 Electrical Evaluation of Implanted Layers

As a preliminary to the determination of carrier concentration and mobility using Hall measurements it is useful to have a simple technique capable of monitoring gross changes in electrical conduction. In particular it is useful to know whether the semi-conductor is n-type or p-type. A simple technique is the thermal probe and is discussed in some detail below. This is followed by a discussion of the Hall effect applied to implanted layers and then a description of the apparatus used to determine Hall coefficient etc.

4.4.1 Thermal Probe

The thermal probe is a simple technique for determining conductivity type which requires no permanent contact to the semi-conductor surface. This technique was used by Granville and Hogarth (58) to monitor conductivity changes in Ge and InSb and by Fane (11) to define p-n junctions in GaAs.

A hot (100°C) gold wire probe and a cold (room temperature) gold wire probe are touched onto the surface of the semi-conductor. The hot probe will supply thermal energy to the majority carriers which will then diffuse away from the heated area, creating a potential difference between the hot and cold probes. The sign of the potential difference is an indication of the carrier type (i.e. n or p). In the equipment used by the author each probe was mounted in a micro-manipulator, the hot probe being heated by, but isolated from, a 15 watt soldering iron bit. The soldering iron bit was supplied from a 250 volt variable D.C. supply to minimise A.C. pickup. The hot and cold probes were connected by a 10 Meg ohm resistor, the voltage developed across the resistor being read on a digital voltmeter. This voltage could be used in a semi-quantitative
Fig. 10 Schematic diagram of thermal probe assembly.

- 0 to 240 volts D.C. heater
- Power supply
- Digital voltmeter
- Micro-manipulator
- Specimen
- Hot probe (gold wire)
- Cold probe (gold wire)
- Soldering iron
- 'Sintox'
- Electrical insulation
manner to measure the electrical activity. A diagram of the thermal
probe assembly is shown in fig. (10).

4.4.2 Hall Effect Measurements

The relevant theory of the Hall effect was outlined in section 3.3.5
and consequently only the aspects of importance to implanted layers will
be considered here.

The geometry of implanted layers i.e. a thin uniform sheet, satisfies
Van der Pauw's (59) conditions for resistivity and Hall coefficient
determination. The relationships of interest can be defined with the aid
of fig. (11) which illustrates a square specimen with a point contact
at each corner.

![Fig. 11](image)

If $V_{34}$ is the voltage measured as a result of a current $I_{12}$ then resistance
values can be defined by :

$$R_{12} = \frac{V_{34}}{I_{12}} \quad R_{23} = \frac{V_{41}}{I_{23}}$$

Then the resistivity is given by :

$$\rho = \frac{\pi d}{2 \ln 2} \left( \frac{R_{12}}{R_{23}} + R_{23} \right) \cdot F$$

Where $d$ is the specimen thickness and $F$ is a function of $R_{12}$ and
is given in Van der Pauw's paper.
In a similar manner the Hall constant is given by:

\[ R_H = \frac{d}{B} \frac{V_{24}}{I_{13}} \]

Where \( B \) is the magnetic field at right angles to the plane of the specimen.

In practice, since the implanted layer thickness was not known, sheet resistivity and surface carrier concentrations were calculated i.e.

\[ \rho_s = \frac{\rho}{d} \quad \text{and} \quad n_s = \frac{R_H}{d} \]

A computer program was developed by the author to calculate sheet resistivity, sheet Hall constant and effective mobility from the measured voltages and currents.

Some implants were made with the square geometry illustrated in fig.(11) and the expected error due to finite contact size was estimated from Van der Pauw's expressions to be less than 5% of the absolute values.

An experimental investigation into the effects of finite contact size was carried out by Stein (60). He used silicon specimens with evaporated contacts at the corners as shown in the diagram below:

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He found that the errors in the absolute values were less than 2% for ratios of \( a/d \) less than 0.2.

Later implants by the author were of the clover leaf geometry suggested by Van der Pauw.

4.4.3 Isolation of Implanted region

Meaningful measurements of the electrical properties of implanted layers require that the specimen current is confined to the implanted
layer, i.e. the implanted layer must be electrically isolated from the substrate. This can be achieved by one of two means:

i) **Implantation into High Resistivity Substrate**

The implanted layer must be formed on a substrate of resistivity much higher than the expected resistivity of the layer. Because of the difference in thickness of implanted layer and substrate this requires a substrate of resistivity greater than about $10^6$ ohm cm. GaAs of resistivity $10^8$ ohm cm is available commercially and is known as semi-insulating GaAs. Such material was used for a large number of the implantations reported here.

ii) **Implantation into a Substrate of Opposite Conductivity Type**

Implantation of an n-type dopant into a p-type substrate can produce type conversion in the implanted layer. The resulting p-n junction can then provide the necessary electrical isolation between the implanted layer and the substrate. Cd and Te were implanted into n-type and p-type substrates respectively in the hope that type conversion could be achieved. The isolation produced by such implants was assessed by measuring diode characteristics of the implanted junction and is discussed in more detail in section 4.3.4.

4.4.4 **Temperature Range of Interest**

A study of the temperature dependence of conductivity and the Hall effect can give fundamental information on scattering mechanisms and ionisation energies of impurities; scattering mechanisms being directly connected with chemical purity and structural perfection. The temperature range of interest will be determined by the ionisation energies of the extrinsic impurities and for hydrogenic impurities this usually means the range from $4^0\text{K}$ (liquid helium) to $300^0\text{K}$ (room temperature) but a great deal of information can be obtained over the more readily obtainable temperature range $100^0\text{K}$ to $300^0\text{K}$. 
Electrical measurements were made at temperatures between room temperature and 77°K using a liquid nitrogen cooled cryostat. The specimen was mounted on the cold finger of the cryostat with a thin film of silicone vacuum grease to ensure good thermal contact. To minimise heat loss by radiation a cover could be screwed onto the cold finger so that the specimen was in a region of constant temperature. The cryostat was mounted in a vacuum system to minimise condensation and heat loss. Measurements were made at pressures typically better than 5 x 10^{-5} torr.

The temperature of the cold finger was measured with a constantin-chromel thermocouple mounted near to the specimen. The thermocouple reference junctions were kept at 0°C in a regularly stirred bath of crushed ice and water. The thermocouple had a sensitivity of 25 micro-volts per °K at 77°K.

During a series of measurements the specimen was first cooled to 77°K and readings taken as the specimen warmed up. Although there will always be a difference in temperature between the specimen and the cold finger due to thermal lag it was felt that the warm up rate of the cryostat was sufficiently slow that the temperature of the cold finger could be taken as the temperature of the specimen. The thermocouple e.m.f. was indicated on a digital voltmeter with an accuracy of ± 1 micro-volt and during warming up the temperature could be maintained constant, while readings were recorded, to within ± 20 micro-volts, corresponding to an error of ± 1°K at 77°K.

As well as the liquid nitrogen cryostat another holder was used for electrical measurements. This holder is shown in fig.(12) and consists of four large diameter, lightly spring loaded, gold probes. The ends of the probes were carefully rounded to minimise pressure on the contact areas. This holder was designed specifically for layer removal.
Fig.(12) Four point probe used with evaporated and implanted contacts.
Using Van de Pauw's analysis for a resistivity calculation requires the measurement of voltage and current in two positions. Likewise a Hall effect measurement requires the measurement of voltage and current in four positions. To eliminate effects due to non-linear contacts, misalignment with magnetic field and to reduce the effects of second order physical processes such as the Ettingshausen and Nernst effect the measurement in each position is repeated with current and magnetic field reversed. This results in a total of twelve pairs of voltage and current to be measured. In practice the specimen is supplied with a constant current and the measurement reduces to the measurement of twelve voltages.

A switching box was available to sequentially switch the specimen current and connect the measuring voltmeter to the desired specimen contacts. The switching relays were P.T.F.E. insulated and could be operated semi-automatically from a footswitch controlled uniselector.

The specimen current was supplied from a constant source consisting of high value resistors (1 Meg - 50 Meg) in series with high voltage batteries (120V - 720V) the current required being selected by switching the corresponding resistor and battery into circuit. The specimen current was calculated from the voltage measured across a 1% 100 K.ohm resistor in series with the current supply. The constant current source was mounted in a hermetically sealed, P.T.F.E. lined box. All electrical connections were with screened leads and PET terminations.

The cryostat could be mounted between the poles of a Newport 4 inch electromagnet, the magnet coils being supplied from a Kingshill constant current power supply. This power supply enabled the magnet current to be switched off without the need to reduce the current to zero. This was a particularly useful facility ensuring optimum reproducibility. The reproducibility of the magnetic field was measured by switching through the measuring sequence several times and monitoring the Hall voltage...
developed in a specimen. In this way the reproducibility was found to be better than 0.1% (a short term figure).

All voltages were measured using a Solartron L.M. 1604 digital voltmeter having an input impedance of $10^{11}$ ohms and a sensitivity of 1 micro-volt.
Using L.S.S. theory as a guide, electrical properties associated with the dopants of interest can be expected to occur over a range of depths of the order of $10^2-10^4 \text{Å}$. Consequently the controlled removal of layers of the order of $10^2-10^4 \text{Å}$ is required to obtain depth profiles.

Techniques of layer removal such as abrasive polishing and ion-sputtering were considered but rejected since they are likely to introduce damage and as discussed in section 2, defects in GaAs can be electrically active. Abrasive techniques however, have been successfully employed by Carter to determine the depth distribution of radio-active ions implanted into GaAs. (Ref. 21)

Therefore it was decided to rely upon chemical etching techniques of layer removal, particularly since experience of polishing and controlled etching was gained as a part of specimen preparation procedures. Zelivinskaya (24) has since reported the use of a weak bromine in methanol etch to determine the profiles of implanted zinc ions in GaAs. He relied on a previous calibration of etching rate obtained by weight loss measurements.

A Talystep was available for the accurate measurement of step heights and in conjunction with masking techniques the amount of material removed by an etch was measured directly. It is particularly important to be able to measure step heights on implanted layers directly, since the etch rate of implanted layers may vary with carrier concentration, residual damage etc. and it is unwise to rely on etch rate calibrations obtained from virgin material.

The etchants considered as suitable for layer removal were the polish etches bromine in methanol and sulphuric acid plus hydrogen peroxide in water. The properties of each etch is considered in some detail below.
Apiezon-W wax was used as a masking material. This wax was found to be insoluble in the etches considered and also insoluble in acetone which was used as a cleaning solvent. The wax was applied to the surface of the GaAs by warming the specimen on a hot plate (150°C) and touching the surface with a fine point coated in wax. In this manner an area as small as 0.2mm. in diameter could be masked and during layer removal several masks could be applied to the specimen surface.

4.5.1 Bromine in Methanol Etchant

Analar quality bromine and methanol were used to prepare a variety of concentrations of bromine in methanol ranging from 0.01% to 1.0%. The etch rate of each solution was determined by measuring the step height on bulk n-type GaAs after etching for 5 minute intervals in each concentration. The etch rate is plotted against concentration in fig.(13) and it can be seen that a suitable etch for layer removal might be a concentration of 0.01% having an etch rate of some 100Å/min. However, an undesirable effect was observed with this etch in that severe variations in etch rate occurred at the mask boundary such that the step edge could be a factor of 2 greater than at areas well away from the mask. The effect is shown in fig.(15) which is a trace of a step obtained after etching in 0.5% etch. The variation in etch rate is readily apparent and occurs for all concentrations of this etch. The cause of this non-planar etching is not known but such a variation in etching rate ruled out the bromine methanol etch for layer removal applications.

It was also found that the bromine methanol etch could weaken over a period of hours. A 0.01% etch visibly changed colour after standing overnight (10 hours) indicating loss of bromine.

4.5.2 Sulphuric Acid and Hydrogen Peroxide Etch

Analar quality sulphuric acid and hydrogen peroxide (100 vols.) plus distilled water were used to make various concentrations of this etch. The concentrations quoted refer to concentrations of the mixture
Fig.(13)  Etch rate versus etch concentration for Bromine in methanol etchant
Etch rate versus concentration for H₂SO₄ + H₂O₂ etchant

Fig. (14)  Etch rate versus concentration for H₂SO₄ + H₂O₂ etchant
(\(\text{H}_2\text{SO}_4 \times \text{H}_2\text{O}_2 \times \text{H}_2\text{O}\))

Conc. = 0.2%  Etch time = 10 mins.

\[\text{Br}_2 \times \text{Methanol}\]

Conc. = 0.2%  Etch time = 10 mins.

Fig. 15  Examples of steps produced by etchants considered for layer removal.
(\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2) \text{ in water. Concentrations in the range 0.1\% to 10\% were used and the etch rate determined in the same manner as described for the bromine methanol etches. The etch rate is plotted against etch concentration in fig(14). In contrast to the bromine methanol etch, this etch produced sharp square steps at all concentrations. A trace of a step obtained after etching in a 0.2 \% etch is also shown in fig.(15). This etch was therefore considered suitable for layer removal and a concentration of 0.25\%, with an etch rate of about \text{60A/min.} was decided upon as a standard etch.

4.5.3 Practical Layer Removal

Specimens for layer removal experiments were usually 5mm. square with an implanted cloverleaf plus contact pads (evaporated or implanted). Before etching the specimens were first thoroughly degreased in an ultrasonic bath containing solvents. It was planned that all final rinses be in analar grade acetone since this solvent, on drying, did not break up into isolated patches on the surface, but evaporated quickly leaving a stain free surface; acetone is also miscible with water.

After degreasing the specimen was transferred, still wet, to a beaker containing acetone and rinsed several times with acetone, care being taken to ensure that the specimen did not dry between stages. After a final rinse in fresh acetone the specimen was allowed to dry on a filter paper. The specimen, then ready for masking, was placed upon a glass slide on a hot plate (150°\text{C}). Several apiezon-W wax masks were applied to the implanted region by touching the surface of the specimen with a fine point coated in wax. In this manner masks as small as 0.2\text{mm. in diameter could be applied to the implanted layer. The masks were applied to the cloverleaf arms but not overlapping the contact areas. At least one mask remained on the sample surface for the duration of the layer removal experiment to monitor the total amount of material removed.}
The etching procedure is given in list form for clarity below:

1. Remove specimen from acetone and immerse in distilled water without letting the specimen dry; agitate to remove acetone.
2. Remove from water and immerse in etch; etch for the prescribed time without agitation.
3. Remove from etch and immerse in water to quench the etch.
4. Remove from water and immerse in acetone and rinse.
5. Remove from acetone and allow to dry by evaporation.
6. Carry out measurement.

This procedure was repeated and after a convenient number of etches one of the masks was removed with a fine spill of filter paper soaked in trichloroethylene and the step measured. The etch rate was calculated from this measurement to determine the amount of material removed at each etch. The sample was then re-masked and the procedure repeated.

The use of acetone rinses in stages 1 and 4 described above was found to assist the wetting of the specimen before immersion in the etch and also to produce stain free surfaces after drying. The distilled water and acetone baths were renewed at regular intervals to minimize cross contamination.
4.6 Implantation Facilities and Techniques

This section briefly describes the practical aspects of the implantation process.

4.6.1 Accelerators

Implantations were carried out using both the 180Kev and 600Kev machines available within the department. The majority of implants were carried out using the 600Kev machine. This machine has been described elsewhere by P.J. Cracknell et al (62). Implantations using this machine were made using the 90° exit beam line from the analysing magnet. This magnet was capable of bending ions up to a maximum mass-energy product of 45 a.m.u.-Mev for this beam line.

Implantations using the 180Kev accelerator were made on the 20° beam line. The maximum mass-energy product for this line being 8 a.m.u.-Mev.

4.6.2 Specimen Holders

Specimen holders must meet several requirements: they must provide clean surroundings for the specimen so that risk of contamination is minimised; they should be able to take more than one specimen to ensure reproducibility between specimens requiring the same dose; they must be able to support masks capable of defining the implant region and it is useful if the holders can be used for other specimen procedures to maintain dimensional accuracy. More detailed studies of implantation effects, such as channelling studies, will require holders capable of alignment (or mis-alignment) with respect to the beam direction.

Specimens for the 180Kev machine were mounted onto 0.7 inch square aluminium backing plates using silver dag as an adhesive. The smallest amount of dag was used to ensure that no dag was squeezed out around the edges of the specimen and therefore could not be seen by the ion beam. The dag also acted as an electrical connection between the specimen and
Fig. (16)  Implantation specimen holders and masks.
the backing plate. If needed two specimens could be mounted together using this procedure. After implantation the specimens were removed by rinsing in acetone to remove the silver dag. Each aluminium square was held in one position of a rotatable holder by phosphor bronze clips, the aluminium square being electrically isolated from the holder by means of a thin sheet of mica.

The specimen holder could take a total of 6 specimens although one specimen position was left blank to act as a 'dummy' for setting up of the beam. The holder could be rotated about a vertical axis by means of gears controlled from outside the target chamber. Electrical connections were made to each specimen in turn by spring contacts to the aluminium backing plate, the specimen being connected to earth through an integrating ammeter to monitor beam current and total charge collected (dose).

The specimen holder could also accommodate a secondary electron suppressor and beam defining aperture in front of the sample. The beam on-off control was a vacuum gate valve immediately in front of the target chamber.

Specimen holders for the 600Kev accelerator were designed in modular form, the holder assembly consisting of a sliding carriage controlled from outside the target chamber by means of a screw-rod. The holder assembly also contained the secondary electron suppressor, aperture and beam shutter. In addition the sliding carriage could be heated, by means of a heating coil behind the carriage, to enable implantations at temperatures up to 200°C.

The specimen holders themselves could be screwed onto a backing plate that in turn could be clamped to the sliding carriage. A total of 4 specimen modules could be mounted side by side onto the backing plate. Again, one of the modules was fitted with a blank to enable setting up of the beam. Each module could take two specimens held in place with spring loaded clasps. A variety of masks could be screwed onto the modules
directly in front of the specimens. The temperature of the sample during a 'hot' implant was monitored by a thermocouple mounted on one of the holders. The holders were electrically isolated from earth and all electrical connections were by means of co-axial sockets on the assembly flange.

A photograph of these specimen holders is shown in fig.(16).

4.6.3. Profiles

The concentration of ions entering an amorphous target will follow a Gaussian type distribution in depth. The concentration of electrically active dopants might also be expected to follow a similar distribution. Such a variation of carrier concentration with depth is rarely useful in device applications and from an experimental point of view can lead to difficulties in the analysis of Hall effect, conductivity etc.

A more practicable profile can be obtained by implanting at various selected energies and doses to produce a more nearly constant carrier concentration as a function of depth. This aspect of implantation has been considered in some detail by Allen (63) who developed a computer program to select energies and doses necessary to produce flat profiles in silicon.

For the dopants of interest in this thesis it was felt that a suitable flat profile could be achieved by implanting at two energies, which would not significantly complicate the implant procedure.

For these implants the highest energy available for the ions of interest (Te and Cd) was limited to 150Kev. The second (low) energy of implant was calculated by assuming that the Gaussian distribution could be approximated to a rectangular distribution of width $2\Delta R_p$. In this manner the low energy of implant was selected from the tables of Johnson and Gibbons (42) so that the depth $(R + \Delta R_p)$ corresponding to the low energy coincided with the depth $(R - \Delta R_p)$ corresponding to the
Fig. 17 Predicted atomic profile for Cd and Te implants at two energies.

<table>
<thead>
<tr>
<th>Energy</th>
<th>Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$ = 150 keV</td>
<td>100%</td>
</tr>
<tr>
<td>$E_2$ = 60 keV</td>
<td>40%</td>
</tr>
</tbody>
</table>

Concentrations calculated for a total dose of $7 \times 10^{14}$ ions cm$^{-2}$.
high energy. The relative doses for each energy were estimated using the expression relating the average concentration at the peak of a Gaussian to the number of implanted ions per unit area, i.e.

\[ n = \frac{N}{2.5 \Delta R_p} \]

where \( n \) = concentration at peak of Gaussian
\( N \) = number of implanted ions per unit area
\( \Delta R_p \) = deviation from projected range

The doses and energies so estimated were then used in a computer program to determine the complete profile by the addition of the Gaussians corresponding to each energy of implant. The composite profile obtained is shown in fig.(17). The calculations were carried out for Te and Cd but only one curve is shown since the masses of Te and Cd are so similar that their ranges and distributions differ by less than 5%.

4.6.4 Ion Beam Conditions

Many of the advantages of ion implantation (see section 1.3) result from the precise control of the ion beam parameters. In particular, ion beam current determines the implanted dopant concentration. Also, control of the ion beam position is essential for the production of devices by writing techniques. The ion beam must also contain no unwanted ion species, i.e. no impurities must be present.

In the context of this thesis only ion beam purity and current are relevant, these factors are discussed in the following sections.

4.6.4.1 Ion Beam Purity and Uniformity

Selection of the ion species to be implanted was carried out by monitoring the beam current falling on a dummy specimen as the analysing magnet current was increased. Beam current and magnet current were
Fig. (18) Example of an ion beam spectrum
plotted on an X-Y chart recorder as y co-ordinate and x co-ordinate respectively. In this manner a spectrum of ion mass (strictly charge/mass) was obtained. The ion of interest was then identified by comparison of the spectrum with published isotope abundance data. An example of the spectra obtained is shown in fig.(18); in practice the magnet current was set so that the most abundant isotope was selected.

Beam uniformity over the implant area was optimised by using a de-focussed beam (about 3-5cm diameter) and large amplitude electrostatic scanning of the beam in the horizontal and vertical planes.

4.6.4.2 Ion Beam Dosimetry

The dose range used in this work is from $10^{12}$ ions/cm$^2$ to $10^{16}$ ions/cm$^2$. In order to operate within practicable implantation times of the order 10 to $10^3$ seconds this dose range requires a beam current density in the range 0.1 to 1.0 microamps/cm$^2$. In practice a beam current density of 0.5 microamps/cm$^2$ was aimed for.

The measurement of implanted dose therefore reduces to the measurement of a positive ion current falling on the specimen with the assumption that each ion incident upon the specimen contributes one unit of charge to the total beam current. This assumption may be in error due to the presence of multiply charged ions in the beam, neutral components of the beam and the emission of electrons from the specimen surface. Other effects not directly connected with the implantation process may also influence the measured current; these effects include the presence of stray electrons in the target chamber and leakage paths from the specimen to earth.

Many of the unwanted species of the beam, such as multiply charged and neutral components, can be separated by magnetic analysis and only leads to difficulty in rare cases (e.g. separation of S from O). The effects of leakage currents and stray electrons can be minimised by careful design of the target chamber and specimen surroundings.
This leaves secondary electron emission as the greatest source of error in measuring implanted doses. In practice secondary electron emission effects are minimised by returning the electrons to the specimen. This is achieved by the application of electrostatic or magnetic fields around the specimen.

The secondary electron suppressor employed during implantation consisted of a metal plate placed in front of the specimen. The optimum negative potential was applied to the suppressor by monitoring the specimen current as the suppressor potential was increased. As the emission of electrons was suppressed the specimen current steadily decreased to a constant value. This constant value was considered to be due to the positive ion beam only.

In practice the suppressor potential was set at 200 volts corresponding to an electric field at the specimen of about 100 volts/cm.
5.1 General

In this section the results of electrical measurements on implanted layers are presented. In general, preliminary measurements at each stage of the specimen treatment were made using the thermal probe. This technique was used as a qualitative means of assessing the changes in electrical properties of implanted layers. More detailed measurements were then made using Hall effect and resistivity measurements to determine carrier concentrations and mobilities.

In particular, results relating to the dependence of layer resistivity, carrier concentration and mobility on implanted ion species, implanted dose, implant temperature and anneal temperature are presented.

Changes in the electrical properties of GaAs can occur as a result of heat treatment. The first of the following section, section 5.2, therefore reports the results of electrical measurements on specimens subjected to annealing schedules similar to those planned for implanted layers.

Sections 5.3 and 5.4 then report the observed changes in electrical properties brought about by implantation and annealing respectively. In section 5.4 anneal temperatures of below 450°C are considered. These effects could be associated with radiation damage rather than any conventional doping properties of the implanted ion species.

Section 5.5 then reports the results of annealing at temperatures greater than 450°C, when the observed effects could be related to the doping effects of the implanted ion species.
5.2 Heat Treatment of Bulk GaAs

Thermal probe and sheet resistivity measurements were carried out on semi-insulating and n-type GaAs substrates annealed for 15 minute periods at temperatures up to 850°C, with and without SiO₂ surface protection.

5.2.1 Thermal Probe Measurements

The results of thermal probe measurements are shown in fig. (19) where thermal probe voltage is plotted against anneal temperature. From these curves it is apparent that p-type activity is introduced at anneal temperatures of 700°C and greater. In fact, some compensation of the n-type specimens may be occurring at anneal temperatures as low as 500°C. At anneal temperatures greater than 700°C the surface layer of the n-type specimens becomes converted to p-type. Etching off the surface layer restores the n-type indications of the bulk material. Similar measurements on semi-insulating GaAs annealed at 700°C and progressively etched in 2% bromine methanol indicated that a thermal probe reading characteristic of the bulk GaAs could only be obtained after the removal of a layer 5 microns thick from the surface.

The effects of surface encapsulation in SiO₂ are also shown in fig. (19), the specimens so encapsulated showing a reduction in the magnitude of the p-type activity at anneal temperatures up to 800°C.

5.2.2 Sheet Resistivity Measurements

Values of the sheet resistivity of heat treated semi-insulating GaAs are given in table (3). The surface of the GaAs was protected with a film of SiO₂ during annealing.

<table>
<thead>
<tr>
<th>Tₐ °C</th>
<th>Sheet Resistivity ohms.cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>10⁶</td>
</tr>
<tr>
<td>700</td>
<td>10⁵-10⁶</td>
</tr>
<tr>
<td>800</td>
<td>10⁴-10⁵</td>
</tr>
<tr>
<td>850</td>
<td>10³-10⁴ (10² unprotected)</td>
</tr>
</tbody>
</table>

Table (3)
Fig. 19 Thermal probe reading versus anneal temperature for heat treated GaAs substrates.
Because of noisy contacts no Hall voltage could be detected on these specimens. However a maximum Hall voltage of about 1mV could be estimated from the measurement sensitivity of the equipment. This Hall voltage, at a specimen current of 5 micro-amps and a magnetic field of 5 k. gauss, yields a maximum value for the Hall constant of the order of \(10^5\) to \(10^6\) cm\(^2\).A\(^{-1}\). A Hall constant of this order corresponds to a sheet carrier concentration of the order of \(5 \times 10^{12}\) to \(5 \times 10^{13}\) carriers.cm\(^{-2}\).

If 5 microns is taken as a representative depth to which the effect occurs then this sheet concentration corresponds to a minimum volume concentration of the order of \(10^{17}\) carriers.cm\(^{-3}\).

A spot measurement of a n-type specimen annealed at 850\(^\circ\)C showed the presence of a p-type surface layer but the specimen retained bulk n-type properties. The electrical parameters measured before and after anneal were:

<table>
<thead>
<tr>
<th></th>
<th>Sheet resistivity ohms.cm(^{-2})</th>
<th>Mobility cm(^2).V.(^{-1}).sec(^{-1})</th>
<th>Sheet carrier concentration electrons.cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before anneal</td>
<td>0.30</td>
<td>2,970</td>
<td>7.2 \times 10^{15}</td>
</tr>
<tr>
<td>After anneal at 850(^\circ)C</td>
<td>0.71</td>
<td>2,830</td>
<td>3.1 \times 10^{15}</td>
</tr>
</tbody>
</table>

5.2.3 Variation of Resistivity with temperature

In order to obtain information regarding the nature of the defect responsible for the p-type activity introduced as a result of heat treatment, the sheet resistivity of semi-insulating GaAs heat treated at 750\(^\circ\)C was measured as a function of temperature.

Sheet resistivity is plotted against \(1/T^0\)K in fig.(20 ) and yields a thermal activation energy of 0.11eV.
Fig. (20) Resistivity versus $T^{-1}$ for thermally generated p-type activity on semi-insulating GaAs substrate.
5.3 **Electrical Properties of Layers as Implanted**

The changes in electrical properties of GaAs substrates as a result of heavy ion bombardment were monitored using thermal probe and resistivity measurements.

### 5.3.1 Thermal Probe Measurements

A summary of the specimens measured using the thermal probe after implantation is given in Table 4. Fig. (21) shows the thermal probe reading plotted against implanted dose for Cd, Te, Zn, Ar and Se implants into semi-insulating substrates. Fig. (22) shows similar data for Zn implants into n-type substrates.

From Fig. (21) it can be seen that implantation of doses greater than $1 \times 10^{12}$ ions/cm$^2$ into semi-insulating GaAs substrates produces a p-type layer. Over the dose range $1 \times 10^{12}$ to $1 \times 10^{14}$ ions/cm$^2$ all implanted ion species follow a similar pattern of increasing p-type activity with increasing dose. At doses greater than about $1 \times 10^{14}$ ions/cm$^2$ the comparatively heavy ions Cd and Te show a saturation effect with only a slight increase in p-type activity over the dose range $1 \times 10^{14}$ to $3 \times 10^{16}$ ions/cm$^2$. This saturation effect is not observed for the 'light' ions Zn, Ar and Se, the p-type activity increasing steadily over the dose range $5 \times 10^{12}$ to $1 \times 10^{16}$ ions/cm$^2$.

The measurements in Fig. (21) indicated by full lines were taken 7 days after implantation. It is apparent that a reduction in thermal probe reading occurs over this period of time, the effect being pronounced for the higher doses. These effects will be discussed in section 6.3.

Fig. (22) shows the data for zinc implantations into n-type substrates. In this case the p-type activity induced as a result of implantation leads to compensation of the substrate and consequently a reduction in n-type activity. Eventually, at doses greater than about
<table>
<thead>
<tr>
<th>Substrate type</th>
<th>Semi-insulating</th>
<th>n-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy key</td>
<td>200 150 400 150</td>
<td>60 60</td>
</tr>
<tr>
<td>Ion</td>
<td>Ca Te Ar Se Zn Zn</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>□ ○ × ■ ● Θ △</td>
<td></td>
</tr>
</tbody>
</table>

Table 4  Key for fig.(21) page 93  
and fig.(22) page 94
Fig. 21  Thermal probe reading versus implanted dose for implants at room temperature (20°C)

See table 4 for key, page 92
Fig. (22) Thermal probe reading versus implanted dose for Zn implanted layers in N type substrate

See table 4 for key. Page 92.
2 x 10^{13} \text{ions/cm}^2$, the induced p-type activity is sufficient to cause type conversion of the substrate and p-type activity is observed to increase with increasing dose.

In fig. (22) the specimens A and B were implanted at the same time and nominally received the same dose. After implantation however, there were visible signs on the beam defining aperture that the beam had been displaced in the direction of specimen B. It is therefore thought that specimen B received a greater dose than specimen A. This difference in dose was apparently sufficient to cause type conversion in specimen B but not in specimen A. Specimen A does show signs of compensation however.

### 5.3.2 Resistivity Measurements

Again no Hall voltages greater than the noise voltages could be detected on specimens after implantation. Therefore only sheet resistivity measurements were possible. A list of the specimens measured is given in tables (5, 6, and 7) while Fig. (23) shows the sheet resistivity of specimens after implantation plotted against total dose. This figure shows two curves: one relating to room temperature implants, the other being a combination of points from 100°C and 180°C implants. The variation of resistivity with implanted dose for the 'hot' implants follows a similar pattern to the variation of thermal probe reading with dose for room temperature Te and Cd implants i.e. a sharp decrease in resistivity of two orders of magnitude over the dose range $1 \times 10^{12}$ - $3 \times 10^{13} \text{ions/cm}^2$ and then a saturation effect in the dose range $3 \times 10^{13}$ - $1 \times 10^{16} \text{ions/cm}^2$ with a decrease in resistivity of only a factor of 2 over this dose range. Data for room temperature Te and Cd implants were only available over the dose range $3 \times 10^{13}$ - $1 \times 10^{16} \text{ions/cm}^2$ and shows a similar trend to the hot implants, the resistivity decreasing by a factor of 2 over this dose range. Over the
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Ion</th>
<th>Energy Kev</th>
<th>Dose ions.cm$^{-2}$</th>
<th>Substrate type</th>
<th>Sheet Resistivity ohms.cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Cd</td>
<td>150 + 60</td>
<td>7 x 10$^{13}$</td>
<td></td>
<td>5.0 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7 x 10$^{14}$</td>
<td></td>
<td>4.0 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7 x 10$^{15}$</td>
<td></td>
<td>3.5 x 10$^5$</td>
</tr>
<tr>
<td>X</td>
<td>Te</td>
<td>150</td>
<td>3 x 10$^{13}$</td>
<td>Semi-insulating</td>
<td>4.0 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3 x 10$^{14}$</td>
<td></td>
<td>3.0 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3 x 10$^{14}$</td>
<td></td>
<td>3.2 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3 x 10$^{14}$</td>
<td></td>
<td>3.9 x 10$^5$</td>
</tr>
<tr>
<td>O</td>
<td>Cd</td>
<td>150 + 60</td>
<td>7 x 10$^{13}$</td>
<td>n-type</td>
<td>3.5 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7 x 10$^{14}$</td>
<td></td>
<td>2.5 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7 x 10$^{14}$</td>
<td></td>
<td>3.0 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7 x 10$^{15}$</td>
<td></td>
<td>1.8 x 10$^5$</td>
</tr>
</tbody>
</table>

Table 5  Sheet resistivity of Cd and Te room temperature implants (20°C) before annealing.

These results are also plotted in fig. (23) page 99
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Ion</th>
<th>Energy Kev</th>
<th>Dose ions.cm⁻²</th>
<th>Substrate type</th>
<th>Sheet resistivity ohms.cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
<td>150 + 60</td>
<td>7.0 x 10¹³</td>
<td></td>
<td>6.3 x 10⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.0 x 10¹⁴</td>
<td></td>
<td>3.0 x 10⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.4 x 10¹⁵</td>
<td>Semi-insulating</td>
<td>2.8 x 10⁴</td>
</tr>
<tr>
<td>□</td>
<td>Te</td>
<td>150 + 60</td>
<td>1.4 x 10¹³</td>
<td></td>
<td>1.7 x 10⁵</td>
</tr>
<tr>
<td>□</td>
<td></td>
<td></td>
<td>6.0 x 10¹³</td>
<td></td>
<td>9.0 x 10⁴</td>
</tr>
<tr>
<td>□</td>
<td></td>
<td></td>
<td>1.4 x 10¹⁵</td>
<td></td>
<td>4.0 x 10⁴</td>
</tr>
<tr>
<td>□</td>
<td></td>
<td></td>
<td>7.0 x 10¹⁵</td>
<td></td>
<td>4.0 x 10⁴</td>
</tr>
<tr>
<td>□</td>
<td>Cd</td>
<td>150 + 60</td>
<td>7.0 x 10¹³</td>
<td></td>
<td>5.3 x 10⁴</td>
</tr>
<tr>
<td>□</td>
<td></td>
<td></td>
<td>7.0 x 10¹⁴</td>
<td></td>
<td>5.0 x 10⁴</td>
</tr>
<tr>
<td>□</td>
<td></td>
<td></td>
<td>7.0 x 10¹⁴</td>
<td></td>
<td>5.0 x 10⁴</td>
</tr>
<tr>
<td>□</td>
<td></td>
<td></td>
<td>7.0 x 10¹⁴</td>
<td></td>
<td>4.0 x 10⁴</td>
</tr>
<tr>
<td>□</td>
<td></td>
<td></td>
<td>7.0 x 10¹⁵</td>
<td></td>
<td>3.6 x 10⁴</td>
</tr>
<tr>
<td>□</td>
<td></td>
<td></td>
<td>7.0 x 10¹⁵</td>
<td></td>
<td>5.8 x 10⁴</td>
</tr>
</tbody>
</table>

Table 6: Sheet resistivity of Cd and Te 100°C implants, before annealing. These results are also plotted in fig. (23), page 99.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Ion</th>
<th>Energy Kev</th>
<th>Dose ions.cm(^{-2})</th>
<th>Substrate type</th>
<th>Sheet resistivity ohms.cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>△</td>
<td>Cd</td>
<td>150 + 60</td>
<td>1.4 x 10(^{10}), 7.0 x 10(^{12}), 7.0 x 10(^{12}), 1.4 x 10(^{13}), 7.0 x 10(^{13}), 7.0 x 10(^{14})</td>
<td>Semi-insulating</td>
<td>3.0 x 10(^{6}), 3.0 x 10(^{5}), 3.3 x 10(^{5}), 2.0 x 10(^{5}), 8.0 x 10(^{4}), 3.0 x 10(^{4})</td>
</tr>
<tr>
<td>x</td>
<td>Te</td>
<td>150 + 60</td>
<td>1.4 x 10(^{13}), 7.0 x 10(^{13}), 3.0 x 10(^{13})</td>
<td>n-type</td>
<td>1.3 x 10(^{5}), 6.0 x 10(^{4}), 1.0 x 10(^{5})</td>
</tr>
<tr>
<td>△</td>
<td>Cd</td>
<td>150 + 60</td>
<td>7.0 x 10(^{13}), 7.0 x 10(^{13}), 7.0 x 10(^{14}), 7.0 x 10(^{14}), 7.0 x 10(^{15})</td>
<td>n-type</td>
<td>9.0 x 10(^{4}), 9.0 x 10(^{4}), 4.8 x 10(^{4}), 5.2 x 10(^{4}), 3.8 x 10(^{4})</td>
</tr>
</tbody>
</table>

**Fig.7**  Sheet resistivity of Cd and Te 180°C implants before annealing.

These results are also plotted in fig.(23) page 99.
Fig. 23  Sheet resistivity versus implanted dose for various ions implanted into
n-type and semi-insulating substrates.

See tables 5, 6 and 7 for key
dose range for which comparison can be made \((3 \times 10^{13} - 1 \times 10^{16})\) the room temperature implants have a value of sheet resistivity greater by a factor of 6 than the hot implants. There is no significant difference in resistivity between 100°C and 180°C implants. Room temperature implants have a mean resistivity (in the saturation region) of \(3 \times 10^5\) ohms/cm\(^2\) while the corresponding resistivity for 100°C and 180°C implants is \(5 \times 10^4\) ohms/cm\(^2\).

5.3.3 Variation of Resistivity with temperature

Measurements of sheet resistivity as a function of temperature were carried out on a variety of specimens after implantation including Cd, Te and Ar implants at various doses and implant temperatures. All specimens measured showed a similar variation of resistivity with temperature. Fig. (24) shows a typical result for Te and Cd implants. In this figure sheet conductivity is plotted against \(1/T^\circ\text{K}\). The change in resistivity of more than two orders of magnitude is thought to be due to carrier de-ionisation and a thermal activation energy of 0.064eV was determined from fig.(24). Specimen A in fig.(24) deviates from the general pattern shown by the other specimens in that, over most of the low temperature regime, the conductivity is characterised by a lower thermal activation energy of about 0.01eV. This specimen was implanted with a particularly high dose \((7 \times 10^{15}\) ions/cm\(^2\)\) of Te.

Noise limited the maximum detectable Hall voltage to 0.05mv with a specimen current of 5 micro-amps and magnetic field of 5K.Gauss. This corresponds to a maximum sheet Hall constant of the order \(2 \times 10^{-11}\) cm\(^2\)/C and therefore a minimum surface carrier concentration of the order \(3 \times 10^{14}\) carriers/cm\(^2\) with a mobility of the order 0.1 - 1.0 cm\(^2\)/V.sec.

If it is assumed that the effects responsible for conduction extend to a depth comparable to the ion range (about 500\(^8\)) then this surface concentration corresponds to a volume concentration of the order \(10^{19}\) /cm\(^3\) at room temperature.
Fig. 24  Sheet Resistivity versus Temperature for Un-annealed Implanted Layers
5.4 Annealing at Temperatures up to 450°C

The effects observed as a result of annealing implanted layers at temperatures up to 450°C could in general, be related to the annealing of radiation damage. The results are presented in two sections corresponding to thermal probe and sheet resistivity measurements respectively.

5.4.1 Thermal Probe Measurements

A summary of the specimens measured at various anneal temperatures is given in table (8). The variation of thermal probe reading with anneal temperature is plotted in fig.(25).

All specimens show a similar behaviour with a reduction in p-type activity after annealing at 300°C when thermal probe readings characteristic of the semi-insulating substrate are recorded. Further annealing at temperatures up to 500°C does not result in any significant change in thermal probe reading although some specimens, implanted with the higher doses, do show a marked increase in p-type activity after annealing at 600°C.

The curve relating to the Zn implant in fig.(25) differs from the general pattern followed by the Te and Cd implants in that annealing above 300°C results in an increase in p-type activity. This specimen was implanted with a high dose \(1 \times 10^{15}\) ions/cm\(^2\) at a relatively low energy (60KeV) and it is thought that p-type activity associated with the doping properties of the Zn was being observed over the annealing temperature range.

5.4.2 Resistivity Measurements

Measurements of sheet resistivity as a function of anneal temperature were made for Te, Cd, Zn and Ar implants. Many specimens were measured and all showed a similar behaviour. Fig.(26) is therefore only a selection of typical curves to illustrate the variation of resistivity with anneal temperature. These curves show some
Table (8) Summary of specimens annealed up to 450°C and measured using the thermal probe.
See also fig.(25) page 104

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Ion</th>
<th>Energy KeV</th>
<th>Dose ions.cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>△</td>
<td>Cd</td>
<td>100</td>
<td>$1 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$5 \times 10^{12}$</td>
</tr>
<tr>
<td>□</td>
<td></td>
<td></td>
<td>$5 \times 10^{13}$</td>
</tr>
<tr>
<td>○</td>
<td></td>
<td></td>
<td>$3 \times 10^{14}$</td>
</tr>
<tr>
<td>×</td>
<td>Te</td>
<td>100</td>
<td>$6 \times 10^{14}$</td>
</tr>
<tr>
<td>▼</td>
<td></td>
<td></td>
<td>$1 \times 10^{16}$</td>
</tr>
<tr>
<td>□</td>
<td>Zn</td>
<td>60</td>
<td>$1 \times 10^{15}$</td>
</tr>
</tbody>
</table>
Fig. (25) Thermal probe reading versus anneal temperature for Cd, Te and Zn implanted layers in semi-insulating GaAs.

See table (8) for key page 103
Fig. 26  Sheet Resistivity versus Anneal Temperature for Anneal Temperatures up to 450°C.
interesting characteristics which are presented in the following two sub-sections corresponding to room temperature implants and 'hot' implants respectively.

5.4.2.1 Room Temperature Implants

Room temperature implants show a drop in sheet resistivity at anneal temperatures up to 150°C - 200°C followed by a steady increase in resistivity up to anneal temperatures of about 450°C when resistivities of the same order as the semi-insulating substrates are recorded. The initial drop in resistivity is thought to be the result of re-ordering of the crystal lattice with a consequent increase in carrier mobility. At anneal temperatures greater than 200°C the removal of electrically active defect centres apparently dominates the changes in resistivity and the resistivity therefore rises.

5.4.2.2 'Hot' Implants

Specimens implanted at 100°C and 180°C do not exhibit the initial decrease in resistivity shown by room temperature implants since, it is thought, some re-ordering of the crystal lattice has already occurred as a result of implantation at elevated temperatures. This is also shown in a generally lower resistivity after implantation for the 'hot' implants as seen in fig.(26). The 'hot' implants do show the steady increase in resistivity, associated with the removal of electrically active centres, at anneal temperatures above 200°C.

5.4.2.3 Analysis of Isochronal Annealing Data

The curves of sheet resistivity against anneal temperature were analysed as outlined in appendix 1 with the assumption that the increase in sheet resistivity at anneal temperatures greater than about 150°C was due solely to the removal of defect centres (i.e. any increase in mobility as a result of lattice re-ordering was ignored). The results are shown in fig.(27), where \( \ln(\ln \frac{N_A}{N_A}) - 1 \) is plotted against \( \frac{1}{T_A} \).
ANNEAL TEMP. $T^\circ C$

![Graph with data points and lines representing energy levels at different temperatures.](image)

**Fig. 27** Analysis of Isochronal Annealing Data
(TA in °K).

NA is the number of electrically active centres after annealing at a temperature TA. It can be seen that at anneal temperatures greater than 250°C (i.e. 1/TA less than 1.9 x 10^{-3}) the points approximate to a straight line, implying that the annealing process is a first order process. The gradient of the straight lines in fig.(27) yields an activation energy of 0.54eV.

5.5 Annealing Above 450°C

In general the electrical properties of implanted layers, after annealing at temperatures greater than 450°C, were associated with the conventional doping properties of the implanted ion species. The results reported in this section relate primarily to the electrical properties of Te and Cd implanted layers and are presented separately in the following two sections.

5.5.1 Te Implants into GaAs

Measurements were made on Te implanted layers in semi-insulating GaAs substrates held at room temperature, 100°C and 180°C during implantation. A summary of the doses covered and the measured electrical properties after 600°C anneal is given in table (9).

From this table it can be seen that annealing of room temperature implants at 600°C results in high resistivity layers of the same order as the substrate. In fact some of these layers were annealed at 800°C but only p-type activity, associated with the thermal degradation of the substrate was recorded.

A high dose (1 x 10^{16} ions/cm^2) specimen annealed at 850°C for 2 minutes (similar to Foyt (35)) did show n-type activity, although with a low carrier concentration of 5 x 10^{12} electrons/cm^2.
<table>
<thead>
<tr>
<th>Dose ions.cm(^{-2})</th>
<th>Energy KeV</th>
<th>T(_{\text{impl}}) °C</th>
<th>T(_{\text{anneal}}) °C</th>
<th>Sheet Resistivity ohms cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0x10(^{12})</td>
<td>100</td>
<td>20</td>
<td>600</td>
<td>greater than 10(^5)</td>
</tr>
<tr>
<td>6.0x10(^{13})</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>5.0x10(^{14})</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.0x10(^{16})</td>
<td>&quot;</td>
<td>&quot;</td>
<td>850/2mins</td>
<td>1.2x10(^3)</td>
</tr>
<tr>
<td>2.8x10(^{13})</td>
<td>60+150</td>
<td>&quot;</td>
<td>600</td>
<td>greater than 10(^5)</td>
</tr>
<tr>
<td>2.8x10(^{14})</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.4x10(^{13})</td>
<td>60+150</td>
<td>100</td>
<td>600</td>
<td>greater than 10(^5)</td>
</tr>
<tr>
<td>2.8x10(^{13})</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>7.0x10(^{13})</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>7.0x10(^{14})</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.2x10(^4)</td>
</tr>
<tr>
<td>1.4x10(^{13})</td>
<td>60+150</td>
<td>180</td>
<td>600</td>
<td>greater than 10(^5)</td>
</tr>
<tr>
<td>7.0x10(^{13})</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>7.0x10(^{14})</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1.5x10(^2)</td>
</tr>
</tbody>
</table>

Table (9) Summary of Te implants into semi-insulating substrates
Implantation at temperatures of 100°C and 180°C shows an improvement in electrical properties after annealing at 600°C, but only for doses of $7 \times 10^{14}$ ions/cm$^2$ (and greater). Doses less than $7 \times 10^{14}$ ions/cm$^2$ form high resistivity layers after annealing at 600°C.

The electrical parameters for room temperature, 100°C and 180°C implants at a dose of $7 \times 10^{14}$ ions/cm$^2$ are given in table (10) for comparison.

Implantation at 180°C seemed particularly promising and therefore further implants at this temperature were made with doses of $7 \times 10^{14}$, $1.4 \times 10^{15}$ and $7 \times 10^{15}$ ions/cm$^2$.

The electrical properties of these specimens after a 600°C anneal, are given in table (11). These points plus further measurements obtained at anneal temperatures up to 800°C are plotted in fig.(28).

Each specimen follows a similar pattern involving three anneal stages, the temperature range of each stage being a function of implanted dose. During Stage 1, all specimens show a sharp decrease in resistivity with a corresponding increase in carrier concentration and improvement in mobility. This is followed by stage 2, a region where little change in the electrical parameters occurs. Stage 3 is then characterised by a dose dependant anneal temperature above which all specimens show a degradation in electrical properties characterised by a decrease in carrier concentration, increase in resistivity and deterioration of mobility.

The temperature range of each stage for the doses encountered is given in table (12).
<table>
<thead>
<tr>
<th>Implanted Temperature (°C)</th>
<th>R.T. (°C)</th>
<th>Sheet Resistivity (ohms/cm²)</th>
<th>Hall Constant (cm²/V·sec)</th>
<th>Carrier Concentration (electrons/cm²)</th>
<th>Hall Mobility (cm²/V·sec)</th>
<th>% Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100</td>
<td>$1.2 \times 10^4$</td>
<td>$2.0 \times 10^7$</td>
<td>$3.2 \times 10^{11}$</td>
<td>$1.0 \times 10^{11}$</td>
<td>not measured</td>
</tr>
<tr>
<td>180</td>
<td></td>
<td>$1.5 \times 10^2$</td>
<td>$3.6 \times 10^5$</td>
<td></td>
<td></td>
<td>2.50</td>
</tr>
</tbody>
</table>

Table (10)

Electrical parameters of Te implanted layers at R.T., 100°C and 180°C after 600°C anneal.
<table>
<thead>
<tr>
<th>Dose ions.cm$^{-2}$</th>
<th>Sheet carrier conc. electrons.cm$^{-2}$</th>
<th>Mobility cm$^2$.V$^{-1}$.sec$^{-1}$</th>
<th>Sheet resistivity ohms.cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0 x 10$^{14}$</td>
<td>1.4 x 10$^{13}$</td>
<td>2,600</td>
<td>1.9 x 10$^2$</td>
</tr>
<tr>
<td>1.4 x 10$^{15}$</td>
<td>1.3 x 10$^{13}$</td>
<td>2,180</td>
<td>2.3 x 10$^2$</td>
</tr>
<tr>
<td>7.0 x 10$^{15}$</td>
<td>8.0 x 10$^{12}$</td>
<td>1,990</td>
<td>3.8 x 10$^2$</td>
</tr>
</tbody>
</table>

Table 11: Electrical parameters of Te layers implanted at 180°C and annealed at 600°C.
Fig. 28 Carrier concentration and mobility versus anneal temperature for Te implanted layers in semi-insulating substrates. Implant temperature = 180°C.
<table>
<thead>
<tr>
<th>Dose (ions/cm²)</th>
<th>Annealing stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>7.0 x 10¹⁴</td>
<td>550 - 600°C</td>
</tr>
<tr>
<td>1.4 x 10¹⁵</td>
<td>550 - 600°C</td>
</tr>
<tr>
<td>7.0 x 10¹⁵</td>
<td>500 - 550°C</td>
</tr>
</tbody>
</table>

Table 12  Annealing stages of Te layers implanted into semi-insulating GaAs at 180°C
5.5.2 Cadmium implants into GaAs

Cadmium implants were made into semi-insulating and n-type substrates at room temperature, 100°C and 180°C. The electrical properties of the semi-insulating and n-type substrates are summarised in appendix 2. The electrical properties of Cd implanted layers, after annealing at temperatures greater than 450°C, are presented in two subsections; i.e. implants into semi-insulating substrates and implants into n-type substrates respectively.

5.5.2.1 Cadmium implants into semi-insulating substrates

Preliminary Cd implants were at room temperature and covered the dose range $3 \times 10^{13}$ to $3 \times 10^{15}$ ions.cm$^{-2}$. These specimens were annealed at 650°C and electrical measurements made. The values of sheet carrier concentration, sheet resistivity and mobility are given in table (13).

From this table it can be seen that doses of less than $5 \times 10^{13}$ ions.cm$^{-2}$ produce low carrier concentration, high resistivity layers. At doses of $3 \times 10^{14}$ and $3 \times 10^{15}$ ions.cm$^{-2}$ high carrier concentration, low resistivity p-type layers are formed having percentage activities in the range 10% to 23%.

Further cadmium implants at room temperature, 100°C and 180°C were carried out with doses of $7 \times 10^{13}$, $7 \times 10^{14}$ and $1.4 \times 10^{15}$ ions.cm$^{-2}$.

The specimens implanted with doses of $7 \times 10^{13}$ and $1.4 \times 10^{15}$ ions.cm$^{-2}$ were annealed at temperatures of up to 800°C but the $7 \times 10^{14}$ ions.cm$^{-2}$ specimen was annealed at 600°C only, prior to profile measurement. These specimens and their electrical properties are summarised in table (14).

Fig. (29 and 30) shows the variation of sheet carrier concentration and mobility with anneal temperature for these specimens.

The $7 \times 10^{13}$ ions.cm$^{-2}$ specimens show electrical activity after annealing at 650°C, the 180°C implant showing a considerably greater activity over the room temperature and 100°C implants (65% as against 16% and 10% respect.)
<table>
<thead>
<tr>
<th>Dose ions.cm(^{-2})</th>
<th>Sheet resistivity ohms.cm(^{-2})</th>
<th>Sheet carrier concentration holes.cm(^{-2})</th>
<th>Mobility cm(^2).V(^{-1}).sec(^{-1})</th>
<th>Percentage activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0 \times 10^{13}</td>
<td>9.0 \times 10^6</td>
<td>2.0 \times 10^{10}</td>
<td>37</td>
<td>0.07</td>
</tr>
<tr>
<td>5.0 \times 10^{13}</td>
<td>1.0 \times 10^7</td>
<td>2.0 \times 10^{10}</td>
<td>27</td>
<td>0.04</td>
</tr>
<tr>
<td>3.0 \times 10^{14}</td>
<td>2.3 \times 10^3</td>
<td>7.0 \times 10^{13}</td>
<td>33</td>
<td>23.0</td>
</tr>
<tr>
<td>3.0 \times 10^{15}</td>
<td>1.0 \times 10^3</td>
<td>3.0 \times 10^{14}</td>
<td>20</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Table 13 Electrical parameters of Cd layers implanted into semi-insulating substrates at room temperature (20°C), after annealing at 650°C.
<table>
<thead>
<tr>
<th>Anneal Temp °C</th>
<th>Dose = $7 \times 10^{13}$ ions.cm$^{-2}$</th>
<th>Dose = $7 \times 10^{14}$ ions.cm$^{-2}$</th>
<th>Dose = $1.4 \times 10^{15}$ ions.cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{impl}$ °C</td>
<td>$T_{impl}$ °C</td>
<td>$T_{impl}$ °C</td>
</tr>
<tr>
<td>600</td>
<td>20</td>
<td>100</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>high</td>
<td>high</td>
<td>$1.9 \times 10^5$</td>
</tr>
<tr>
<td>650</td>
<td>8.0 x $10^4$</td>
<td>1.2 x $10^4$</td>
<td>7.1 x $10^3$</td>
</tr>
<tr>
<td>700</td>
<td>4.2 x $10^3$</td>
<td>2.7 x $10^4$</td>
<td>2.4 x $10^3$</td>
</tr>
<tr>
<td>750</td>
<td>1.5 x $10^3$</td>
<td>4.9 x $10^3$</td>
<td>1.7 x $10^3$</td>
</tr>
<tr>
<td>800</td>
<td>2.7 x $10^3$</td>
<td>1.6 x $10^4$</td>
<td>3.0 x $10^3$</td>
</tr>
</tbody>
</table>

Table 14: Sheet resistivity of Cd implanted layers in semi-insulating substrates after annealing at temperatures in the range 600°C to 800°C.

(see fig.29 and 30 for plots of carrier concentration and mobility versus anneal temperature for these specimens)
Fig. 29 Carrier concentration and mobility versus anneal temperature for Cd implanted layers in semi-insulating substrates.

\[
\text{Dose} = 7 \times 10^{13} \text{ ions.cm}^{-2}
\]
Fig. 30 Carrier concentration and mobility versus anneal temperature for Cd implanted layers in semi-insulating substrates.

Dose = $1.4 \times 10^{15}$ ions.cm$^{-2}$
Annealing at temperatures above 650°C did not result in any significant improvement in carrier concentration for the 180°C implant, the activity being about 70%-100% over this anneal temperature range. The room temperature and 100°C implants however, show an increase in carrier concentration for anneal temperatures up to 750°C when a percentage activity of about 65% is obtained.

The 100°C, 7 x 10^{13} ions/cm^2 layer showed inhomogeneity in resistivity measurements at some anneal temperatures and therefore large errors in the calculation of resistivity and mobility resulted. However, the variation of mobility with anneal temperature for the room temperature and 180°C implants was measured and is shown in fig. 29. There is little difference between the values of mobility for these specimens at any particular anneal temperature, both specimens showing a similar variation of mobility with anneal temperature. At anneal temperatures of 650°C to 750°C the mobility shows a dramatic improvement with a maximum value of about 95 cm^2/V.sec at 750°C. At anneal temperatures greater than 750°C the mobility shows an equally dramatic deterioration, falling to a value of 40 cm^2/V.sec at 800°C.

Specimens implanted with a total dose of 1.4 x 10^{15} ions/cm^2 show measurable p-type activity at anneal temperature of 600°C with a carrier concentration in the range 3 x 10^{13} - 1 x 10^{14} holes/cm^2. At an anneal temperature of 600°C the 180°C implant shows a greater percentage activity than the 100°C or room temperature implants, the activities being given in table (15).

The 180°C implant shows a steady increase in carrier concentration for anneal temperatures up to 800°C with a final concentration of 1.1 x 10^{15} holes/cm^2 (80% activity) whereas the 100°C implant shows an increase in carrier concentration for anneal temperatures up to 650°C but...
then remains constant at $3.5 \times 10^{14}$ holes/cm$^2$ (25% activity) for anneal temperatures between 650°C and 800°C. The room temperature implant shows a steady rise in concentration for anneal temperatures greater than 700°C, having a final concentration of $3 \times 10^{14}$ holes/cm$^2$, similar to the 100°C implant at an anneal temperature of 800°C.

<table>
<thead>
<tr>
<th>Implant Temperature°C</th>
<th>Sheet Carrier Concentration holes/cm$^2$</th>
<th>% Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>$1.2 \times 10^{14}$</td>
<td>8.0</td>
</tr>
<tr>
<td>100</td>
<td>$6.7 \times 10^{13}$</td>
<td>4.8</td>
</tr>
<tr>
<td>R.T.</td>
<td>$3.5 \times 10^{13}$</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table (15)

Carrier concentration and % activity for layers implanted with a dose of $1.4 \times 10^{15}$ Cd ions/cm$^2$ after annealing at 600°C.

The variation of mobility for these specimens is shown in fig.(30).

The mobility for the 180°C implant does not show any significant improvement at anneal temperatures greater than 600°C, in fact the highest mobility recorded for the specimen is at an anneal temperature of 600°C with a value of 50 cm$^2$/V.sec. Between anneal temperatures of 650°C and 800°C the mobility has a value of about 35cm$^2$/V.sec. In contrast, the 100°C and R.T. implants show an increase in mobility for anneal temperatures of 600°C to 700°C. Above an anneal temperature of 700°C the 100°C implant remains at a constant mobility of about 80cm$^2$/V.sec. whereas the room temperature implant shows a drop in mobility from 50cm$^2$/V.sec. at 700°C to 30cm$^2$/V.sec. at 750°C, remaining at this value up to an anneal temperature of 800°C.
The specimens implanted with a dose of $7 \times 10^{14}$ ions/cm$^2$ were only annealed at 600°C and then a stripping experiment carried out to obtain information regarding the depth distribution of carriers and their mobility. The measured sheet resistivity, sheet carrier concentration and mobility after annealing at 600°C are given in table (16).

<table>
<thead>
<tr>
<th>Implant Temperature °C</th>
<th>Sheet Resistivity ohms/cm$^2$</th>
<th>Mobility cm$^2$/V.sec</th>
<th>Sheet Carrier Concentration holes/cm$^2$</th>
<th>% Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>$6.6 \times 10^2$</td>
<td>63</td>
<td>$1.5 \times 10^{14}$</td>
<td>21</td>
</tr>
<tr>
<td>100</td>
<td>$5.8 \times 10^3$</td>
<td>43</td>
<td>$2.5 \times 10^{13}$</td>
<td>3.5</td>
</tr>
<tr>
<td>R.T.</td>
<td>$1.1 \times 10^3$</td>
<td>30</td>
<td>$1.9 \times 10^{14}$</td>
<td>27</td>
</tr>
</tbody>
</table>

Table (16)

Electrical parameters of layers implanted with a dose of $7 \times 10^{14}$ Cd ions/cm$^2$ after annealing at 600°C.

The 180°C and room temperature implants show high values of carrier concentration with percentage activities of 21% and 27% respectively. The 180°C implant has a better mobility than the room temperature implant. The 100°C implant shows considerably lower activity than either the 180°C or room temperature implant.

5.5.2.2 Cadmium implants into N-type Substrates

Cadmium was implanted into n-type substrates at doses of $7 \times 10^{13}$, $7 \times 10^{14}$ and $7 \times 10^{15}$ ions/cm$^2$ at room temperature, 100°C and 180°C.

Sheet resistivity, sheet carrier concentration and mobility were measured for these specimens after annealing at temperatures up to 800°C. The resulting curves are shown in figs. (31,32, 33) and described in the following subsections.
(i) \[ \text{Dose} = 7 \times 10^{13} \text{ions/cm}^2 \]

The specimens implanted with a total dose of \( 7 \times 10^{13} \text{ions/cm}^2 \) show a similar anneal behaviour to the equivalent implants into semi-insulating substrates: low resistivity layers are formed after annealing at 650°C, the 'hot' implants having a higher carrier concentration than the room temperature implants at this anneal temperature. Annealing to 700°C gives a slight improvement in carrier concentration for the 100°C and 180°C implants and a large improvement for the room temperature implant. At all anneal temperatures the 100°C implant shows a higher value of carrier concentration than the 180°C implant by a factor of about 2.5. Annealing at temperatures above 700°C results in a reduction in carrier concentration for all specimens with eventually the formation of a high resistivity layer after annealing of the 180°C implant at 800°C.

All specimens implanted with a dose of \( 7 \times 10^{13} \text{ions/cm}^2 \) show a marked improvement in mobility at anneal temperatures in the range 650°C-700°C, particularly so in the case of the room temperature implant. There appears to be no significant difference in mobility for the room temperature, 100°C or 180°C implants. Above an anneal temperature of 700°C the mobility levels off to a value of about 110 cm²/V·sec.

(ii) \[ \text{Dose} = 7 \times 10^{14} \text{ions/cm}^2 \]

Specimens implanted with a total dose of \( 7 \times 10^{14} \text{ions/cm}^2 \) produced low resistivity layers after annealing at 600°C. Annealing to 650°C results in an improvement in carrier concentration although annealing above 650°C for the room temperature implant and above 750°C for the 100°C implant causes a reduction in carrier concentration. Again mobility increases at anneal temperatures in the range 600°C-700°C then levels off at anneal temperatures in the range 750°C-800°C. There appears to be no significant difference between the electrical properties of room temperature, 100°C or 180°C implants, although measurements on the 180°C implant were
Fig. 31 Carrier concentration and mobility versus anneal temperature for Cd implanted layers in n-type substrates

Dose = $7.0 \times 10^{13}$ ions.cm$^{-2}$
Fig. 32  Carrier concentration and mobility versus anneal temperature for Cd implanted layers in n-type substrates

\[ \text{Dose} = 7.0 \times 10^{11} \text{ ions.cm}^{-2} \]
Fig. 33 Carrier concentration and mobility versus anneal temperature for Cd implanted layers in n-type substrates.

\[ \text{Dose} = 7.0 \times 10^{15} \text{ ions.cm}^{-2} \]
only possible up to an anneal temperature of 650°C.

(iii) Dose = $7 \times 10^{15}$ ions/cm$^2$

A specimen implanted with a total dose of $7 \times 10^{15}$ ions/cm$^2$ did not show the usual initial increase in resistivity at low anneal temperatures (up to 400°C). At anneal temperatures up to 340°C this specimen had an almost constant sheet resistivity of $4 \times 10^4$ ohms/cm$^2$, above 340°C the sheet resistivity fell and p-type activity could be measured. Sheet resistivity, carrier concentration and mobility for this and other specimens implanted with a total dose of $7 \times 10^{15}$ ions/cm$^2$ at room temperature and 100°C are shown in fig.(33).

After annealing at 340°C the 180°C implant had a carrier concentration of $1.1 \times 10^{14}$ holes/cm$^2$ but a very low mobility of $2.0\text{cm}^2/\text{V.sec.}$; annealing up to 600°C shows only a slight increase in carrier concentration to $2.5 \times 10^{14}$ holes/cm$^2$ but a marked increase in mobility to $20\text{cm}^2/\text{V.sec.}$

Further annealing up to 650°C shows a slight decrease in carrier concentration but a dramatic increase in mobility to $70\text{cm}^2/\text{V.sec.}$, unfortunately no measurements at anneal temperatures greater than 650°C could be made.

In contrast, the room temperature and 100°C implants followed the usual low temperature annealing pattern and p-type activity could only be measured after annealing at 600°C. All specimens, including the 180°C implant, have a similar sheet carrier concentration at these anneal temperatures of about $1-2 \times 10^{14}$ holes/cm$^2$. Annealing at temperatures up to 750°C results in a gradual decrease in carrier concentration for the room temperature and 100°C implants.

The 100°C implant shows a marked improvement in mobility after annealing in the range 600°C-700°C; above 700°C the mobility does not improve significantly and has a value of about 85cm$^2$/V.sec. The room temperature implant requires anneal temperatures of 700°C-750°C to show
any marked improvement in mobility comparable to the other specimens. After annealing at 750°C the room temperature implant has a mobility of $65 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$.

5.5.3 Carrier concentration and mobility profiles of Cd implanted layers.

Carrier concentration and mobility profiles were obtained for Cd implanted layers in semi-insulating and n-type substrates.

Table (17) is a summary of the specimens for which profiles were obtained. The results are presented in two sections corresponding to implants into semi-insulating and n-type substrates respectively.

5.5.3.1 Profiles in semi-insulating substrates

The profiles of carrier concentration and mobility for specimens implanted with a dose of $7 \times 10^{14}$ ions.cm$^{-2}$ are shown in fig.(34) and fig.(35) and will be described separately.

(i) Room temperature (20°C) implant

Over the depth range for which measurements were possible this specimen had a flat carrier concentration profile with a value of $2.0 \times 10^{19}$ holes.cm$^{-3}$. This value of carrier concentration extended from about 50 Å below the surface to a depth of 700 Å. Beyond the depth of 700 Å the resistivity of the layer rose sharply and no further measurements of Hall constant could be made. The last measured value of the Hall constant, at a depth of 700 Å, indicated that a free surface carrier concentration of about $1.0 \times 10^{13}$ holes.cm$^{-2}$ remained in the layer.

The integrated concentration from the surface to a depth of 700 Å corresponds to a surface sheet concentration of $1.4 \times 10^{14}$ holes.cm$^{-2}$. The total surface concentration is therefore $(1.4 \times 10^{14}) + (1.0 \times 10^{13})$ holes.cm$^{-2}$ i.e. $1.5 \times 10^{14}$ holes.cm$^{-2}$ which is close to the measured sheet concentration before stripping of $1.9 \times 10^{14}$ holes.cm$^{-2}$. 
<table>
<thead>
<tr>
<th>Dose ions. cm(^{-2})</th>
<th>(T_{\text{impl}}) °C</th>
<th>(T_{\text{anneal}}) °C</th>
<th>Substrate Type</th>
<th>Sheet Carrier Concentration, holes.cm(^{-2})</th>
<th>Integrated Carrier conc. holes.cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7 \times 10^{14})</td>
<td>20</td>
<td>600</td>
<td></td>
<td>1.9 \times 10^{14}</td>
<td>1.5 \times 10^{14}</td>
</tr>
<tr>
<td>(7 \times 10^{14})</td>
<td>100</td>
<td>600</td>
<td>semi-insulating</td>
<td>2.5 \times 10^{13}</td>
<td>2.4 \times 10^{13}</td>
</tr>
<tr>
<td>(7 \times 10^{14})</td>
<td>180</td>
<td>600</td>
<td></td>
<td>1.5 \times 10^{14}</td>
<td>1.5 \times 10^{14}</td>
</tr>
<tr>
<td>(7 \times 10^{14})</td>
<td>20</td>
<td>600</td>
<td>N-type</td>
<td>6.9 \times 10^{13}</td>
<td>6.2 \times 10^{13}</td>
</tr>
<tr>
<td>(7 \times 10^{14})</td>
<td>20</td>
<td>750</td>
<td></td>
<td>4.8 \times 10^{13}</td>
<td>5.1 \times 10^{13}</td>
</tr>
</tbody>
</table>

**Table 17** Summary of O$_3$ implanted specimens for which carrier concentration and mobility profiles were obtained.
The mobility within the layer does not vary significantly from a constant value of about 30 cm$^2$.V$^{-1}$.sec$^{-1}$ except at depths greater than 600 $\AA$ where it starts to fall sharply.

This combination of low mobility and small carrier concentration at depths of greater than 700 $\AA$ explains the rapid rise in resistivity beyond this depth.

The predicted atomic profile is also shown in fig.(34) by the curve marked L.S.S. and as can be seen, although the peak carrier concentration does not equal the peak atomic concentration, the carrier concentration profile does not extend to any depth appreciably greater than the predicted distribution.

(ii) 100°C Implant

The sheet resistivity and carrier concentration of this specimen, measured before stripping, show poor electrical activity, see table (17). This poor activity is also revealed in the carrier concentration profile shown in fig.(35).

The surface region is denuded of free carriers, the concentration rising to a peak value of $5 \times 10^{18}$ holes.cm$^{-3}$ at a depth of 500 $\AA$ i.e. near the end of the predicted atomic distribution. The carrier concentration then falls steadily to a value of $2 \times 10^{18}$ holes.cm$^{-3}$ at a depth of 950 $\AA$.

The last measured value of the Hall constant, at a depth of 950 $\AA$, indicates that the concentration of free carriers left in the layer is about $2 \times 10^{12}$ holes.cm$^{-2}$ (sheet concentration) which, if the carrier concentration falls at the same rate beyond 950 $\AA$, will extend to no more than a further 150 to 200 $\AA$.

The carrier concentration appears to fall less sharply than the predicted atomic profile and possibly penetrates to a depth of about 300 $\AA$ beyond the predicted distribution.
Fig. 34 Carrier concentration and mobility profiles for Cd implanted layers in semi-insulating substrates.

Dose = $7.0 \times 10^{14}$ ions.cm$^{-2}$
Fig. 35 Carrier concentration and mobility profile for Cd implanted layer in semi-insulating GaAs. Dose = $7 \times 10^{14}$ ions cm$^{-2}$.
The integrated carrier concentration between 200 Å and 1,000 Å corresponds to a surface concentration of $2.2 \times 10^{13}$ holes.cm$^{-2}$ and therefore the total sheet concentration in the layer is $(2.2 \times 10^{13})+(2.0 \times 10^{12})$ holes.cm$^{-2}$ i.e. $2.4 \times 10^{13}$ holes.cm$^{-2}$. This, again, is close to the measured sheet concentration before stripping of $2.5 \times 10^{13}$ holes.cm$^{-2}$.

The mobility within the layer shows a steady decrease from a peak of $35 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$ at 450 Å to $10 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$ at a depth of 950 Å.

(iii) 180°C Implants

The carrier concentration and mobility profiles for this specimen are shown in fig.(35) and show some interesting characteristics.

In particular, the measured carrier concentration profile extends to a depth of 6,000 Å - considerably greater than the predicted L.S.S. range of about 700 Å. The concentration rises from a value of $1 \times 10^{18}$ holes.cm$^{-3}$ at the surface to a value of $4.5 \times 10^{18}$ holes.cm$^{-3}$ at a depth of 1,000 Å. The concentration then falls to a value of $3.2 \times 10^{18}$ holes.cm$^{-3}$ at a depth of 1,600 Å and remains at this level to a depth of 3,300 Å. Beyond 3,300 Å the concentration falls steadily to a value of $4.0 \times 10^{17}$ holes.cm$^{-3}$ at a depth of 6,000 Å.

It is thought that the concentration at a depth of 6,000 Å is a measure of the concentration of compensating centres in the substrate material.

The Hall constant at a depth of 6,000 Å indicates that about $1.0 \times 10^{12}$ holes.cm$^{-2}$ (sheet concentration) remain in the layer. If the rate of fall of carrier concentration at 6,000 Å is maintained then the carrier concentration profile would extend a further 500 Å into the substrate.

The integrated carrier concentration to a depth of 6,000 Å corresponds to a sheet concentration of $1.5 \times 10^{14}$ holes.cm$^{-2}$, exactly that found by sheet measurement before stripping.
The mobility profile shows little structure, being virtually constant at a value of 55 to 60 cm² V⁻¹ sec⁻¹ to a depth of 4,750 Å and then gradually falling to a value of 25 cm² V⁻¹ sec⁻¹ at a depth of 6,000 Å.

5.5.3.2 Profiles in n-type substrates

Specimens were implanted with a total dose of $7.0 \times 10^{14}$ ions cm⁻² at room temperature, 100°C and 180°C into n-type substrates and annealed at 600°C.

Unfortunately the 100°C and 180°C implants were broken during annealing and measurements could only be made on the room temperature implants.

In fact two specimens were implanted at room temperature with a dose of $7.0 \times 10^{14}$ ions cm⁻²; one was annealed at 600°C and the other was annealed at 750°C. The resulting profiles of carrier concentration and mobility are shown in fig. (36) and are described in the following two sections.

(i) 600°C anneal profile

The carrier concentration profile after annealing at 600°C shows a steady increase from a value of about $1.0 \times 10^{18}$ holes cm⁻³ at the surface to a value of $8.0 \times 10^{18}$ holes cm⁻³ at a depth of 750 Å. Beyond 750 Å the resistivity of the layer rises sharply and no measurements of the Hall constant could be made. The value of the Hall constant at the depth of 750 Å indicates that a sheet carrier concentration of $3.5 \times 10^{13}$ holes cm⁻² remained in the layer.

The integrated concentration between 150 Å and 750 Å corresponds to a sheet concentration of $2.7 \times 10^{13}$ holes cm⁻² and therefore the total sheet concentration of the layer is $(3.5 \times 10^{13}) + (2.7 \times 10^{13})$ holes cm⁻² i.e. $6.2 \times 10^{13}$ holes cm⁻². The measured value of the sheet concentration before stripping being $6.9 \times 10^{13}$ holes cm⁻².

The mobility within the layer also rises gradually with increasing
Fig. (36) Carrier concentration and mobility profiles for Cd implant into n-type substrate at room temp.

Dose = $7.0 \times 10^{14}$ ions cm$^{-2}$
depth from a value of about 15 cm\(^2\) V\(^{-1}\) sec\(^{-1}\) near to the surface to a value of 30 cm\(^2\) V\(^{-1}\) sec\(^{-1}\) at a depth of 700 \AA. The measured Hall constant and resistivity at a depth of 750 \AA indicate that the mobility in the remaining layer drops to about 15 cm\(^2\) V\(^{-1}\) sec\(^{-1}\).

(ii) 750°C Anneal profile

After annealing an identical specimen at 750°C a different carrier concentration profile was obtained.

This specimen had an identical value for the sheet carrier concentration after annealing at 600°C as the specimen annealed at 600°C only, i.e. 6.9 \times 10^{13}\text{ holes.cm}^{-2}.

The carrier concentration for this specimen gradually falls from a peak value of about 8.0 \times 10^{18}\text{ holes.cm}^{-3} at the surface to a value of 3.0 \times 10^{18}\text{ holes.cm}^{-3} at a depth of 650 \AA.

The value of the Hall constant at a depth of 650 \AA indicates that a sheet carrier concentration of 1.25 \times 10^{13}\text{ holes.cm}^{-2} remains within the layer.

The integrated concentration to a depth of 650 \AA corresponds to a sheet carrier concentration of 3.86 \times 10^{13}\text{ holes.cm}^{-2} and therefore the total sheet concentration for the layer is (3.86 \times 10^{13}) + (1.25 \times 10^{13}) \text{ holes.cm}^{-2} i.e. 5.11 \times 10^{13}\text{ holes.cm}^{-2}. The measured value for the sheet concentration, before stripping, was 4.8 \times 10^{13}\text{ holes.cm}^{-2}.

The mobility within the layer shows a significant improvement over the 600°C anneal specimen, having an almost constant value of about 75 cm\(^2\) V\(^{-1}\) sec\(^{-1}\) from the surface to a depth of 500 \AA. Beyond 500 \AA
the mobility appears to carry on rising to a value of about 100 cm\(^2\) V\(^{-1}\) sec\(^{-1}\).

The value of the Hall constant and resistivity at a depth of 600 \AA indicate that the mobility within the remaining layer is also about 100 cm\(^2\) V\(^{-1}\) sec\(^{-1}\).
This section takes the form of a discussion of the experimental results reported in Chapter 5 with an attempt to relate these results to the established properties of GaAs.

In many cases it has been possible to correlate the observed behaviour of implanted GaAs with the known properties of bulk GaAs. In some cases, however, the observed effects fall outside the range of experimental studies on bulk GaAs and therefore any conclusions are of a hypothetical nature and require more experimental measurements to classify the behaviour.

In particular the effects due to heat treatment of GaAs are not fully understood and also the high impurity concentrations encountered in this thesis are outside the range of experimental study on conventionally doped (diffused) GaAs.

6.1 Heat Treatment of GaAs

Thermal probe and resistivity measurements reported in section 5.2 revealed that heat treatment of bulk GaAs at temperatures in excess of about 700°C resulted in the formation of acceptor like centres. This is in general agreement with the experimental evidence of other workers reported in section 2.1. The measurements of section 5.2 indicated that the concentration of these acceptors was greater than \(10^{17}\) acceptors/cm\(^3\) and that they were characterised by a very low mobility of the order \(1\text{cm}^2/\text{Vsec.}\) or less.

It is therefore of primary importance to keep annealing temperatures of implanted layers as low as possible, preferably below 700°C, in order to minimise spurious effects not directly related to the implantation process.
It is also apparent that encapsulation of the specimen in SiO₂
does not stop the loss of arsenic or gallium from the surface at high
anneal temperatures. Therefore if high anneal temperatures are essential
it will be necessary to modify the anneal procedure, perhaps by
improved surface protection or annealing in an arsenic rich atmosphere.

6.2 Radiation damage effects

In section 5.3 the results presented showed that p-type electrical
activity was introduced in GaAs as a result of heavy ion implantation.
This p-type activity could not be related to any conventional doping
properties of the implanted ion species but was rather a function of
implanted ion mass.

This independance of ion species but dependance on ion mass
suggests that the observed effects are a result of radiation damage to
the crystal. The increased rate of damage production associated with
the heavier atoms (Te and Cd) results in the formation of a completely
disordered, amorphous layer at doses greater than about $5 \times 10^{13}$ ions.cm⁻²
with a consequent saturation of p-type activity. This saturation might
be expected to occur at higher doses for the lighter ions (Zn,Ar and Se)
and indeed thermal probe measurements, fig.(21), do not show a saturation
effect for these ions over the dose range covered.

The saturation of damage effects as measured by electrical means
occurs at similar doses to those responsible for the saturation of other
effects associated with radiation damage i.e. crystal perfection as
measured using electron microscopy (22) and Rutherford back-scattering
(21).

The saturation of damage and the formation of an amorphous layer is
thought to be due to the overlapping of damage regions associated with
individual particle tracks. The onset of saturation at a dose of about
$5 \times 10^{13}$ ions.cm⁻² indicates that the damage produced along each track
can be associated with a cross sectional area having a radius of 10 Å.

Implants of Te and Cd at 100°C and 180°C still showed p-type activity. In fact implantation at these temperatures produced lower resistivity layers than corresponding room temperature implants, there being no significant difference in resistivity between 100°C and 180°C implants. These hot implants still showed a saturation effect at doses greater than 5 x 10^{13} ions.cm^{-2}.

In some ways this was a very surprising behaviour since Rutherford back-scattering measurements by Bell (§5) of lattice disorder introduced after the implantation of Te into GaAs at 100°C and 180°C revealed that a dramatic reduction in radiation damage effects. This was particularly the case for 180°C implants where the measured lattice disorder was less than 5% of that introduced after a room temperature implant. Clearly the electrical activity associated with radiation damage cannot be correlated with gross lattice disorder as measured by Rutherford back-scattering techniques.

The reordering of the crystal lattice as a result of hot implants is thought to be the cause of the generally lower resistivity of damage layers formed at elevated implant temperatures, the improved crystallinity resulting in an increase in mobility of the carriers responsible for the p-type activity.

Measurements of sheet resistivity as a function of temperature yield an activation energy for the acceptor centres created by radiation damage of 0.064 eV above the valence band. This activation energy is somewhat lower than other reported values of about 0.10eV for acceptors created by gallium vacancies in GaAs (see section 2). However, the high concentration of acceptor centres (at least 10^{19} per cm^{3}) created by bombardment is likely to result in some impurity band spreading.
(as discussed in section 3.3.3) with a consequent reduction in activation energy. It is therefore thought that the acceptor centres created by bombardment could be associated with gallium vacancies.

6.3 Annealing of Radiation damage

Thermal probe and resistivity measurements reported in section 5.4 showed that the observed effects of radiation damage could be annealed out by heat treatment at temperatures of up to about 450°C. After annealing at this temperature high resistivity layers were formed and no effects associated with the dopant properties of the implanted ion were observed.

An interesting change in thermal probe reading with time was observed and reported in section 5.3.1, this change being particularly pronounced for high dose specimens. This change in thermal probe reading, indicating a reduction in p-type activity, may be due to room temperature annealing of the damaged layer. However, because of the sensitivity of the thermal probe technique to surface effects this change may also be due to the growth of a surface oxide film similar to that reported in ref. The effect was not investigated in any greater detail.

The resistivity of room temperature implants shows an interesting decrease at anneal temperatures of up to 200°C. Bicknell (64) reported the reordering of GaAs into a twinned crystalline structure at anneal temperatures of about 150°C and it is felt that the drop in resistivity over this anneal temperature range is due to an increase in carrier mobility as a result of re-crystallisation. Above anneal temperatures of 200°C the resistivity increases rapidly due, it is thought, to the removal of electrically active centres. This removal of carriers is apparently complete at anneal temperatures of about 450°C when resistivities of the same order as the semi-insulating substrate are recorded.

The implants at 100°C and 180°C do not show an initial decrease in resistivity when annealed, presumably because any reordering of the
crystal lattice as a result of annealing is masked by the dramatic re-ordering that results after implantation at these temperatures.

Analysis of the isochronal annealing data indicates that the process of annealing is first order at anneal temperatures greater than about 200°C, characterised by an activation energy of 0.54 eV.

6.4 Implanted dopant effects

The following discussion of the observed effects after annealing implanted layers at temperatures of greater than 450°C will deal with Te and Cd implants separately.

6.4.1 Te implants

The formation of low resistivity n-type layers by the implantation of Te at room temperature has proved extremely difficult. The only observed n-type activity being from a high dose \(1 \times 10^{16} \text{ ions.cm}^{-2}\) specimen annealed at 850°C for two minutes.

Implantation at elevated temperatures, 180°C in particular, resulted in a dramatic improvement, n-type layers being formed after annealing at a much lower temperature (600°C - 650°C). These specimens, implanted at 180°C and annealed to higher temperatures, did not show any significant improvement in electrical properties. In fact at high anneal temperatures a degradation of electrical properties was seen above a dose dependant anneal temperature (see table 12). This degradation is characterised by a sharp drop in carrier concentration and decrease in mobility and eventually the formation of high resistivity layers. The reduction in carrier concentration at high anneal temperatures is thought to be due to either of two causes or a combination of both, i.e. the introduction of compensating centres as a result of heat treatment, or the physical loss of Te from the layer.

It has been well reported in the literature (see section 2.1) and
observed by the author (see section 5.2) that heat treatment of GaAs at temperatures greater than 700°C results in the formation of acceptor-like centres, the consensus of opinion being that these centres are associated with gallium vacancies. The author's work, reported in section 5.2, indicates that the number of acceptors introduced by heat treatment has a minimum value of the order $10^{17}$ per cm$^3$.

If it is assumed that the electrical activity associated with the implanted dopant extends to a depth of the same order as the L.S.S. range then the observed sheet carrier concentrations, of about $1 \times 10^{13}$ electrons.cm$^{-2}$, correspond to a volume concentration of the order $10^{18}$ to $10^{19}$ electrons.cm$^{-3}$. The introduction of greater than $10^{17}$ acceptors.cm$^{-3}$ by heat treatment would therefore result in a significant decrease in carrier concentration by compensation of the Te donors. This explanation however does not account simply for the observed dose dependance of the anneal temperature above which deterioration takes place since all three specimens in fig.(28) have much the same carrier concentration and therefore should be influenced to the same extent by compensation effects.

Since all specimens do have a similar carrier concentration (i.e. concentration of Te in electrically active sites) the higher dose specimens have a greater proportion of the implanted Te in electrically non-active sites (perhaps $V_{Ga}^-\text{Te}$ complexes) and it is perhaps therefore reasonable to assume that the removal of Te from electrically active sites into electrically non-active sites will be suppressed, by concentration gradients, for the higher dose implants. This explanation could account for the reduced effect of compensation centres upon the carrier concentration for the high dose specimens.

The reduction in carrier concentration could also be explained by the physical loss of Te from the layer, either by diffusion into the protective SiO$_2$ film or diffusion into the substrate. Rutherford back-scattering measurements by Bell(65) on Te implants at room temperature do suggest that Te is being lost from the layer although it is not yet
clear whether this loss is due to diffusion into the substrate or into the protective film.

The maximum carrier concentration of about $2 \times 10^{13}$ electrons.cm$^{-2}$ observed for Te implants corresponds to a volume concentration of the order $10^{18}$ to $10^{19}$ electrons.cm$^{-3}$ and is virtually independent of dose in the range $7 \times 10^{14}$ to $7 \times 10^{15}$ ions.cm$^{-2}$. This saturation of carrier concentration is very similar to the observed behaviour of diffused Te in bulk GaAs at high concentrations (see section 2.1) where a maximum concentration of about $1 \times 10^{19}$ electrons.cm$^{-3}$ was obtained for atomic concentrations greater than $1 \times 10^{19}$ atoms.cm$^{-3}$. The peak concentration corresponding to an implanted dose of $7 \times 10^{14}$ ions.cm$^{-2}$ is about $1 \times 10^{20}$ atoms.cm$^{-3}$. It is therefore reasonable to assume that, at these concentration, the Te not directly accounted for by the free carrier concentration is in electrically non-active sites similar to those postulated by the authors quoted in section 2.1 to explain the behaviour of Te in GaAs at high concentrations i.e. Te - $V_{Ga}$ complexes.

The formation of these complexes could also account for the poor electrical activity observed for room temperature implants. Vacancies will almost certainly be created in large numbers by the act of ion implantation and conditions will therefore favour the formation of donor - vacancy complexes. It was also pointed out in section 2 that these complexes are thought to be electrically inactive and stable at temperatures of up to 850°C.

**6.4.2 Cd implants**

In contrast to room temperature Te implants, measurements with the thermal probe on room temperature implanted Cd layers indicated that p-type activity could be produced after annealing at 600°C. In fact specimens annealed at 650°C formed p-type layers with high carrier concentrations for doses of $5 \times 10^{13}$ ions.cm$^{-2}$ and greater.
The formation of low resistivity, high carrier concentration layers may be dependent on the formation of an amorphous layer after implantation. Annealing at 650°C only shows good electrical activity for specimens implanted with doses greater than about \(5 \times 10^{13} \text{ ions.cm}^{-2}\), a similar dose to that required to form an amorphous layer. This pattern is observed in both semi-insulating and n-type substrates.

Implantation of Cd at elevated temperatures results in improved activity at low anneal temperatures (600°C to 650°C), particularly for 180°C implants and low dose specimens. Layers implanted at elevated temperatures and annealed in the range 600°C - 650°C generally have a higher carrier concentration and marginally higher mobility than equivalent room temperature implants. In fact a high dose (7 x 10^{15} ions.cm^{-2}) Cd implant at 180°C into a n-type substrate showed measurable electrical activity at anneal temperatures as low as 340°C (see fig. 33) the improved activity at these anneal temperatures being due to an improvement in mobility rather than an increase in carrier concentration.

There does not appear to be any significant difference between the electrical properties of Cd implanted layers in either n-type or semi-insulating substrates for anneal temperatures of up to 750°C. If anything layers implanted into n-type substrates have a marginally higher mobility after annealing in this temperature range.

The observed effects after annealing at temperatures greater than about 750°C do appear to be a function of the substrate material. Annealing of layers implanted into semi-insulating substrates at temperatures greater than 750°C does not produce the drastic drop in carrier concentration observed for Te implanted layers at these anneal temperatures. The Cd implanted layers do show a decrease in mobility at anneal temperatures of greater than 750°C, particularly for the low dose implant (7 x 10^{13} ions.cm^{-2}). At these anneal temperatures little
change in carrier concentration is observed (see fig. 29 and 30).

This degradation of mobility may be an indication of the introduction of thermally generated acceptor centres similar to those postulated to explain the Te anneal results. The introduction of these centres would increase the number of scattering centres and therefore reduce the mobility. Electrical measurements on heat treated semi-insulating GaAs (see section 5.2) have shown that large numbers of acceptor-like defects are introduced by heat treatment at temperatures of about 750°C. These defects can be characterised by an extremely low mobility (of the order of 1.0 or less). The introduction of such acceptors into the implanted layer would not significantly alter the measured value of the sheet Hall constant (from which the sheet carrier concentration is calculated) but would result in a decrease in carrier mobility because of the greater number of scattering centres.

Annealing of layers implanted into n-type substrates at temperatures greater than about 700°C to 750°C results in the reduction of carrier concentration but little change in mobility. This reduction in carrier concentration at high anneal temperatures may be the result of diffusion of Cd into the substrate since any compensation effects within the implanted layer would be expected to result in a reduction of mobility also.

It is difficult to ascertain whether thermally induced defects are introduced to the same extent as in semi-insulating substrates because the variation of mobility in the n-type substrates is complicated by the overall reduction in carrier concentration at high anneal temperatures, i.e. any decrease in mobility as a result of the introduction of thermally generated defects may be counteracted by a general increase in mobility as a result of the decrease in carrier concentration.
6.5 Carrier concentration and mobility profiles

Carrier concentration and mobility profiles were obtained for Cd implanted layers in semi-insulating and n-type substrates. These will be discussed separately.

6.5.1 Profiles in semi-insulating substrates

These profiles were obtained for Cd implanted layers after annealing at 600°C. The characteristics of each profile appear to be a function of implant temperature.

6.5.1.1 Room temperature implant

The carrier concentration profile for the room temperature implant does not extend to any significant depth greater than the predicted L.S.S. distribution. Also the peak carrier concentration in the layer of about $2 \times 10^{19}$ holes cm$^{-3}$ does not equal the predicted peak atomic concentration of about $2 \times 10^{20}$ atoms cm$^{-3}$.

The mobility within the layer is lower than the mobility measured in bulk GaAs of a similar carrier concentration (see section 3.3.4.2), indicating that radiation damage has not been completely removed at this anneal temperature (600°C). In fact from figures 29 and 30 it can be seen that the anneal temperature range 550°C to 650°C is a very sensitive region where large changes in carrier concentration and mobility can occur, optimum electrical activity being achieved at anneal temperatures of about 650°C or greater.

In retrospect it appears that a more meaningful comparison of profiles could have been made if the specimens had been annealed at a temperature in the range 650°C to 700°C.

6.5.1.2 100°C Implant

The 100°C implant profile shows signs of incomplete annealing of the radiation damage at this anneal temperature (600°C). This specimen shows low electrical activity having a low carrier concentration near
to the surface. The comparatively good mobility near the surface however, does indicate that few scattering centres are present in this region and may be an indication that the implanted cadmium distribution does not follow the predicted L.S.S. distribution but extends to a greater depth. In fact the measured carrier concentration profile extends beyond the predicted range for a significant depth (about 300 Å).

6.5.1.3 180°C Implant

The 180°C carrier concentration profile extends to a depth considerably greater than the predicted L.S.S. distribution and shows a similar drop in carrier concentration near to the surface as the 100°C implant.

The limit to the measurable carrier concentration of \( 4 \times 10^{17} \) holes \( \text{cm}^{-3} \) at a depth of 6,000 Å is thought to be due to compensation of the p-type activity by the background impurities of the semi-insulating substrate.

The deep profile seen after implantation at 180°C and possibly 100°C can be explained either by the diffusion of cadmium into the substrate as a result of the elevated temperature of implant, or by channelling of the ion beam during implantation.

An estimate of the diffusion coefficient required to produce the 180°C profile from a concentration of cadmium on the specimen surface equal to the implanted dose was made by using the equation relating the concentration of dopants to depth and time for diffusion from a limited source i.e.:

\[
N(x,t) = \frac{S}{\sqrt{\pi D t}} \exp\left( -\frac{x^2}{4D t} \right)
\]
where \( S \) = number of impurities per unit area in the source
\( x \) = depth
\( t \) = time
\( D \) = diffusion coefficient

The resulting curve that approximated to the measured profile is shown in fig. (35) and the corresponding diffusion coefficient is of the order \( 10^{-13} \text{ cm}^2\text{.sec}^{-1} \). This is three orders of magnitude higher than the measured diffusion coefficient of cadmium in GaAs at 600°C (\( 10^{-16} \text{ cm}^2\text{.sec}^{-1} \)) and therefore the deep profile cannot be explained by simple diffusion of cadmium. It is feasible that the cadmium may diffuse rapidly during implantation, being enhanced by the large number of vacancies created during implantation.

Channelling of the ion beam during implantation is also very likely to cause deep profiles. Calculations outlined in section 3.1.4 yield a critical angle for channelling at these energies of about 5°. During implantation no effort was made to align, or mis-align, the specimen with respect to the beam direction and it is thought likely that the specimen could inadvertently have been aligned with the beam to within about 5°. Rutherford back-scattering measurements by Bell (65) of radiation damage after implantation at 180°C have revealed a great reduction in lattice disorder. Therefore it is thought that the probability of channelling at these implant temperatures is further increased (i.e. no amorphous layer is formed which would tend to block channels and de-channel the beam).

It is hoped that future work would reproduce these deep profiles and that careful consideration of implant conditions will determine the cause of the deep profiles, in particular implantation in channelling directions and well away from channelling directions. It would also be
interesting to implant Cd at room temperature and follow this with an implant of an inert gas ion (e.g. Argon) at 180°C to try and determine the role of radiation induced defects upon the carrier concentration profile. If the deep profiles are the result of radiation enhanced diffusion then, hopefully, the defects created by the inert gas ions at an implant temperature of 180°C would modify the profile of the room temperature Cd implantation.

6.5.2 Profiles in n-type substrates

The carrier concentration and mobility profiles for room temperature Cd implants were obtained after annealing at 600°C and 750°C.

The shape of these profiles suggest that Cd may be diffusing into the substrate at high anneal temperatures.

The fall in carrier concentration and low mobility near to the surface after annealing at 600°C suggest that the effects of radiation damage have not been completely removed at this anneal temperature. Annealing at 750°C results in an increase in carrier concentration near to the surface and a dramatic increase in mobility throughout the implanted layer. However, after annealing at 750°C, the carrier concentration falls steadily at depths greater than about 400 μ due, it is thought, to the diffusion of cadmium into the substrate. After diffusing into the n-type substrate the p-type properties of the cadmium would be compensated by the n-type dopants in the substrate.

This diffusion of cadmium into the n-type substrate is likely to modify the electrical characteristics of the p-n junction and it is anticipated that future measurements of diode characteristics as a function of anneal temperature will be able to determine the extent of any diffusion.
The experimental properties of implanted layers in GaAs can be summarised as follows:

1. Implantation of heavy ions creates a damaged surface layer.
2. This damaged layer is characterised by acceptor like defects having a thermal activation energy of 0.064 eV.
3. These acceptor like centres cannot be correlated with gross lattice disorder as observed using R.B.S. techniques.
4. The effect of these defects can be reduced by annealing in the temperature range 100°C to 450°C.
5. The removal of these defects by annealing is a first order process with an activation energy of 0.54 eV.
6. Anneal temperatures of at least 500°C are required before electrical properties characteristic of the implanted ion species are observed.
7. Implantation at elevated temperatures (particularly 180°C) results in an improvement in carrier concentration and mobility at the lower anneal temperatures.
8. Acceptor like centres are introduced by the heat treatment of GaAs at temperatures of greater than 700°C.
9. These thermally generated acceptors are characterised by an activation energy of 0.10 eV and are thought to be associated with gallium vacancies.
10. These acceptors compensate the n-type properties of implanted Te for all but the highest doses.
11. These acceptors are responsible for a reduction in mobility of Cd implanted p-type layers.
12. Implanted Cd profiles extend to depths greater than the predicted L.S.S. distribution for implants at elevated temperatures.
13. Annealing at elevated temperatures results in the inward diffusion of Cd.

The dramatic improvement in electrical properties after implantation at elevated temperatures is very encouraging and it is hoped that future work will be aimed at implantations at higher temperatures than 180°C.

Implants at such temperatures should require lower anneal temperatures to obtain satisfactory electrical activity. A difficulty does arise however, in that deep profiles are obtained after implantation at elevated temperatures. Future work must also be aimed at isolating the cause of these deep profiles. In particular implants in channeling and non-channeling directions would be useful.

At present the electrical properties of implanted layers are limited by the deterioration of GaAs as a result of heat treatment at temperatures of greater than 700°C. This problem is not peculiar to ion implantation but is a general feature of GaAs technology - the effects associated with the heat treatment of GaAs are not fully understood. Improved annealing techniques are required to limit the formation of defects but, as mentioned above, these problems are not peculiar to the process of ion implantation.

Hopefully, implantation at elevated temperatures will reduce the anneal temperatures required to obtain acceptable electrical properties.

In conclusion it is felt that the observed effects cannot be related to differences between specimens or material preparation techniques and this is therefore used as an argument in favour of more experiments using less expensive bulk grown GaAs in order to understand the gross changes brought about by ion implantation and heat treatment.
N represents the number of reactants left after annealing isochronally at temperature \( T \), i.e. the number of free carriers.

The rate of reaction at temperature \( T \) is given by:

\[
\frac{dN}{dt} = K \cdot N^\gamma
\]

\( \gamma \) = order of reaction

\( K = A \cdot \exp \frac{-\varepsilon}{kT} \) = a constant

\( \varepsilon \) = activation energy of annealing process

**Assuming 1st Order Kinetics**

\( \gamma = 1 \) therefore

\[
\frac{dN}{dt} = A \cdot N \cdot \exp \frac{-\varepsilon}{kT}
\]

\[
\frac{dN}{N} = A \cdot \exp \frac{-\varepsilon}{kT} \cdot dt
\]

\[
\ln N = A \cdot t \cdot \exp \frac{-\varepsilon}{kT} + \text{constant}
\]

at \( t = 0 \quad N = N_0 \)

therefore constant = \(-\ln N_0\)
therefore \( \ln \frac{N}{N_0} = A.t \exp - \frac{\varepsilon}{kT} \)

therefore \( \frac{N}{N_0} = \exp - Bt \)

where \( B = A \exp - \frac{\varepsilon}{kT} \)

For isochronal annealing \( B \) will not be a constant and therefore the integration must be between successive temperatures.

at \( T_a \), \( B_a = A \exp - \frac{\varepsilon}{kT_a} \)

then \( \frac{N_{a-1}}{N_a} = \exp - B_a t \)

\[
\ln \frac{N_{a-1}}{N_a} = -B_a t = A.t \exp - \frac{\varepsilon}{kT_a}
\]

or \( \ln \ln \frac{N_{a-1}}{N_a} = \ln A.t - \frac{\varepsilon}{kT_a} \)

therefore a plot of \( \ln \ln \frac{N_{a-1}}{N_a} \) against \( 1/T_a \) should be a straight line with a slope of \( -\frac{\varepsilon}{k} \).
APPENDIX II

PROPERTIES OF SUBSTRATE MATERIALS USED

Crystal Number = X2081 Supplier = M.C.P.

Dopant Te (n-type)
Carrier concentration $3.6 \times 10^{16}$ electrons cm$^{-3}$
Mobility 3,040 cm$^2$V$^{-1}$sec$^{-1}$
Resistivity 0.058 ohm.cm.
Orientation 110

Crystal Number = X2203 Supplier = M.C.P.

Dopant Cr
Carrier concentration -
Mobility Greater than $10^8$ ohm.cm.
Orientation 110

A specimen of this crystal was analysed by the chemistry department of the University and was found to contain not greater than 10 p.p.m. of Chromium.

The analysis was by means of emission spectroscopy with a detection limit of 10 p.p.m.
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