ABSTRACT

Some of the effects of implanting tellurium and tin into single crystal gallium arsenide are described in this thesis. The distribution and retention of tellurium and tin implanted into GaAs, the properties of the ion implantation damage and the electrical properties of the ion implanted impurities were studied as a function of the implantation temperature, dose and anneal temperature between 150°C and 700°C. Silicon dioxide (SiO$_2$) was used as the encapsulant for the majority of those specimens annealed at temperatures in excess of 500°C. A few comparative measurements were made with silicon nitride (Si$_3$N$_4$) as the encapsulant material. The effectiveness of silicon dioxide as an encapsulant for GaAs is discussed. The Rutherford backscattering and Hall effect techniques were used to investigate the depth distribution of the physical and electrical properties of the ion implanted layers.

It was shown that the damage induced conductivity was confined to a thin surface layer for implantation temperatures of 20°C and 100°C, but deeper diffusing tails in the electrical conductivity versus depth profile were observed for implantation temperatures of 180°C and 250°C. The dependence of the damage induced conductivity on analysis temperature could be described theoretically by a model in which it was assumed that the conduction mechanism was similar to that of an amorphous semiconductor with a non-uniform density of states in the region of the Fermi energy level. Although the ion implanted Te does not redistribute for annealing temperatures up to 700°C, the ion implanted Sn diffuses towards the surface of the crystal. The results presented indicate that, for anneal temperatures up to 700°C, only a small percentage of the ion implanted Te and Sn became electrically active. The reasons for this low activity are discussed.
ACKNOWLEDGEMENTS

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This thesis is dedicated to my wife, Teresa, for her support, understanding and patience during the period it was being prepared.
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Gallium arsenide is technologically of interest as a semiconductor material because of its high electron mobility and large band gap. This combination of properties has made GaAs one of the more promising starting materials for high speed device applications suitable for working at moderately high temperatures. As these types of devices are likely to require an inhomogeneous distribution of electrically active impurities, an interest has been established in the dopant properties of various elements in GaAs. Much of the work concerned with forming inhomogeneous distributions of the impurities published prior to the commencement of the work described in this thesis, was based on diffusion and epitaxial growth techniques. These techniques have the disadvantage that they are predominantly high temperature processes which, unless suitable steps are taken, allow the dissociation of the surface and the degradation of the electrical properties in the surface regions. Acceptor impurities can be diffused readily into GaAs. However, the low diffusion coefficients of donor atoms \(^{1,2}\) make it necessary to diffuse n-type layers at temperatures where the substrate surface is badly degraded. Hence there is a need for an alternative doping technique to diffusion for GaAs.

In recent years, it has been shown that ion implantation is a useful technique for doping semiconductors \(^{3,4,5}\). Some of the advantages of using ion implantation over the more conventional diffusion process are:

(i) The ability to control precisely the concentration of the dopant atoms over many orders of magnitude.
(ii) Good control over the depth profile, allowing special dopant profiles to be easily fabricated.
(iii) It is essentially a low temperature process.
(iv) A wider selection of impurities may be used.

The biggest disadvantage of this technique is that it introduces a large amount of radiation damage which may cause the surface layers of the crystal to become amorphous. This radiation damage will modify the electrical properties of the implanted dopant.
The ability to introduce impurities into the surface layers of a semiconductor makes the use of ion implantation attractive as a processing technique to dope those crystals, such as GaAs, which are liable to dissociate at elevated temperatures. However, the electrical properties of semiconductors are very sensitive to crystalline defects such as those created by the ion implantation process, and it is usually necessary to anneal the material after implantation to reduce the concentration of such defects. The annealing temperatures are usually lower than that required for diffusion, thus keeping advantage 3 above. However, the annealing process may still cause the dissociation of the surface layers of a compound semiconductor.

When GaAs is heat treated at temperatures above 600°C, arsenic is lost from the surface layers creating As vacancies which can diffuse into the crystal. These vacancies create deep electrically active compensating centres with acceptor-like properties. As the As loss will tend to make acceptor layers more p-type and donor layers less n-type, this will make the generation of low resistivity n-type layers more difficult. One method of overcoming this problem when annealing GaAs at high temperatures, is to coat the crystal with an encapsulating layer which will preserve the atomic composition at the surface by inhibiting the loss of either the As or the Ga atoms. In the study described here, the GaAs was coated with a deposited layer of silicon dioxide. A few comparative measurements were made using silicon nitride as the encapsulating layer.

Before a process such as ion implantation can be used as a technique in the development or production of solid state devices, it is necessary to characterise the effects of the implanted atoms on the physical and electrical properties of the crystal. Some preliminary work\textsuperscript{7-13} had indicated that GaAs could be doped to form a low resistivity p-type layer using ion implantation, but the formation of low resistivity n-type layers was proving difficult. It was therefore decided to investigate some of the problems associated with using ion implantation as a technique to form low resistivity n-type layers in GaAs. This thesis describes some of the effects of implanting the donors, Te and Sn, into GaAs. The effects of the post implantation anneals on the electrical and physical properties were examined.
For those specimens heat treated to a temperature in excess of 500°C, the samples were encapsulated using deposited SiO₂. The effectiveness of this material as an encapsulant is discussed in section 5.2. The thesis describes the distribution and retention of Te and Sn, the quantity of crystalline disorder and the electrical properties of the surface layers all as a function of the implantation and anneal temperatures. The implantation energy was 150 keV.

Using the Hall effect technique, the resistivity, Hall mobility and Hall constant of the ion implanted layer was studied as a function of the temperature of analysis and as a function of depth. The Rutherford backscattering technique was used to study the distribution of the implanted impurity and the crystalline disorder. These techniques, along with the experimental details are described in chapter 3.

The experimental results are described in chapter 4. These results are examined in more detail in chapter 5. Among the topics discussed in this chapter are the effectiveness of SiO₂ as an encapsulant, the electrical properties of the crystalline disorder, the atomic distribution of Te and Sn and the donor properties of ion implanted Te and Sn in GaAs. The main conclusions taken from this discussion are given in chapter 6.

When this work was started in 1970, ion implantation was showing promise as a tool for improving the performance and yield of silicon devices, but at that time had not been accepted as a production technique. Since that date, there have been many advances, and this technique has gained acceptance as a production tool for the manufacture of a wide range of silicon devices with a near ultimate performance (see for example ref. 14). In GaAs, ion implantation has now been used to fabricate such devices as FET's¹⁵,¹⁶ laser diodes¹⁷ and Impatt diodes¹⁸. A review of the current literature relating to the formation of ion implanted n-type layers in GaAs, the distribution of the ion implanted impurity and the annealing of the radiation damage is given in chapter 2.
2. REVIEW OF SOME OF THE PROPERTIES OF ION IMPLANTED GaAs

This section will give a brief review of the literature dealing with the formation of electrically active ion implanted n-type layers in GaAs, the annealing of the radiation damage, and the distribution of the ion implanted impurity.

2.1 Formation of Low Resistivity Layers in GaAs by Ion Implantation

The formation of low resistivity ion implanted p-type layers exhibiting a high percentage of electrically active acceptor centres has been demonstrated for Cd, Zn, Mg, and Be. The peak electrical activity of these layers was close to the solubility limit of the dopant in GaAs. In contrast, only a small percentage of donor atoms normally becomes electrically active after annealing to similar temperatures. High donor activity has been observed for Se and Si implantations, but for these cases the ion doses investigated, and hence the carrier concentration within the peaks were low. At higher doses the percentage of the implanted ions which are electrically active decreases (see for example refs. 11, 13, 20).

In the last few years there has been much effort to determine the optimum conditions for the maximum electrical activity of donor ions implanted into GaAs. The effects on the measured electrical activity of the substrate, the implantation temperature, the encapsulant used during the high temperature anneals, and dual implantations have all been considered as variables and have been shown to have some effect on the measured activity. These variables will be discussed below.

(i) Effects Attributed to the Substrate

Hunsperger and Hirsch investigated the effect of implanting S with a dose around $5 \times 10^{12} \text{cm}^{-2}$ into semi-insulating substrates obtained from various manufacturers. It was thought that the observed spread in the doping efficiencies was due to the differences in the chromium content between the various substrate materials. However, for high doses the effects of compensation within the substrate would be less important.
(ii) Effect of the Implantation Temperature

Many workers\textsuperscript{12-24} have investigated the properties of the implanted layers as a function of the implantation temperature. They have found that if the implantation is conducted at temperatures in excess of 150°C, the resultant ion implantation damage is partially annealed during the implantation process\textsuperscript{4,21,22,23}, and that the minimum annealing temperature required to show donor activity was lower than that for a similar specimen implanted at 20°C\textsuperscript{22,23,24,25}. It was noted by Woodcock et al.\textsuperscript{20} that with the heavier ions such as Se and Sn, it was necessary to implant at a temperature above room temperature in order to get significant electrical activity, whilst with the lighter ions such as Si and S significant electrical activity could also be obtained after a room temperature implantation. The annealing temperature required to give donor activity was found to be greater than 500°C for all cases. It was found, by these workers that higher annealing temperatures than this were required for optimum electrical activity and it has been found to be advantageous to anneal up to a temperature of 900°C\textsuperscript{22,25}.

Harris\textsuperscript{12} has investigated the effects of implanting C and Si into GaAs at a substrate temperature between 77 and 300°K. He found that there was an annealing stage around 300°K and that defects formed during the low temperature implantations did not completely anneal out at 800°C. Other workers\textsuperscript{27,28} have noted that there are two stages for annealing of the radiation damage from the crystal lattice, one around 300°C for those specimens which do not have a completely amorphous surface layer, and the other around 600°C for specimens with initially amorphous layers. It has been shown by Guivarch et al.\textsuperscript{29} for 1 MeV Zn implanted at room temperature that there is still a measurable quantity of crystalline damage after a 900°C anneal. It has been shown by Itoh and Kushivo\textsuperscript{9,30} that As vacancies could be generated during a 500°C, Zn implant, and that these vacancies could diffuse to great depths into the crystal. The As vacancies generated formed stable donor - vacancy complexes within the substrate giving an intrinsic region which could be several microns thick.

The measurements of the electrical activity and of the ion implantation damage described above, indicate that for ion implanted
donors in GaAs, it is desirable to keep the damage produced during the ion implantation process to a minimum, and to implant at temperatures above room temperature. However, the substrate temperature must not be too high, otherwise As will be lost from the GaAs surface. This is in complete contrast to the case of the implantation of donors into silicon\(^{31}\), in which it was found advantageous to form an amorphous surface layer.

(iii) Encapsulant Used

When GaAs is annealed at temperatures in excess of 500°C, steps must be taken to ensure that the specimen surface does not dissociate. This is usually done by depositing a layer such as SiO\(_2\) or Si\(_3\)N\(_4\) on to the specimen surface before annealing. It is known that Ga readily diffuses through thermally grown SiO\(_2\) on Si\(^{32-36}\), and hence it is likely that Ga will outdiffuse through the deposited SiO\(_2\) from the GaAs substrate creating Ga vacancies within the surface layers of the crystal. Photoluminescence data for Te implanted GaAs samples given by Harris et al.\(^{22}\) has been interpreted as showing that when SiO\(_2\) was used as the encapsulant for a 750°C anneal the number of \([V_{Ga} + Te]\) complexes formed was much greater than when Si\(_3\)N\(_4\) was used as an encapsulant. The donor activity was higher for the silicon nitride encapsulated specimens. Bell et al.\(^{35}\) have observed that a gallium oxide was formed on the surface of a Te implanted GaAs specimen when SiO\(_2\) was used as the encapsulant for a 750°C anneal, but that this oxide was not formed when the specimens were encapsulated with silicon nitride. These results indicate that Si\(_3\)N\(_4\) may exhibit better encapsulant properties than SiO\(_2\). It has been noted that when Si\(_3\)N\(_4\) is used the electrical properties of the ion implanted layer have not been very reproducible after annealing\(^{36,37}\). Very reproducible electrical properties have been obtained by using evaporated Al as the encapsulant\(^{38}\). The main disadvantage of this encapsulant is that it can only be used for anneal temperatures up to about 700°C due to the formation of Ga\(_{1-x}\)Al\(_x\)As on the surface at higher annealing temperatures. A double layer encapsulant system of Al on a thin layer of thermally grown Ga\(_2\)O\(_3\) has been used up to temperatures of 800°C by Sealy and D'Cruz\(^{39}\). This system has been shown to exhibit superior encapsulant properties to the single layers of Ga\(_2\)O\(_3\) which have been grown at the same laboratories\(^{40,41}\). Other encapsulant systems
which have been used include AlN\textsuperscript{15}, Al\textsubscript{2}O\textsubscript{3}\textsuperscript{42} and polycrystalline silicon\textsuperscript{42}. With all of these encapsulant systems it was noted that, after annealing, the percentage of those implanted donors which are electrically active was low.

2.2 Lattice Location of the Ion Implanted Impurity

Lattice location data using the light ion channelling technique have been analysed for Te\textsuperscript{43} and Sn\textsuperscript{44}. These workers have investigated the angular dependence of the backscattered yield for the three major channelling directions, deducing that the implanted Te is substitutional after a 200°C implantation (dose of $6 \times 10^{18}$ m\textsuperscript{-2}, energy 70 keV) and that between 40% and 60% of a Sn impurity is substitutional for a room temperature implant annealed at 310°C (dose $7 \times 10^{15}$ m\textsuperscript{-2} energy 40 keV). Other workers\textsuperscript{7,23,24} have analysed data for one major direction, usually the $<110>$, and have found that only a small proportion (less than 10%) of the Te atoms were on non-substitutional sites for implantations at 180°C and 350°C, and for anneal temperatures up to 900°C.

2.3 Atomic Distribution of the Ion Implanted Impurity

Several techniques have been used to determine the atomic depth profiles of implanted ions in GaAs. By using radioactive isotopes and a layer removal technique, profiles have been determined for Kr\textsuperscript{45}, S\textsuperscript{47}, Zn\textsuperscript{47} and Na\textsuperscript{47}. Profiles of radioactive Kr and Tl\textsuperscript{48} were deduced from a study of the number of ions retained within the crystal lattice as a function of the ion implantation dose. The atomic profile of P\textsuperscript{49} has been determined using Auger electron spectroscopy with a sputter etching technique. The above data has indicated that the peaks in the atomic distribution are at a similar depth to that predicted by the L.S.S. theory, but that the tail in the distribution is deeper than predicted. The deeper penetration of the impurity has been attributed to channelling effects\textsuperscript{47} and to damage enhanced diffusion\textsuperscript{49}.

The profiles of the ion implanted impurity after annealing have not been determined in any great detail. It has been shown by
Bell et al.\textsuperscript{35} using electron spectroscopy combined with an ion sputtering gun and by Harris et al.\textsuperscript{22} using the backscattering technique that when a Te implanted specimen is annealed at a temperature above 750°C using SiO\textsubscript{2} as the encapsulant, there is a build up of Te on the GaAs surface. For specimens encapsulated with Si\textsubscript{3}N\textsubscript{4}, it was found that the movement towards the surface of the Te was small for a 750°C anneal\textsuperscript{35}, and was not observed after a 900°C anneal.\textsuperscript{27} The observed differences in the shapes of the Te depth profiles when Si\textsubscript{3}N\textsubscript{4} is used instead of SiO\textsubscript{2} as the encapsulant has been attributed to the oxidation of the surface Ga atoms and the etching in hydrofluoric acid of the Ga\textsubscript{2}O\textsubscript{3} in preference to the Te for those specimens encapsulated with SiO\textsubscript{2}\textsuperscript{35}. No oxidation of the Ga atoms was observed for these specimens encapsulated with Si\textsubscript{3}N\textsubscript{4}.

2.4 Depth Profiles of the Electrical Activity

Profiles of the electrical activity with depth have been determined for a wide range of implantation and annealing conditions. If the ions are implanted at a substrate temperature of 180 or 200°C and then annealed to a temperature less than 800°C, then the peaks in the curves of the electron concentration with depth are deeper than that predicted by the LSS theory for S\textsuperscript{20}, Se\textsuperscript{20,38}, Sn (using a Si\textsubscript{3}N\textsubscript{4} encapsulant); for Te\textsuperscript{41} (SiO\textsubscript{2} encapsulant); Se\textsuperscript{38} (Al encapsulant); and Sn\textsuperscript{39} (Al on Ga\textsubscript{2}O\textsubscript{3} encapsulant). For the case of ions implanted at 20°C into GaAs and then annealed up to 750°C, Te\textsuperscript{41} gives the peak in the electron concentration deeper than that predicted, whereas for Si\textsuperscript{20} and S\textsuperscript{22}, the peaks were at depths similar to the L.S.S. theory. Implanting at 300°C or higher and annealing at temperatures around 900 - 950°C have given peaks in the electron concentration at depths similar to that predicted for Si\textsuperscript{20,42} and Te\textsuperscript{25,26}.

These differences observed in the profiles may be due to the differing implantation and annealing temperatures used by the various groups. In all cases, the tails in the distribution of the electrical activity with depth were more deeply penetrating than predicted by the theory. Müller et al.\textsuperscript{26} investigated the temperature dependence of the depth distribution of the electrical activity of sulphur, implanted at 350°C, over the temperature range 750°C to 900°C and
observed that the higher the annealing temperature the more deeply penetrating the tail becomes. The deep profiles observed by Miyazaki et al. for a 900°C, 60 min. anneal have been attributed to the diffusion of silicon. For this case, the electron concentration approached the limiting value normally observed for Si in bulk grown GaAs.

2.5 Dual Implantations

Heckingbottom and Ambridge published a paper which suggested that if impurity atoms are implanted into a III-V compound, and if these predominantly reside on one sublattice, then a number of vacancies will be created on the other sublattice. It was suggested by these authors that if stoichiometry was maintained by performing a second implantation with either a III or V atom to fill these vacancies, an increase in the percentage activity should be obtained. There has been little experimental data published to verify this theory. Recently, Ambridge et al. have demonstrated that the electrical activity for a dual implantation of Ga + Se was higher than a single implant of Se (doses $2 \times 10^{16} \text{m}^{-2}$). Moreover, the profiles of the electrical activity indicated that the enhanced activity occurred at the depth where the Ga concentration was a maximum.
3. EXPERIMENTAL TECHNIQUES

3.1 Sample Processing

3.1.1 Material Preparation

The bulk grown GaAs material was bought from several suppliers in the form of ingots. These were sawn into wafers approximately 2 mm thick using a diamond saw. These slices were then polished on a Hyprocel-Pan-W pad with a solution of 1% Br in methanol, removing about .25 mm of material at this stage. After polishing, the slices were diced into 5 × 7 mm specimens using a wire saw, thoroughly degreased in trichloroethylene and acetone, and attached to a P.T.F.E. disc using black apiezone wax. The polished surfaces were then etched for 10 mins. in a rotating beaker containing a solution of 0.75% Br in methanol. The specimens were removed from the P.T.F.E. disc by dissolving out the black wax in trichloroethylene, cleaned in acetone and stored in plastic boxes until required. Prior to ion implantation, the specimens were further degreased in a reflux degreasing bath containing iso-propyl-alcohol (I.P.A.).

The slices of epitaxial material were diced up using a wire saw into specimens 4 × 5 mm and degreased in trichloroethylene and acetone. They were also given a further wash with I.P.A. in a reflux degreaser just prior to implantation. A summary of the material parameters are given in table 1.

The specimen orientation was checked on one specimen from each slice using the Laue back reflection X-ray technique. This specimen was not used in subsequent investigations.

3.1.2 Ion Implantation

All the specimens were implanted on the 90 degree port of the University of Surrey 600 keV heavy ion accelerator which was then situated in the laboratory on the Dennis site. At that time the machine was capable of implanting Te and Sn at ion energies ranging from 15 keV to 300 keV.
<table>
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<tr>
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<th>Supplier</th>
<th>Orientation</th>
<th>Type</th>
<th>Dopant</th>
<th>Doping Concentration</th>
<th>Mobility m² V⁻¹ s⁻¹</th>
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<td>B-SI</td>
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<td>E-N/SI</td>
<td>Te</td>
<td>1x10²² m⁻³</td>
<td>0.6</td>
</tr>
<tr>
<td>S18R2C</td>
<td></td>
<td>100</td>
<td>E-N/SI</td>
<td>Te</td>
<td>1x10²¹ m⁻³</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Key to Table

B  Bulk grown
E  Epitaxially grown
M  Mullard Research Laboratories, Redhill
MCP  M.C.P. Electronics Ltd., Wembley
N  N-type
N/SI  N-type on semi-insulating substrate
P  P-type
RRE  Royal Radar Establishment, Malvern
SI  Semi-insulating substrate

Table Listing the Dopant Parameters for the GaAs ingots

Table 1
Energy and mass analysis of the ion beam was carried out using a magnetic separator. The various atomic isotopes were well resolved, and the ion beam was identified by the relative heights of the major isotopes. Ion doses were measured using a current integrator. Secondary electrons from the target were suppressed by a flat plate 1 cm from the sample, which had a potential relative to the specimen of -300 V. Further details of this facility are given by Cracknell et al.\(^5\)

The specimens were implanted singly using a beam defining aperture of 1.5 cms x 1 cms. Reproducibility of the ion dose was checked by implanting several specimens and measuring the number of implanted atoms which had been implanted into the substrate using the Rutherford backscattering technique as described in section 3.3. The relationship between the measured number of implanted atoms as a function of the nominal ion dose measured by the current integrator is shown in Fig. 1. It can be seen from this figure that although the reproducibility of the measured ion dose was within the measurement accuracy of the backscattering technique, the measured number of implanted atoms was approximately 1.7 times the nominal dose. This discrepancy may be due to a neutral component of the ion beam, or due to inadequate suppression of the secondary electrons.

All the ions were implanted in a non-channelled direction by misaligning the specimens by 7° from the <110> . Specimens were implanted with a substrate temperature of 20°C, 100°C, 180°C or 250°C. The ion energy was 150 keV and the dose rate was \((4 \pm 3) \times 10^{16}\) ions m\(^{-2}\)s\(^{-1}\).

### 3.1.3 Annealing of Specimens

All the specimens were annealed for 15 mins. in a resistance heated furnace with a quartz tube which was purged with dry N\(_2\). The samples were placed on an etched GaAs furnace boat with the ion implanted surface in contact with the boat.

When annealing specimens at temperatures in excess of 500°C, the ion implanted surface was coated with SiO\(_2\) which was grown by the pyrolytic decomposition of silane gas in oxygen at a temperature of 400°C, as described by Tansey\(^5\).
The Number of Implanted Atoms Measured using the Backscattering Technique as a Function of the Implanted Dose Measured using the Current Integrator

FIGURE 1
The oxide thickness was 400 ± 100 nm thick. A few specimens were coated, by the Mullard Research Laboratory, with 200 nm of sputtered $\text{Si}_3\text{N}_4$. This was deposited at a temperature of 350°C.

3.1.4 Layer Removal Technique

The layer removal technique used was based on a chemical etching system described by Sansbury and Gibbons$^{13}$. The etching solution was composed of $\text{H}_2\text{O}_2$ (assay about 98%), $\text{H}_2\text{SO}_4$ (conc.) and deionised water, in the ratio of 1:1:x where x was the quantity of deionised water which was varied as explained below. A small blob of black wax was put on the specimen surface to act as a mask against the etchant. The stripping procedure consisted of washing the slice in distilled water, transferring the specimen into the etchant such that the surface of the slice remained wet, etching for a known time, and then transferring the slice back into a beaker of distilled water such that a bubble of the etchant remained on the specimen until it was quenched in water. This procedure ensured that the specimen surface did not dry out at any time during the etching cycle, and reduced the risk of the GaAs being etched unevenly.

The etch rate on the $\langle110\rangle$ face of bulk grown GaAs is shown as a function of the concentration of the etchant in Fig. 2. These specimens were etched for a time greater than 1 hr. in a slowly rotating beaker, the step height being measured with an interference microscope. It was noted that after etching the surface roughness was dependent on the concentration of the etch, the smoothest results being obtained with the etch concentrations of $x = 100$ and $x = 500$.

Undercutting at the step edge was observed. This was due to turbulence of the etchant at the step edge and was eliminated when etching in a free standing beaker. Later measurements, on the step heights produced by a series of 30 sec. etches on ion implanted material, indicated that the etch rate was a function of either the crystalline damage or of the chemical effects of the implanted dopant. It was noted that specimens with a high degree of disorder etched about 50% slower in the disordered region. Some high dose Te implanted specimens annealed at 650°C also etched approximately 50% slower than
Etch Rate versus Etch Concentration
For the $H_2SO_4, H_2O_2, H_2O$ System

FIGURE 2
the underlying bulk material. The step heights in these cases were measured using a Rank Taylor Hobson Talystep. Using this technique step heights as small as 5 nm could be measured to within 10% of the step height. Using an etch concentration of 1:1:100, the surface roughness for step heights less than 100 nm was less than 10% of the step height, and steps could be etched up to about 1 μm before serious surface degradation was observed. The surface roughness was found to increase as the number of etching cycles increased.

After etching off 100 nm of GaAs from the surface, it was observed, from the <110>-aligned Rutherford backscattering measurements that the Ga and As surface peaks were similar in height. However for the case of heavily doped Te implanted samples, build up of Te on the surface was observed indicating that the Te etches at a much slower rate than the Ga or As.

The amount of material etched off was checked by measuring the step height after between 1 and 4 stripping cycles.

3.2 Electrical Profile Determination from Hall Effect Measurements

3.2.1 Theory

Hall effect and conductivity measurements were made using the technique developed by Van der Pauw. In this technique one may determine the resistivity, \( \rho \), and the Hall constant \( R_H \) of irregularly shaped samples from the following equations:

\[
\rho = \frac{\pi d}{\ln 2} \left( \frac{R_{ABCD} + R_{BCDA}}{2} \right) f \left( \frac{R_{ABCD}}{R_{BCDA}} \right) \]

\[
R_H = \frac{d}{B} \cdot \Delta R_{BDAC} \]

where:

d is the specimen thickness
B is the applied magnetic field
\( R_{ABCD} \) is defined as the potential difference \( V_D - V_C \) between contacts

\( f(x) = \frac{x + \sqrt{x^2 - 1}}{2} \)
D and C per unit current through the contacts A and B, where A, B, C, D refers to four successive contacts fixed at arbitrary places along the circumference of the sample.

f is a function of \( \frac{R_{ABCD}}{R_{BCDA}} \) and is described in reference 52.

From a single Hall effect and conductivity measurement, one can determine a weighted average mobility, carrier concentration and resistivity of a sample. As these measurements will give the average doping concentration throughout the sample, some means must be found of either isolating the implanted layer from the bulk material, or arranging the experiment such that there is only a thin layer of the material being measured. This may be done practically by implanting the donors into semi-insulating material, into p-type material, or into a thin epitaxially grown n-type layer on a semi-insulating or p-type substrate.

It has been shown by Baron et al.\(^{31}\) that if one removes a thin layer from the surface of the specimen and repeats the Hall effect measurements then the average mobility, \( \mu_H(x) \), carrier concentration \( n(x) \), and resistivity \( \rho(x) \), of the layer removed can be determined from the equations:

\[
\mu_H(x) = \frac{\frac{d(R_s \sigma_s^2)}{dx}}{\frac{d\sigma_s}{dx}} \quad \text{.............................. (3.3)}
\]

\[
n(x) = \frac{\mu_H(x)}{e \mu_c(x)} \left( \frac{d\sigma_s}{dx} \right)^2 / \frac{d(R_s \sigma_s^2)}{dx} \quad \text{.............................. (3.4)}
\]

\[
\rho(x) = \frac{1}{\frac{d\sigma_s}{dx}} \quad \text{.............................. (3.5)}
\]

\( R_s \) is the sheet Hall coefficient

\( \sigma_s \) is the sheet conductivity

\( e \) is the electronic charge

Hence by successively removing thin layers of material from the
semiconductor surface we can determine the depth distribution of the net electrical activity. By integrating the total number of ions as a function of depth, we can deduce the total concentration of electrically active ions, assuming that the compensating effect of the damage is negligible.

3.2.2 Experimental Details

Hall effect measurements were taken as a function of the temperature of analysis (between 78°K and 300°K), as a function of the annealing temperature (between 50°C and 700°C) and as a function of the amount of material etched from the surface of the specimen. To minimise second order effects, each Hall effect and conductivity measurement was repeated with the current and magnetic fields reversed. An automatic switch sequence was used which allowed current to flow through the current terminals of the specimen, and connected the voltage terminals to the digital voltmeter. The switching box also controlled the magnet and specimen currents.

Voltages were measured using a Solartron D.V.M. (type No. LM1604). The current source consisted of a 1 kV battery in series with a switched resistor which had a value between $10^7$ and $10^{11}$ ohms. The magnitude of the current was determined by measuring the voltage dropped across a standard 10 K ohm resistor. To reduce heating effects of the ion implanted layers, the specimen current was kept as small as possible typically between $10^{-8}$ and $10^{-5}$ A. The voltages measured were between 10 and 200 mV. Changes in the resistivity which could be attributed to the resistive heating of the ion implanted layer by the analysing current were not observed. The magnetic field was set to 5 kG ± 5%. The magnetic field was not measured on a routine basis, but the electric current through the coils of the electromagnet was measured and reset to within 0.5% of a known value. The magnet current was derived from a Kingshill power supply (type No. S6010B) which was used in a constant current mode. Care was taken to minimise hysterisis effects by reversing the magnet current several times before measuring the Hall effect voltage.
For the low temperature measurements, the samples were mounted in a cryostat. This consisted of a thin, hollow copper cylinder which could be internally cooled with liquid nitrogen. The specimen was attached to the outside of the cylinder which was mounted inside a vacuum chamber situated between the pole pieces of an electromagnet. The pressure inside the chamber was $1 \times 10^{-6}$ torr. The specimen temperature was measured by the output of a copper constantan thermocouple with the reference junction in an ice bath. Details of the other sample holders used, along with other details of the equipment are contained in refs. 51 and 55.

Electrical contact to the specimen was made in one of three ways:

A. Small tin contacts were alloyed onto the ion implanted surface, near the corners of the specimens. These contacts were alloyed onto the GaAs at a temperature of 250°C in an atmosphere of nitrogen with a trace of moist HCl gas. This method of making electrical contact to the ion implanted layers was used for those specimens annealed at temperatures in excess of 500°C.

B. Using four gold probes, one in each corner of the slice. This method was used in the isochronal annealing sequences, and for the layer removal measurements of unannealed specimens.

C. Attaching fine copper wires to the slices using silver dag. This method was used for making electrical contact with a specimen, when it was mounted in the cryostat for the low temperature investigation.

The maximum sheet resistivity which could be measured was limited by the input impedance of the digital voltmeter. At a sheet resistivity of $10^8$ ohms per sq., the error due to the input impedance of the D.V.M. was 2%. The estimated error in the resistivity was 1% for sheet resistivities below $10^7$ ohms per sq. For a well annealed n-type specimen, the estimated error in $R_H$ was 2%. The error in determining the conductivity, and of the value of the reciprocal Hall coefficient as a function of depth was estimated to be between 20 and 30%. This large error is due to the relatively small changes measured in the sheet values of $\rho(x)$ and $R_H(x)$ as the material was etched away.
The finite size of the electrical contacts resulted in an estimated systematic error of 10% (from the equations given by Van der Pauw\textsuperscript{52}). This was checked by measuring several specimens before and after etching into clover leaf shaped patterns. It was observed that the etched specimens had approximately a 5% larger Hall coefficient than the unetched specimens.

### 3.3 The Rutherford Backscattering Technique

#### 3.3.1 Theory

##### 3.3.1.1 Introduction

This technique relies on the close interaction of fast moving light particles (such as protons or helium ions) with the atomic nucleus of the target atoms. If a target is bombarded with a beam of monoenergetic light ions and the energy of those particles undergoing a single large angle scattering is analysed into a plot of the number of backscattered particles as a function of energy, then the exact position and shape of this energy spectrum can provide quantitative information on the atomic composition of the target as a function of depth\textsuperscript{45}.

The main features of the backscattering technique are illustrated for the case of an amorphous target which has been implanted with ions of a heavier mass in Fig. 3. The energy spectrum of the backscattered particles consists of a sharp edge, which corresponds to the elastic scattering from the substrate atoms in the surface region, followed by a smooth slowly varying yield at lower energies which corresponds to scattering from the substrate atoms at progressively greater depths. The ions backscattered from the heavier implanted impurity atoms will have a smaller elastic energy loss than those backscattered from the substrate atoms. Hence the edge of the impurity spectrum occurs at a higher energy than the substrate. As the implanted impurity ions are generally confined to a relatively thin surface region (often less than .1 micron for heavy ions implanted into a light substrates at moderate implantation energies) the impurity spectrum consists of a fairly sharp peak.
THE MAIN FEATURES OF THE BACKSCATTERING TECHNIQUE FOR THE QUANTITATIVE ATOMIC ANALYSIS OF AN ION IMPLANTED TARGET

FIGURE 3
3.3.1.2 Profile Determination

The energy of an ion after undergoing a large angle scattering from an atomic nucleus is given by the formula due to Rutherford (see ref. 4 page 138),

\[ E_f = E_i \left( \frac{M_1 \cos(\alpha) + \left[M_2^2 - M_1^2 \sin^2(\alpha)\right]^{1/2}}{M_1 + M_2} \right)^2 \]  \hspace{1cm} (3.6)

where \( E_i \) = energy of ion immediately before scattering

\( E_f \) = energy of ion of mass \( M_1 \) immediately after being scattered through an angle \( (180^\circ - \alpha) \) by an atomic nucleus of mass \( M_2 \).

It can be seen from eqn. 3.6 that for a fixed scattering angle and ion mass, the ratio of the energy of the ion immediately after undergoing a scatter to that immediately before scattering is only dependent on the mass of the scattering centre.

When a high energy ion beam is incident on the surface of an amorphous layer, only a very small proportion of the beam will undergo a large angle scattering due to the surface atoms. The rest of the ions will penetrate the surface and lose energy. A few of the ions will undergo a large angle collision at some depth, \( t \), below the surface of the substrate, continue to lose energy until the specimen surface is reached, and then (assuming the scattering angle is between certain limits) be detected by the energy detection system.

The energy \( E_2(t) \) of the ions reaching the detector will be given by\(^5\)

\[ E_2(t) = k \left[ E_1 - \int S(E_1)dt + \int S(E_2)dt \right] \]  \hspace{1cm} (3.7)
where \( S(E) \) is the stopping power of the ion as a function of energy and subscripts 1 and 2 refer to the ingoing and outgoing paths of the ion beam.

\( k \) is the ratio \( E_f/E_i \) from equation 3.6.

\( \theta \) is the angle between the incoming light ion beam and the direction of the normal of the specimen surface projected onto the plane containing the incoming ion beam and the detector (detector/ion beam plane).

\( \phi \) is the angle between the incoming light ion beam and the direction of the normal projected onto the plane containing the incoming ion beam which is perpendicular to the detector/ion beam plane.

and the other terms are defined in figure 3.

Consider a surface layer a few hundred angstroms thick. In this region, \( S(E_1) \) and \( S(E_2) \) approximate to constants. Then equation 3.7 becomes:

\[
E_2(t) = k E_1 - \frac{t}{\cos(\theta)} \left( \frac{k S(E_1)}{\cos(\theta)} + \frac{S(E_2)}{\cos(\alpha-\theta)} \right) \quad (3.8)
\]

For a high energy light ion the electronic stopping power is the dominant process. If there are negligible inelastic energy loss mechanisms present, and as \( S(E) \propto E^2 \) for an electronic stopping mechanism, then:

\[
S(E_2) = k^2 S(E_1)
\]

substituting for \( S(E_2) \) in equation 3.8 and putting

\[
T = \frac{t}{\cos(\theta)} \left( \frac{k}{\cos(\theta)} + \frac{k^2}{\cos(\alpha-\theta)} \right) \quad (3.9)
\]

we obtain:

\[
E_2(t) = k E_1 - T S(E_1) \quad (3.10)
\]

where \( T \) is the effective path length of the ion.
Hence, the energy axis can be directly transferred into a linear depth scale. It should be noted that as \( S(E) \propto E^2 \) and the separation of the GaAs and Te edges is 113 keV for a 1.5 MeV He ion beam, the assumption that \( S(E) \) is approximately constant will lead to an error of about 2\% in the depth scale.

In order to determine the impurity profile from the energy spectrum, it is necessary to determine a relationship between the number of backscattered ions and the concentration of scattering centres. Consider the numbers of backscattered ions due to a heavy impurity at a depth, \( t \), in the substrate. From scattering theory, the number of ions detected due to a single large angle scattering at an energy \( E_i \) is given by:-

\[
C_i = \rho_i \frac{d\sigma}{d\Omega} (E_i) \Delta t Q \Omega_d
\]  

where

\( \rho_i \) is the density of impurity ions at the depth \( t \).

\( \frac{d\sigma}{d\Omega} (E_i) \) is the scattering cross-section of the ion/impurity system.

\( \Delta t \) is the thickness of the layer under investigation

\( Q \) is the total number of projectiles

\( \Omega_d \) solid angle of the detector

A similar equation is obtained for the scattering of the ions by the substrate,

\[
C_s = \rho_s \frac{d\sigma}{d\Omega} (E_s) \Delta t Q \Omega_d
\]

where \( \rho_s \) is the density of substrate ions

Dividing equation 3.12 by 3.11 and rearranging we obtain:
The scattering cross-section of an ion is given by the Rutherford scattering formula\(^3\) (for close interactions of the atomic nuclei),

\[
\rho_i = \frac{c_i}{c_s} \cdot \rho_s \cdot \left( \frac{d\sigma_s}{d\Omega} (E_s) \right) \left( \frac{d\sigma}{d\Omega} (E_1) \right) \tag{3.13}
\]

where subscript \(1\) refers to the moving ion

subscript \(2\) refers to the substrate atom

\(Z\) is the atomic number

\(M\) is the atomic mass

\(E\) is the energy of the ion in MeV

\(\beta\) is the scattering angle in centre of mass co-ordinates

It can be seen from eqn. 3.14 that the last bracket of equation 3.13 is independent of the ion energy and of the geometry of the detection system. Hence if we know the atomic concentration of the substrate we can directly relate the number of detected particles in any one channel of the impurity peak to an atomic concentration.

For the purpose of these calculations the value of the substrate density was taken to be that of the bulk material (i.e. \(4.43 \times 10^{28}\) atoms m\(^{-3}\)). However this figure may be in error for our heavily doped ion implanted samples due to:

(a) the direct replacement of the Ga or As atoms by the impurity atom. In the worst case, for a \(1 \times 10^{20}\) m\(^{-2}\), 150 keV Te implant, the peak impurity concentration will be of the order of \(1 \times 10^{27}\) atoms m\(^{-3}\), i.e. of the order of 2\% of the bulk concentration. If the Te directly replaces the Ga or As, then a reduction in the Ga or As yields of 2\% should result.
(b) Lattice expansion as a result of the impurity added.

(c) Increased number of vacancies due to the radiation damage.

All of these effects will reduce the concentration of the Ga and As atoms in the surface layers. However, this decrease was below the sensitivity of the experiment.

The shape of the impurity peaks will be distorted by pulse-pile up and by the close proximity of the GaAs edge. This type of distortion was corrected for by subtracting the energy spectrum of an unimplanted control sample from the energy spectrum of the implanted specimen. The control spectrum was determined under identical conditions to the implanted cases.

There are several practical limitations to the use of the backscattering technique:-

1. The implanted ion generally has to be heavier than the substrate material, otherwise the impurity peak will become lost in the very much higher substrate yield.

2. The silicon surface barrier ion detectors used have resolutions of the order of 12 to 20 keV F.W.H.M. (full width half maximum). This energy resolution is equivalent to depth resolution of the order of 0.02-0.03 micron which is approximately the same as the impurity peak width observed under our experimental conditions (for 150 keV Te in GaAs). The effect of this relatively large detector resolution is to smear out the impurity peak and the edge of the substrate.

3. With the experimental conditions used, it is insensitive to Te impurity concentrations less than 0.05 at. %, and hence was only suitable for investigating the impurity concentration of those samples implanted with 150 keV Te at doses greater than $5 \times 10^{18} \text{m}^{-2}$.

The problem of the large detector resolution may be overcome in one of two ways:-
A. Using a layer removal technique.

Although the solid state detectors smear out the impurity peaks, the total area under the peak will bear a constant relationship to the yield of the continuum for a constant implanted impurity concentration. Hence if one uses a layer removal technique and monitors the change in area of the impurity concentration as material is removed from the front surface, one should be able to produce a depth profile of the impurity concentration. However with the chemical etching technique used (as described in section 3.1.4), it was found that although the gallium and arsenic had equal dissolution rates, the dissolution rate of the Te was very much less. This resulted in a build up of Te on the front surface of the specimen as the GaAs was etched away.

B. The deconvolution technique.

The relatively poor resolution achievable with the detection system may be reduced by correcting the observed energy distribution of the backscattered particles using the deconvolution technique. This was first applied to an ion implanted As peak in silicon by Zeigler and Baglin\textsuperscript{5}. This technique is described in Appendix A, but was found to be limited in its practical value.

3.3.1.3 Information from the <110> channelled spectra

When the direction of travel of the He ion beam is aligned with one of the major crystallographic directions, the ion beam becomes channelled down these crystallographic rows. The chances of a large angle scattering with one of the atomic lattice atoms is very much reduced. The major number of large angle scatterings in this case will be either due to atoms not sitting on normal atomic lattice sites or due to He ions becoming dechannelled and then interacting with the lattice atoms in the normal way. Hence the backscattering spectrum taken for the He ion beam aligned with say the <110> direction can yield information about the relative quantity of crystalline damage, the percentage of the impurity atoms which are not sitting on lattice sites, and on the surface stoichiometry. With this technique it is not easy to measure the crystalline disorder directly, but measurements
taken and compared to a known standard will give an indication of the relative crystalline disorder.

The quantity of crystalline damage is usually defined in one of two ways:-

A. If a damage peak is observed in the aligned backscattered spectrum then the quantity of disorder may be defined as the area under the damage peak which has been normalised to the non-channelled spectrum.

B. An alternative method of defining the relative disorder is the minimum yield behind the damage peak of the channelled backscattered spectra normalised to the non-channelled energy spectra. This quantity is known as $\chi_{\text{min}}$.

For some of the implanted specimens analysed in the work presented in this thesis, no damage peak was observed. For these cases the damage parameter, $\chi_{100}$ was used, where $\chi_{100}$ was defined as the yield of the channelled spectra at 174 keV from the As surface peak normalised to the non-channelled energy spectra. (This was equivalent to 100 channels on the energy spectra).

The percentage of those atoms which do not lie on substitutional lattice sites can be determined from the equation:-

$$\text{Percentage of non substitutional atoms, lying along an axial row} = 100 \times \frac{N_a}{N_r} \quad \text{......... (3.15)}$$

where the interaction yields between the incident and dopant atoms for a channelled and non-channelled incidence are denoted by $N_a$ and $N_r$ respectively.

The use of eqn. 3.15 may lead to a systematic error as no allowance is made for flux peaking, or for the probability of an incident ion which has been dechannelled by some means other than a close encounter with an atom which is not on a lattice site having an
interaction with an impurity atom. However, before an estimate of this percentage error can be made a knowledge of the dechannelling rate under the experimental conditions used has to be determined. In practice, this will be difficult due to the crystalline disorder in the region of the impurity peak. Lattice location of impurity atoms is discussed in the channelling review of reference 57.

In principle the ratio of the number of Ga to As atoms at the surface can be deduced from the relative He ion yields of the back-scattering spectrum. It was found that although the Ga and As edges for the non-channelled spectra were not adequately resolved, the Ga and As surface peaks seen for the \(<110>\) aligned spectra were resolved. The magnitude of these surface peaks is dependent on the degree of surface disorder and on the concentration of the Ga and As atoms in the surface layers.

By considering the following simple model, it will be shown that the measured Ga:As ratio at the surface may underestimate the true Ga:As ratio. When the He ion beam is aligned with the \(<110>\) channel of a perfect GaAs crystal, the ion beam would see rows of As atoms and rows of Ga atoms extending down the channel. If one of the surface Ga atoms is removed, and the ion beam is perfectly aligned with the \(<110>\) channel, then those He ions which would have normally been scattered by the Ga atom which is now missing from the lattice will interact with the next atom in the row down the channel. This atom will be another Ga atom. Hence it can be seen from the simple model that if there are a large number of Ga vacancies within the first few atomic layers of the GaAs crystal, we would not expect a large change in the relative heights of the Ga and As surface peaks, assuming that the GaAs crystalline structure extended without distortion to the surface. However, if the number of Ga vacancies within the surface region is large, it might be expected that some of the As atoms would be pulled away from their normal atomic positions by the interatomic forces, resulting in a lowering of the measured Ga peak and an increase in the measured As peak. This model would also predict a broadening of the Ga surface peak due to the energy loss of the ion beam whilst travelling down the 'channel' before interacting
with the 'first' Ga atom. However, this will be small due to the thinness of the layer being measured. Hence, using the backscattering technique one might expect to see only a small reduction in the As:Ga ratio and little peak broadening if the Ga concentration is reduced by several orders of magnitude within the surface regions of the GaAs.

The height of the As peak is a function of the number of As atoms on the As sublattice only. However, the height of the Ga peak is a function of the number of Ga atoms in the Ga sublattice and of the amount of crystalline disorder on the As sublattice. If it is assumed that the amount of crystalline disorder on the As and Ga sublattices is similar, then the value of \( \chi_{\text{min}} \) is a measure of the disorder on either the Ga or As sublattices. The Ga peak height was therefore defined as the measured Ga peak height minus \( \frac{1}{2} \chi_{\text{min}} \) (non-channelled yield). The surface stoichiometry was then determined from the ratio of the As peak height to the calculated Ga peak height, and correcting this ratio, using an equation similar to equation 3.13 for the differing atomic scattering cross-sections of the Ga and As atoms.

### 3.3.2 Experimental Details

The Rutherford backscattering facility used has been described by Gettings.\(^5^5\) During the course of this work, this whole system was moved from the site at the Dennis Bros. factory to the new accelerator laboratory on the university site. The equipment and beam geometry were not altered after the move.

A beam of 1.5 ± 0.05 MeV He\(^+\) ions with a divergence of 0.05 degree and a diameter of 1 mm. was used to probe the surface layers of the specimens. The energy of the ion beam could be reset to within ±5 keV. The He ions were scattered through an angle of 150° and were detected by an Ortec Si surface barrier detector. Pulse height analysis was made with an Intertechnique 800 channel analyser. The linearity of the electronics has been measured with an Ortec precision pulse generator, and was found to be better than 0.5%.

Energy spectra were taken for a <110> and an associated non-channelled direction. Each spectrum was taken using a beam current...
of 1.5 - 2 nA. The stopping power of the 1.5 MeV He ions in GaAs has been measured to be 360 ± 40 keV \( \mu \text{m}^{-1} \) as described in appendix B.

The resolution of the detector and associated electronics was measured directly by observing the backscattered spectrum of a thin gold film which had been evaporated onto an aluminium substrate. The thickness of the gold film was less than 10 nm. If the incident ion energy is known, the energy scale of the backscattered spectrum can be calibrated. The width of the peak due to the gold film at half its maximum height is then a measure of the detector resolution. In all the experimental determinations of the detector resolution, the peak on the backscattered spectra due to the gold film was symmetrical about its centre point indicating that little ion energy is lost in the gold film.

The detector resolution was measured at the beginning of each day's work.

Initial experiments were conducted using an Ortec detector having an energy resolution of 17 keV. The deconvolution technique, as outlined in appendix A, was used to correct the impurity peaks for the finite detector resolution. This correction resulted in a reduction in the resolution to 12 keV (equivalent to a depth resolution of about 20 nm.). Later measurements were conducted using an Ortec Premium grade detector with a resolution of 12 ± 1 keV. The deconvolution technique was not applied to the impurity peaks of these spectra as no significant change in the resolution could be obtained.

There are several sources of error in this experimental technique:

A. Statistical counting error due to the random nature in which the particles were detected.

B. Correction of the impurity peak for pulse pile up. This error will be larger for smaller ion doses, and in the region deep into the crystal close to where the impurity peak merges with the random edge.
For the impurity profile in the aligned direction, the pulse pile up correction was insignificant, however, the statistical error was higher due to the smaller number of detected particles.

3.4 Thermal Probe

This is a useful instrument for determining the conductivity type of a semiconductor. If a hot gold wire probe and a gold probe which is at room temperature are placed on a semiconductor surface, the thermal energy supplied to the majority carriers by the hot probe will cause these to diffuse away from the hot zone. This will create a potential difference between the hot and cold zones. The sign of this potential difference will be an indication of the current carrier type.

The apparatus used consisted of two gold probes, one of which was heated by a d.c. electric soldering iron. The probes were held in micromanipulators. A DVM was used to measure the potential difference across the two probes. Further details of the Equipment are given by Tansey.
4. EXPERIMENTAL RESULTS

4.1 Introduction

This chapter describes the results of an investigation into some of the properties of GaAs which has been implanted with Sn and Te ions. The results have been described in three sections, one dealing with the physical properties of the ion implanted layer, one relating to the surface properties of the GaAs crystal and the encapsulant, and the third describing the electrical properties of the ion implanted layer. The results from the first two sections describing the physical properties have been derived from the Rutherford backscattering experiments. The electrical properties were investigated using Hall effect measurements. These measurement techniques have been described in chapter 3.

4.2 Physical Properties of the Ion Implanted Layer

4.2.1 Dose Dependence of the Crystalline Damage

The dose dependence of the backscattered energy spectra taken in a $<110>$ channelling direction is shown in Fig. 4 for GaAs specimens implanted with Te at a substrate temperature of 20°C. A peak in this energy spectrum is seen, the maximum height of which is similar to that of the backscattered energy spectrum taken in a non-channelled direction. The width of this peak increases with increasing dose. The dose dependence of the aligned backscattered spectra is shown in Fig. 5 for specimens implanted with Te at a substrate temperature of 180°C. A similar dose dependence was seen for specimens implanted with Sn under identical conditions. The aligned yields increase with increasing dose over the dose range investigated. This yield is small in comparison to the yield observed from GaAs specimens implanted at room temperature. An apparent change in the rate at which the ions are being dechannelled is seen at an energy of $70 \pm 10$ keV from the GaAs edge for both the Te and Sn spectra. It was observed that the shape of the energy spectrum for the highest implantation dose was different from that for the lower doses. It can be seen from Fig. 5 that the Ga peak is no longer resolved from the background, and that
ION ENERGY - 150 keV
IMPLANTATION TEMP. - 20°C
NO ANNEAL
Te DOSE:  
- $5 \times 10^{18}$ m$^{-2}$
- $1 \times 10^{19}$ m$^{-2}$
- $5 \times 10^{19}$ m$^{-2}$

SPECTRA <110> ALIGNED
CHARGE COLLECTED 5 μC
ONE CHANNEL = 1.45 keV
RESOLUTION = 17 keV

Note: - For clarity
only 1 in 3 data points are shown

THE ALIGNED BACKSCATTERING SPECTRA AS A FUNCTION OF DOSE
FOR GaAs IMPLANTED AT 20°C.

FIGURE 4
ION ENERGY - 150 keV
IMPLANTATION TEMP. - 180°C
NO ANNEAL

Te DOSE: -- Curve 1  $1 \times 10^{20}$ m$^{-2}$
2  $5 \times 10^{19}$ m$^{-2}$
3  $1 \times 10^{19}$ m$^{-2}$
4  $5 \times 10^{18}$ m$^{-2}$
5  Unimplanted

MATERIAL - P-TYPE Ingot No. X2314
SPECTRA <110> ALIGNED
CHARGE COLLECTED - 5 μC.
ONE CHANNEL = 1.75 keV
RESOLUTION - 12 keV

THE ALIGNED BACKSCATTERING SPECTRA AS A FUNCTION OF DOSE
FOR GaAs IMPLANTED AT 180°C.

FIGURE 5
the As peak height is lower than the unimplanted level.

4.2.2 Dependence of the Crystalline Damage on the Annealing Temperature

The aligned backscattered yield was investigated for a series of 15 min. isochronal anneals between 350°C and 750°C. This anneal temperature dependence is shown in Fig. 6 for a Te dose of 1 × 10^{19} \text{m}^{-2} implanted at 20°C. The yield decreased with increasing anneal temperature up to 650°C. A significant damage peak was observed even after the 650°C anneal, and the Ga and As surface peaks were not resolved indicating the presence of a disordered surface layer.

A summary of the annealing behaviour with temperature for those specimens implanted at 180°C is shown in Fig. 7. This figure shows the dependence of the relative damage parameter, \( \chi_{100} \) as a function of anneal temperature for both the Te and Sn data. The value of \( \chi_{100} \) does not change appreciably for anneal temperatures up to 450°C. However, above 450°C \( \chi_{100} \) decreases, and is still above the unimplanted level at 700°C. The value of \( \chi_{100} \) after this annealing temperature increases with increasing dose, indicating that some crystalline damage centres are still present.

A comparison was made between the encapsulant properties of SiO\(_2\) and Si\(_3\)N\(_4\). The Rutherford backscattering energy spectra taken after 700°C anneals for those specimens implanted with Sn at 180°C is shown in Fig. 8. It can be seen from this figure that the aligned yield was much lower for those specimens encapsulated with Si\(_3\)N\(_4\) than those using SiO\(_2\). Annealing SiO\(_2\) encapsulated specimens at 750°C caused the degradation of the crystalline surface as seen by a broadening of the Ga and As surface peaks. This degradation was not observed for those specimens encapsulated with Si\(_3\)N\(_4\).

4.2.3 Distribution of the Implanted Impurity before Annealing

The dose dependence of the He ion yield for the non-channelled backscattering energy spectra in the region of the impurity peak for both Sn and Te implanted GaAs is shown in Fig. 9. Using the value of
Non-Channelled Spectrum

Unimplanted Control Spectrum

The aligned backscattering spectra as a function of the anneal temperature for GaAs implanted at 20°C with a Te dose of $1 \times 10^{19}$ m$^{-2}$

Te dose $= 1 \times 10^{19}$ m$^{-2}$
Ion energy $= 150$ keV.
Implantation temp. $= 20°C$
Anneal temp.: ⊳ NIL
△ 350°C
▽ 450°C
× 650°C

Spectra (110) aligned

Note: For clarity, only $\frac{1}{4}$ of the data points are shown

Charge collected 5μC
One channel $= 1.75$ keV
Resolution 12 keV

Figure 6
THE RELATIVE DAMAGE PARAMETER $\chi_{100}$ AS A FUNCTION OF
THE ANNEAL TEMPERATURE FOR SPECIMENS IMPLANTED AT 180°C

FIGURE 7

A - Unimplanted level after a 700°C anneal using SiO$_2$ as the encapsulant
Comparison of the aligned backscattering spectra from those samples encapsulated with $\text{SiO}_2$ and $\text{Si}_3\text{N}_4$.

**Figure 8**
HELUM
ION
YIELD
(COUNTS)

Sn & Te Implant Conditions
ION ENERGY - 150 keV
IMPLANT TEMP. - 180°C
NO ANNEAL
CHARGE COLLECTED 5 μC
ONE CHANNEL ≈ 1.75 keV
RESOLUTION - 12 keV

Non-Channelled Spectra

Sn DOSES:
- $5 \times 10^{19}$ m.$^{-2}$
- $3 \times 10^{19}$ m.$^{-2}$
- $1 \times 10^{19}$ m.$^{-2}$
- $x \times 5 \times 10^{18}$ m.$^{-2}$

Te DOSES:
- $1 \times 10^{20}$ m.$^{-2}$
- $1 \times 10^{19}$ m.$^{-2}$
- $x \times 5 \times 10^{18}$ m.$^{-2}$

The dependence on dose of the non-channelled backscattering spectra in the region of the impurity peaks

FIGURE 9
360 keV \mu m^{-1} for the stopping power of the 1.5 MeV He ions in GaAs it was found that the positions of the peaks in the distribution were similar to that predicted by the L.S.S. theory i.e. approximately 40 nm. However, in contrast to this theory, the shape of the peaks were found to be asymmetric.

4.2.4 Anneal Temperature Dependence of the Impurity Distribution

Non-channelled and \langle 110 \rangle channelled spectra have been collected and these curves analysed to show the changes in the Te and Sn distributions with the annealing temperature.

The impurity peaks for Te and Sn implanted specimens have been plotted in Figs. 10, 11. No movement of the Te could be detected for anneal temperatures up to 650°C, and for doses up to $5 \times 10^{19} \text{m}^{-2}$. In contrast, the Sn implanted specimens show a movement of the impurity towards the surface. The \langle 110 \rangle aligned yield close to the surface increases with increasing anneal temperature indicating that some of the atoms within the surface regions are on non-subsitutional sites. The movement towards the surface is more pronounced for the higher doses.

4.2.5 Retention of the Impurity

Fig. 12 shows the quantity of Sn and Te retained within the crystal as a function of the anneal temperature. This figure shows that for anneals up to a temperature of 650°C there is no significant loss of Sn or Te, but for the highest dose Sn implanted specimen annealed at 700°C the Sn concentration is reduced by 30%.

4.3 Surface Properties of the GaAs Crystal

Because of the similarity in the masses of Ga and As, it was only possible to determine the ratio of Ga to As close to the surface. (see section 3.3.1.3).

A plot of the As to Ga atomic ratio as a function of annealing temperature is given in Fig. 13. There was a slow increase in the As:Ga ratio with increase in the annealing temperature reaching a maximum value of 2:1 at 650°C (As rich). At higher annealing temperatures, the surface was
THE DEPENDENCE ON ANNEAL TEMPERATURE OF THE BACKSCATTERING SPECTRA IN THE REGION OF THE IMPURITY PEAKS FOR Te AND Sn IMPLANTED INTO GaAs WITH A NOMINAL DOSE OF $5 \times 10^{19}$ m$^{-2}$

**FIGURE 10**
THE DEPENDENCE ON ANNEAL TEMPERATURE OF THE BACKSCATTERING SPECTRA IN THE REGION OF THE IMPURITY PEAKS FOR Sn IMPLANTED INTO GaAs WITH NOMINAL DOSES OF $5 \times 10^{18}$ m$^{-2}$ AND $1 \times 10^{19}$ m$^{-2}$
Quoted caption: Quoted text: Figure 12

Figure 12: Quantity of Sn and Te retained within the GaAs crystal as a function of the anneal temperature.
SURFACE STOICHIOMETRY AS A FUNCTION OF THE ANNEAL TEMPERATURE

FIGURE 13
Ga rich, with the ratio of As:Ga equal to 0.7:1 after a 700°C anneal. These results were not dependent on the implanted ion species used, or on the implanted dose, but it was noticed that after a 700°C anneal, those specimens which were encapsulated with Si₃N₄ showed an apparently As rich surface, whereas those coated with SiO₂ showed a Ga rich surface.

4.4 Diffusion into the Encapsulant

A series of experiments were conducted in which the specimens were analysed before and after annealing with the encapsulant in place. If it is assumed that there are no Ga, As or impurity atoms in the encapsulant, then due to the energy loss of the ion beam in the encapsulant, the Ga, As and impurity edges of the backscattering spectra will occur at lower energies than an uncoated specimen. It can be seen from Fig. 14a that after annealing at 700°C, there is a build up of Sn near the SiC/GaAs interface. However, there were no additional counts between that channel associated with the Sn edge and the actual edge indicating that the quantity of Sn in the oxide was below the sensitivity of the experiment. Similar results were obtained with the Te implanted specimens, except that diffusion of the Te was not observed.

This form of analysis was extended to an unimplanted specimen. For this case, the Sn and Te peaks were missing and it was possible to deduce if there was any Ga or As diffusing into the SiO₂ during the anneal. It was found that any diffusion into the SiO₂ was below the sensitivity of the experiment, i.e. less than $1 \times 10^{26} \text{m}^{-3}$.

A similar analysis on Si₃N₄ encapsulated specimens gave similar results, i.e. the concentration of Ga, As, Sn or Te diffusing into the encapsulant was below the sensitivity of the experiment.

Unfortunately the deposition of SiO₂ was not always well controlled and occasionally poor quality films were grown. Fortunately these films were easily distinguished from the good quality films, by their optical appearance. These inferior quality films exhibited poor encapsulant properties. Fig. 14b shows a typical non-aligned spectrum before and after annealing at 650°C, a Sn implanted specimen with a poor SiO₂ layer. It can be directly compared to Fig. 14a for a normal SiO₂.
ANALYSIS OF Sn IMPLANTED GaAs WITH THE SiO₂ ENCAPSULANT ON THE SURFACE OF THE CRYSTAL

FIGURE 14
film. The increased yield in Fig. 14b is probably due to Ga in the oxide. On removing the film the surface Ga and As peaks seen in the aligned backscattered spectrum indicated that the surface was As rich (As:Ga ratio 2.2:1). This ratio was similar to that measured after annealing at 650°C with a good quality SiO₂ film. The Sn distribution, for a dose of $1 \times 10^{19} \text{m}^{-2}$, did not depend on the oxide quality.

4.5 Electrical Properties of the Ion Implanted Layers

4.5.1 Isochronal Anneals

A series of 15 min. isochronal anneals have been made on Sn and Te implanted layers in GaAs. Fig. 15 shows the effects of such an annealing sequence on the sheet resistivity of these layers implanted with a dose of $5 \times 10^{18}$ ions $\text{m}^{-2}$ into semi-insulating GaAs. An increase in the sheet resistivity is seen for increasing anneal temperatures over the temperature range 150°C to 400°C. For the room temperature implanted specimens, the sheet resistivity decreased slightly with increasing anneal temperature for anneals between 50°C and 150°C. This reverse annealing process is consistent with the work of Bicknell et al.²¹

For all anneal temperatures up to 400°C, the Hall voltage was below the sensitivity of the apparatus. This indicates that the number of current carriers must be above $1 \times 10^{25} \text{m}^{-3}$, and that their mobility is smaller than $5 \times 10^{-5} \text{m}^{2}\text{V}^{-1}\text{s}^{-1}$. The thermal probe measurements showed that these layers were p-type.

For anneal temperatures above 500°C the specimens were encapsulated with approximately 0.4 µm of deposited SiO₂. For the 180°C implanted cases, the sheet resistivity decreased rapidly with increasing anneal temperature above 500°C, but for the room temperature implanted cases, the sheet resistivity remained higher than $1 \times 10^{8}$ ohms per sq. for anneal temperatures up to 700°C. The Hall effect voltage could be measured on those specimens which were implanted at 100°C or 180°C and annealed at temperatures greater than 500°C. The sign of this voltage normally indicated that the layer was exhibiting n-type conductivity. Thermal probe measurements also indicated that the conductivity was n-type.

FIGURE 15
Additional information could be determined from the Hall effect measurements. Fig. 16 shows the variation of $1/R_H$ and of the average Hall mobility with the annealing temperature above 500°C. The value of $1/R_H$ increases with anneal temperature up to about 600°C, when a saturation effect occurs for the Sn data. For a 15 min. anneal at 600°C or 650°C the value of $1/R_H$ is higher for the Te data than for the Sn data. The weighted average Hall mobility increases with increasing anneal temperatures up to 700°C.

Higher annealing temperatures were not used as the results from the backscattering experiment suggested that the surface of the GaAs was becoming severely degraded at temperatures in excess of 700°C.

The dose dependence of the electrical activity is shown in Fig. 17. The majority of the data shown in this figure is for specimens annealed at 650°C for 15 mins. using SiO$_2$ as the encapsulant. It was observed that for the Te implantation case, a 600°C 1 hr. anneal produced a larger percentage activity than either a 500°C or 650°C anneal for 15 mins. However, a 1 hr. 650°C anneal for the Sn implanted case produced a lower activity than a 650°C anneal for 15 mins.

The experimental results have indicated that the electrical properties of those implanted layers which have been annealed to temperatures up to 400°C are different to those annealed above 400°C. Below this anneal temperature, the thermal probe has indicated that the layers are p-type and above this temperature the layers are n-type. The p-type layers have a very small Hall mobility in comparison to the n-type layers ($\mu_n/\mu_p > 4000$). As the properties of the n-type layers are essentially different from the damage induced p-type layers, the description of the experimental data will be split into two parts. One part will characterise the electrical properties of the layers which have been annealed to a maximum temperature of 400°C, the other describing the properties of those layers heat treated in the temperature range 500°C to 700°C.

4.5.2 Electrical Properties for Anneal Temperatures up to 400°C

4.5.2.1 Dependence of the sheet resistivity on temperature

Fig. 18 shows the variation of the sheet resistivity as a function
Figure 16

Reciprocal Hall coefficient and average Hall mobility as a function of the annealing temperature.

Anneal Time - 15 min.
Implant. temp. - 180°C
Implant. Doses:
- X Te $5 \times 10^{18}$ m$^{-2}$
- O Sn $5 \times 10^{18}$ m$^{-2}$
- U Sn $1 \times 10^{19}$ m$^{-2}$
Implant. temp. - 100°C
- O Te dose $5 \times 10^{18}$ m$^{-2}$
Anneal Time - 60 min.
Implant. Temp. - 180°C
- O Te dose $5 \times 10^{18}$ m$^{-2}$
- O Te dose $5 \times 10^{19}$ m$^{-2}$
THE NUMBER OF ELECTRICALLY ACTIVE ATOMS AS A FUNCTION OF DOSE

FIGURE 17
The sheet resistivity as a function of the reciprocal analysis temp. for those specimens heat treated to a temperature up to 350°C.

**Figure 18**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 °C</td>
<td>350 °C</td>
</tr>
<tr>
<td>2</td>
<td>20 °C</td>
<td>NONE</td>
</tr>
<tr>
<td>3</td>
<td>180 °C</td>
<td>350 °C</td>
</tr>
<tr>
<td>4</td>
<td>250 °C</td>
<td>350 °C</td>
</tr>
<tr>
<td>5</td>
<td>250 °C</td>
<td>NONE</td>
</tr>
<tr>
<td>6</td>
<td>20 °C</td>
<td>NONE – Ga</td>
</tr>
<tr>
<td>7</td>
<td>100 °C</td>
<td>NONE</td>
</tr>
<tr>
<td>8</td>
<td>180 °C</td>
<td>NONE</td>
</tr>
</tbody>
</table>

Material: S.I. GaAs INGOT A294

With the exception of curve 6, all of the implants were of Te with a dose of \(5 \times 10^{18} \text{ m}^{-2}\) at 150 keV.

Curve 6: Ga implant dose \(1 \times 10^{19} \text{ m}^{-2}\), 100 keV.
of $1/T$ for the ion implanted specimens annealed up to 350°C. Details of the range of specimens analysed is given in Table 2. For each case a similar change in the sheet resistivity was seen over the temperature range 80°K to 300°K. It appeared that these curves were composed of several straight lines, the slopes of which were apparently similar (see Table 2). Using a magnetic field of 0.5 Wb m$^{-2}$, the Hall effect voltage was not measurable for any temperature in the range 80°K to 300°K.

### 4.5.2.2 Variation of the Resistivity with Depth

The sheet resistivity has been measured as a function of the total thickness of material etched off from the surface of the GaAs. The stripping technique used has been described in section 3.1.4. Fig. 19 shows the variation of the sheet resistivity as a function of the material removed for both the 'as implanted' specimens and those annealed at 350°C. For the room temperature implanted samples, the conduction centres were confined to a shallow surface layer but they penetrated more deeply into the crystal for the higher implantation temperatures. On annealing at 350°C, the conduction centres in those specimens implanted at 20°C and 100°C diffused deeper into the crystal, but for those samples implanted at 180°C and 250°C, the conduction centres at great depths within the crystal annealed out.

These curves have been reanalysed to give the conductivity as a function of depth as described in section 3.2.1. The conductivity is a function of the concentration of electrically active conduction centres. It can be seen from Figs. 20 and 21 that the variation of the conductivity with depth is dependent on the implantation temperature. For the 20°C and 100°C implantations, the peaks lie close to the surface, and a deeply penetrating tail in the distribution was not seen. Those specimens implanted with Sn or Te at 20°C and annealed at 350°C gave similar profiles. However, the unannealed data shows a large variation in the position of the Te and Sn peaks. It is possible that this discrepancy between the Te and Sn data in the nominally unannealed state may be due to the fact that the Sn implanted material had been accidentally heated to about 80°C on a hot plate before analysis.

For those specimens implanted at a temperature of 180°C or above two peaks in the distribution were apparent; the first peak occurred at a depth shallower than that predicted by the L.S.S. theory and the second
<table>
<thead>
<tr>
<th>Ion</th>
<th>Dose ions m⁻²</th>
<th>Implant Temp °C</th>
<th>Anneal Temp °C</th>
<th>Slopes of Lines Fitted to Plot of Ln(ρ) Vs. T⁻¹ °K x 10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te</td>
<td>5 × 10¹⁸</td>
<td>20</td>
<td>-</td>
<td>1.2 0.97 0.80</td>
</tr>
<tr>
<td>Te</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
<td>1.2 0.93 0.81 0.58</td>
</tr>
<tr>
<td>Ga</td>
<td>1 × 10¹⁹</td>
<td>&quot;</td>
<td>-</td>
<td>0.99 0.78 0.58</td>
</tr>
<tr>
<td>Sn</td>
<td>5 × 10¹⁸</td>
<td>&quot;</td>
<td>80</td>
<td>1.2 0.96 0.8 0.6</td>
</tr>
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<td>Te</td>
<td>&quot;</td>
<td>&quot;</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>&quot;</td>
<td>&quot;</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>&quot;</td>
<td>&quot;</td>
<td>350</td>
<td>0.96 0.89</td>
</tr>
<tr>
<td>Sn</td>
<td>&quot;</td>
<td>&quot;</td>
<td>350</td>
<td>1.2 0.94 0.77</td>
</tr>
<tr>
<td>Te</td>
<td>&quot;</td>
<td>100</td>
<td>-</td>
<td>0.99 0.80 0.68 0.63</td>
</tr>
<tr>
<td>Te</td>
<td>&quot;</td>
<td>100</td>
<td>350</td>
<td>0.96 0.79</td>
</tr>
<tr>
<td>Te</td>
<td>&quot;</td>
<td>180</td>
<td>-</td>
<td>1.2 0.80 0.65</td>
</tr>
<tr>
<td>Sn</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
<td>1.2 0.96 0.8 0.65</td>
</tr>
<tr>
<td>Sn</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
<td>1.2 0.97 0.81 0.65</td>
</tr>
<tr>
<td>Sn</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
<td>1.1</td>
</tr>
<tr>
<td>Te</td>
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<td>350</td>
<td>1.0</td>
<td>0.92 0.77</td>
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<tr>
<td>Sn</td>
<td>&quot;</td>
<td>350</td>
<td>1.2</td>
<td>0.94 0.87 0.7</td>
</tr>
<tr>
<td>Te</td>
<td>&quot;</td>
<td>250</td>
<td>-</td>
<td>0.98 0.8 0.73</td>
</tr>
<tr>
<td>Te</td>
<td>&quot;</td>
<td>250</td>
<td>350</td>
<td>1.0 0.92 0.77</td>
</tr>
</tbody>
</table>

Slopes of the straight Lines fitted to the curves of Ln (resistivity) Vs. T⁻¹

**TABLE 2**
THE SHEET RESISTIVITY AS A FUNCTION OF THE THICKNESS OF THE MATERIAL ETCHED OFF THE CRYSTAL SURFACE FOR THOSE SPECIMENS HEAT TREATED UP TO A TEMPERATURE OF 350°C

FIGURE 19
The conductivity as a function of depth for those specimens implanted at 20°C and 100°C.

FIGURE 20
The conductivity as a function of depth for those specimens implanted at 180°C and 250°C.

**Figure 21**

- **Te** 180°C
- **Te** 250°C
- **Sn** 180°C

**Ion Implant. Temp.**

- Ion dose: $5 \times 10^{18} \text{ m}^{-2}$
- Ion Energy: 150 keV
- S.i. GaAs - Ingot A294

**Conductivity** (mhos m$^{-1}$)

**Distance from Surface** (nm)
occurred between 150 and 200 nm from the specimen surface. Deeply
penetrating tails in the distribution were seen which partially
anneal out at 350°C.

It can be seen from Figs. 20 and 21 that the magnitude
of the peak in the conductivity versus depth curves is around
1 mho cm\(^{-1}\) for all the implantation temperatures up to 180°C.
The lower peak conductivity for the 250°C implanted specimen was
probably due to the damage centres being partially annealed out
during the ion implantation process. It is apparent from these
figures that the higher sheet conductivity of the 180°C implanted
specimens compared to the 20°C implanted specimens is due to the
deeper distribution of the 180°C implanted specimens, and not due
to a higher peak conductivity.

4.4.3 Electrical Properties for Anneal Temperatures Greater than 400°C

4.4.3.1 Temperature dependence of \(\rho_S\) and \(R_H\)

The variation of resistivity, the reciprocal Hall coefficient
(1/R\(_H\)) and of the Hall mobility as a function of the temperature of
analysis is shown in Fig. 22 for those specimens annealed at
temperatures in excess of 450°C. This variation in the measured
resistivity with temperature is small in comparison to the variation
in the resistivity of those specimens which have not been heat treated.
Typically the value of R\(_H\) does not change appreciably with temperature.
Some specimens showed an unexpected decrease in 1/R\(_H\) with increasing
measurement temperature. It is suspected that this behaviour is not
typical of the implanted Te or Sn in GaAs, but is due to the
encapsulant modifying the surface layers of the crystal, possibly
creating a thin p-type region near the surface.

4.4.3.2 Variation of the electrical activity with depth

Typical variation of the sheet resistivity and reciprocal
Hall coefficient as material is etched off from the surface of the
GaAs crystal is shown in curves A, B and C of Fig. 23. It can be
seen from these curves that as the material is etched away, there
is an increase in the sheet resistivity and Hall coefficient.
However, some curves showed a decrease in the Hall coefficient
near the surface. This behaviour, which is illustrated in curve D
### Table of Ions and Dose Rates

<table>
<thead>
<tr>
<th>Ion</th>
<th>ION DOSAGE</th>
<th>ANNEAL TEMP.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$5 \times 10^{18}$ m$^{-2}$</td>
<td>600°C 60 min.</td>
</tr>
<tr>
<td>Sn</td>
<td>$1 \times 10^{18}$ m$^{-2}$</td>
<td>600°C 15 min.</td>
</tr>
<tr>
<td>Sn</td>
<td>$5 \times 10^{18}$ m$^{-2}$</td>
<td>650°C 15 min.</td>
</tr>
<tr>
<td>Sn</td>
<td>$1 \times 10^{19}$ m$^{-2}$</td>
<td>650°C 15 min.</td>
</tr>
<tr>
<td>Sn</td>
<td>$1 \times 10^{19}$ m$^{-2}$</td>
<td>700°C 15 min.</td>
</tr>
</tbody>
</table>

### Diagram Description

**The Sheet Resistivity, Reciprocal Hall Coefficient, and Hall Mobility as a Function of the Temperature of Analysis for Those Specimens Annealed at Temperatures Between 500°C and 700°C.**

**Figure 22**
The sheet resistivity and sheet Hall coefficient as a function of the material etched off from the specimen surface.

**Figure 23**
of Fig. 23 was only observed for those specimens which exhibited a decrease in $1/R_H$ with increasing temperature as discussed above.

Those curves which show an increase in both the sheet resistivity and $1/R_H$ can be reanalysed to yield the doping concentration and mobility as a function of depth as described in section 3.2.1. This analysis of the data for the Te implantations is shown in Fig. 24. Similar plots for the Sn implantations are shown in Fig. 25. All of these curves show a peak in the doping concentration and a decrease in the measured mobility in the vicinity of the peak. Although it was found that the percentage of electrical activity varied greatly from sample to sample using nominally similar implantation conditions, a general trend in the depth distribution of the electrical activity peaks was observed.

The Te data had a peak in the doping concentration versus depth curve which was deeper than predicted by the LSS theory whilst for the Sn, the peak was closer to the surface than predicted. It was also noted that those Te implanted specimens which annealed at 600°C for 1 hr. had a higher peak doping concentration than those annealed at 650°C for 15 min. However, those specimens annealed at 600°C had a lower electron mobility.

It has already been shown that during the annealing process, the Sn atoms diffuse towards the GaAs surface. Estimates of the percentage activity for typical Sn and Te implanted specimens can be made as a function of depth by comparing typical profiles obtained from the backscattering experiments with those from the Hall effect measurements. Fig. 26 shows the estimated percentage activity as a function of depth for the first few hundred angstroms of the surface. It can be seen from this curve that although the Sn tends to build up in the surface layers during annealing, the percentage of the Sn atoms which are electrically active and not compensated is higher in the surface layers of the GaAs whilst the equivalent Te curves indicate that the percentage of electrically active atoms is increasing with increasing depth. This would seem to imply that some surface effect is modifying the electrical properties of the Sn dopant.
Profiles of the doping concentration as a function of depth for the Te implantations.

Figure 24
Profiles of the doping concentration as a function of depth

Figure 25
ESTIMATED PERCENTAGE OF ELECTRICALLY ACTIVE ATOMS AS A FUNCTION OF DEPTH

FIGURE 26
5. ANALYSIS AND DISCUSSION OF THE EXPERIMENTAL RESULTS

This chapter will discuss and analyse further the experimental data described in chapter 4. Among these subjects discussed are the crystalline damage, the effectiveness of SiO\textsubscript{2} as an encapsulant, the electrical properties of the crystalline disorder, the atomic distribution of Te and Sn, and the donor properties of ion implanted Te and Sn in GaAs.

5.1 Crystalline Damage

This section will only consider that part of the Rutherford backscattering energy spectrum due to the interaction of the He ion beam with the GaAs substrate. The <110> aligned backscattering energy spectra described in sections 4.2.1 and 4.2.2 are interpreted in terms of the crystalline disorder of the ion implanted layers. The damage in the crystal lattice is discussed as a function of the implantation and annealing temperatures.

For those specimens implanted at 20°C with a Te dose greater than 5 × 10\textsuperscript{18} m\textsuperscript{-2}, a peak was observed in the aligned energy spectrum (see Figs. 4 and 6). This peak in the spectrum is due to the interaction of the He ion beam with those Ga or As atoms which are not on normal lattice sites. The area under this peak will therefore be proportional to the quantity of the crystalline damage. For those specimens which have not been annealed, the maximum yield of the damage peak is similar to the yield of the non-channelled spectrum indicating that the surface layer may be either amorphous or very highly disordered. The energy position of the peak shows that the crystalline disorder is confined to a region close to the GaAs surface. On heat treating these specimens, the damage peak was reduced in height and width, the maximum disorder still occurring close to the surface of the specimen. These results indicate that the crystal starts reordering in those regions closest to the undamaged crystal and that this reordering process was not complete after a 650°C anneal.
Bicknell et al\textsuperscript{21} and Sealy\textsuperscript{58} have observed non-crystalline structures from electron microscopy studies of specimens implanted under similar conditions to those above. On heat treating these specimens, Bicknell et al\textsuperscript{21} found that the implanted layer reordered into a completely twinned structure after a 150°C anneal, and Sealy\textsuperscript{58} observed that after a 250°C anneal epitaxial recrystallization of the amorphous layer was complete with the damage remaining in the form of micro-twins and stacking faults. These results are consistent with this work because when the He ion beam is aligned with the crystallographic channels of the bulk material, the chances that a twinned surface structure is also in line with the ion beam is small. Hence this crystallographic structure will produce a damage peak as seen by the backscattering technique.

If the GaAs is implanted with Te or Sn with a substrate temperature of 180°C, the amount of crystalline damage detected by the backscattering technique is small (see Fig. 5). No damage peak was observed in the aligned backscattering spectrum, indicating that the implanted layer was exhibiting an ordered crystalline structure and that there were no lattice atoms lying in the <110> channels. The increase in the aligned yield over the yield of the unimplanted control specimens, is probably caused by the higher dechannelling rate of the He ion beam as it travels through the surface layer of the GaAs crystal which is strained by the residual radiation induced defects. On heat treating these specimens it was found that the aligned backscattered yield did not change appreciably for anneal temperatures less than 450°C, but above this temperature the yield decreased with increasing anneal temperatures up to 700°C (see Fig. 7). After a 700°C anneal, the aligned yield increases with increasing dose, the minimum aligned yield being similar to an unimplanted specimen encapsulated with SiO\textsubscript{2} and annealed at 700°C. However, this value was still higher than an unannealed control specimen, indicating that some of the crystalline defects present after a 700°C anneal may be generated during the heat treatment. Fig. 8 shows that for Sn implanted specimens encapsulated with sputtered Si\textsubscript{3}N\textsubscript{4} and then annealed at 700°C, the aligned yield is lower than those samples implanted
under the same conditions, but encapsulated with deposited SiO$_2$. The aligned yield for the Si$_3$N$_4$ encapsulated specimen was slightly higher than an unannealed control specimen ($\chi_{100\ control} = 4.0 \pm 0.2\%$, $\chi_{100\, Si_3N_4} = 4.2 \pm 0.2\%$, $\chi_{100\, SiO_2} = 5 \pm 0.2\%$). Hence, for a 700°C anneal, Si$_3$N$_4$ is apparently a better encapsulant than SiO$_2$.

These results show that if the ion implantation process was conducted at 180°C instead of 20°C, then the ion implantation damage, before annealing, was greatly reduced. Heat treating the specimens at temperatures of up to 700°C does not eliminate the crystalline damage completely. The residual crystalline disorder was dependent on the encapsulant used. If SiO$_2$ is used, some defects are generated during the heat treatment.

5.2 Silicon Dioxide as an Encapsulant for GaAs

In the previous section, it was shown that, after annealing, the concentration of the crystalline defects was dependent on which encapsulant was used. As it is possible that these differences in the annealing properties of the GaAs were due to the differences in the diffusion properties of Ga or As in these two encapsulants, this section will discuss the effectiveness of SiO$_2$ as an encapsulant for GaAs. Only the diffusion of Ga through the SiO$_2$ will be considered as it is known that As does not readily diffuse through SiO$_2$. The Ga concentration at the GaAs/SiO$_2$ interface will be calculated using the published data for the diffusion coefficients of Ga in GaAs and SiO$_2$. This value will be compared with the experimental data.

The concentration of Ga atoms in the SiO$_2$ at a distance $x$ from the GaAs/SiO$_2$ interface after a diffusion for time $t$, is given by:

$$N(x,t) = C_S \text{erfc}[x/(2\sqrt{D_2t})] \quad \text{.........}(5.1)$$
where $C_s$ is the concentration of Ga atoms at the GaAs/SiO$_2$ interface.

$C_0$ is the initial doping concentration of Ga in GaAs.

$D_1$ & $D_2$ are the diffusivities of Ga in the GaAs and SiO$_2$ respectively.

$m$ is the segregation coefficient (ratio of the concentration of the dopant in the oxide to the concentration in the GaAs at the GaAs/SiO$_2$ interface).

The surface concentration $C_s$ is given by:

$$C_s = \frac{m \cdot C_0 \cdot D_1 / D_2}{m + D_1 / D_2} \quad \text{(5.2)}$$

The concentration of Ga atoms at the GaAs/SiO$_2$ interface is dependent on the relative diffusion coefficients of the Ga in the GaAs and in the SiO$_2$. Goldstein has determined the self-diffusion coefficient of Ga in GaAs over the temperature range 1000-1200°C. This data predicts that after a 650°C anneal, the self-diffusion coefficient of the Ga will be of the order of $10^{-25}$ m$^2$s$^{-1}$, i.e. the diffusion of Ga will be negligible. However, if the number of Ga vacancies at the GaAs surface is large, then the effective diffusion rate of the Ga atoms towards the surface will be the same as the diffusion rate of the Ga vacancies away from the surface into the bulk crystal. Recently Chiang and Pearson have measured the diffusion constants of Ga and As vacancies over the temperature range 700°C-1000°C for low vacancy concentrations. The calculations in this discussion will use this data and will assume that these diffusion coefficients will give a reasonable estimate to both the Ga vacancy motion and the atomic Ga diffusion in the surface regions of the crystal.
It is known that, at temperatures between 800°C and 1250°C, Ga readily diffuses through SiO₂ which has been thermally grown on Si. If it is assumed that this data can be projected to lower temperatures and still give reasonable values for these diffusion coefficients, then the surface concentration of Ga atoms can be calculated from eqn. 5.2 for various values of the segregation coefficient, m. The diffusion profiles of the Ga atoms in the SiO₂ and the profiles of Ga vacancies in the GaAs can then be estimated from eqn. 5.1. This data has been summarised in Fig. 27 for a 650°C anneal. The calculated surface concentrations of the Ga atoms (and vacancies) after a 700°C are very similar to those for a 650°C anneal.

Using the backscattering technique, it was noted in section 4.4 that, for a good quality SiO₂ film, the concentration of Ga atoms in the SiO₂ after annealing at 650°C was below the limit of sensitivity of the technique. This sensitivity limit implied that the Ga concentration was less than 1 × 10²⁶ atoms m⁻³ at 100 nm from the GaAs/SiO₂ interface. Due to the non-uniformity of the oxide and the close proximity of the GaAs edge, it was not possible to estimate the Ga concentration closer to the interface. Comparing this value with the data in Fig. 27, it can be estimated that the segregation coefficient for Ga in GaAs and SiO₂ should be less than 0.01, and that the Ga:As ratio at the interface is between 1:1 and 1:1.2. However, the measured Ga:As ratio was greater than 1:1.9 after a 650°C anneal, and was 1.4:1 after a 700°C anneal. The data given by Bell et al. implies a similar Ga:As ratio at the surface after a 600°C anneal, and that there are a large number of Ga vacancies in the surface regions of the crystal.

There are several discrepancies between the diffusion model and the experimental results:

(i) After a 700°C anneal, the experimental results indicate that the surface of the crystal is Ga rich, whereas the model predicts the GaAs surface should be As rich. The observed experimental behaviour is consistent with the Ga atoms at the GaAs/SiO₂ interface becoming oxidised, and this gallium oxide acting as a barrier to the further outdiffusion of the Ga. This oxidation of the GaAs surface has been observed after a 750°C anneal by Bell et al.
Concentration of either Ga Vacancies or Atomic Ga m^-3

1 x 10^{28}

1 x 10^{27}

1 x 10^{26}

1 x 10^{25}

1 x 10^{24}

1 x 10^{23}

Ga VACANCY DIFFUSION INTO GaAs

Ga DIFFUSION INTO SiO_2

GaAs ← → SiO_2

Distance From GaAs/SiO_2 Interface nm.

100 200 300 400

CALCULATED VALUES FOR THE CONCENTRATION OF Ga ATOMS IN THE SiO_2 AND FOR THE CONCENTRATION OF Ga VACANCIES IN GaAs AFTER A 650°C ANNEAL

FIGURE 27.
The diffusion model underestimates the Ga:As ratio at the surface. This error is probably due to errors in the diffusion constants for Ga in SiO$_2$ and for Ga vacancies in GaAs. It is known that the properties of SiO$_2$ films depend on the method of film preparation and that the films deposited at low temperatures tend to be less dense than those which have been thermally grown on Si, (see for example ref. 60b). Hence, it is possible that the diffusion coefficient of the Ga atoms in SiO$_2$ has been underestimated. If a larger value is assumed for the diffusion coefficient of Ga atoms in SiO$_2$, then the calculated values for the Ga concentration at the interface will be lower giving a higher Ga:As ratio.

It was observed that in the poor quality films there was a significant concentration of Ga atoms in the SiO$_2$. Comparing the backscattering data of Fig. 14b with the calculated Ga diffusion profiles of Fig. 27, it can be seen that the experimental Ga diffusion profile is flatter than the predicted profiles. This indicates that the diffusion coefficient of the Ga atoms in the poor quality films was higher than that predicted by ref. 34. If we assume that the diffusion coefficient of Ga vacancies in GaAs is independent of the quality of the SiO$_2$ films, then the segregation coefficient for Ga at the GaAs/SiO$_2$ interface must be higher than that for the good quality films, otherwise the concentration of the Ga atoms in the SiO$_2$ would be below the sensitivity of the experiment and gallium would not have been detected in the SiO$_2$.

Using the published data for the diffusion coefficients of Ga atoms in SiO$_2$ and for Ga vacancies in GaAs, it has been shown that Ga vacancies will be generated in the surface regions of the GaAs when SiO$_2$ is used as the encapsulant for the high temperature anneals. The experimental results have indicated that the GaAs surface is deficient in Ga after a 650°C anneal and that the surface concentration of the Ga atoms is lower than the calculated value. After a 700°C anneal, the GaAs surface was Ga rich. These discrepancies have been discussed. It was shown that the high values which were calculated for the Ga surface concentration were consistent with underestimating the diffusion coefficient of the Ga in the deposited SiO$_2$. 
5.3 Electrical Properties of the Crystalline Damage

5.3.1 Dependence of the Resistivity on Temperature

The sheet resistivity has been measured as a function of the temperature of analysis. The data has been presented as a plot of \( \log \rho \) vs. \( 1/T \) in Fig. 17. This data may be analysed in several ways, depending on whether it is assumed that the conduction process is due to electrons (or holes) in the conduction (or valence) bands or whether it is due to electrons hopping from one bound state to another by the absorption and emission of a phonon as in the case of amorphous materials (see Appendix C).

In this section the following four theoretical models will be discussed:

A. The conduction is via electrons (or holes) in the conduction (or valence) bands.

B. The conduction is similar to that of an amorphous semiconductor with a uniform density of states in the region of the Fermi energy level.

C. As model B, except that the sample is very thin.

D. The conduction is similar to that of an amorphous semiconductor with a non-uniform density of states in the region of the Fermi energy level.

It will be shown that the experimental results are described best by model D.

A. Conduction by Electrons (or holes) in the Conduction (or valence) Bands

Making the assumptions that the carrier mobility is independent of the analysis temperature, that the conduction is via electrons (or holes) in the conduction (or valence) bands and that the concentration of electrons and holes in the various bands can be
determined from Fermi-Dirac statistics, then the slope of the straight lines fitted to the resistivity data plotted in the form $\ln(\rho)$ vs. $T^{-1}$ can be interpreted as a carrier activation energy. The variation of the resistivity as a function of the reciprocal temperature of analysis has been shown in Fig. 17 for some of the data sets. All of the curves were similar in shape and were apparently composed of several straight lines, the slopes of which have been given in Table 2. If the slopes of these lines are interpreted as carrier activation energies, then the values in this table show that similar energy levels were measured for each sample, even though the implantation conditions varied widely from sample to sample. The carrier activation energies are between 0.05 and 0.1 eV.

If this is the correct analysis of this data, then when the electrons or holes are in the conduction or valence bands, the carrier mobility would be determined by the electronic scattering mechanisms within the crystal. However, the mobility has been estimated, from the Hall coefficient to be less than $5 \times 10^{-5} m^2 V^{-1} sec^{-1}$. This value is too low to be explained theoretically by assuming that the predominant electronic scattering mechanism is due to ionised impurities. This low value of the mobility is indicative of an amorphous type of conduction process (see Appendix C for a brief review of the theoretical aspects of amorphous conduction mechanisms).

B. Conductivity in Thick Amorphous Materials with a Uniform Density of States

Several workers have assumed that the conduction process in amorphous semiconductors is similar to that described theoretically by Mott, and have analysed their data using plots of $\ln(\rho)$ vs. $T^{-\frac{3}{2}}$ (see eqn. C3 in Appendix C). Kato has observed that for temperatures below 150°K, this form of analysis described their experimental results for the dependence on temperature of the resistivity of the damage induced conductivity of ion implanted GaAs. However, it can be seen from Fig. 28, that when our data is analysed in this form only a poor approximation to a straight line
SHEET RESISTIVITY
Ohms per sq.

\[ 1 \times 10^{-5}, 1 \times 10^{-6}, 1 \times 10^{-7} \]

THE DAMAGE INDUCED CONDUCTIVITY AS A FUNCTION OF TEMPERATURE
PLOTTED AS \( \log(\sigma) \) VS \( T^{-\frac{1}{4}} \)

FIGURE 28
is obtained although the general shape of the curves are similar to those given in refs. 62 and 63.

Lewis\textsuperscript{65} has pointed out that it is possible to determine the values for the various parameters in Mott's equation (eqns. C3 and C4) from a straight line fit to the curve obtained by plotting the data in the form \(\ln(\rho T^{\frac{3}{2}})\) vs. \(T^{-\frac{3}{4}}\). The results of using this analysis on the best straight line fit to the data between 80 and 150\textdegree{}K are given in Table 3. Although the values of the slope of the straight line fit, \(T_0\), were of the right order of magnitude for thermally activated hopping\textsuperscript{65}, the values of \(N(E_F)\) were too large to be reconciled with this physical model.

C. Conductivity in Thin Amorphous Materials with a Uniform Density of States

If the thickness of the conducting film is less than three or four times the characteristic hopping distance of the current carriers, then we would expect\textsuperscript{66} the resistivity to be given by:

\[
\rho = \rho_0 \exp(AT^{-1/3})
\]

From eqns. C3 and C9 of Appendix C it is possible to estimate a value for the characteristic hopping distance. From eqn. C3 we obtain:

\[
\alpha^3 = \frac{T_0 N(E_F) k}{C^4}
\]

It has been estimated from the Hall effect measurements that for our films the density of conduction states must be greater than \(10^{25}\) m\(^{-3}\). If it is assumed that \(N(E_F)\) is between \(10^{25}\) and \(10^{26}\) m\(^{-3}\) eV\(^{-1}\) and \(T_0\) is of the order of \(1 \times 10^8\) \textdegree{}K then \(\alpha\) is between \(6 \times 10^9\) and \(6 \times 10^{10}\) m\(^{-1}\) giving the average hopping distance at 100\textdegree{}K to be between 3 and 30 nm (from eqn. C9). Then from Knotek\textsuperscript{59}, the thickness of the film necessary for a transition from a two dimensional to a three dimensional hopping process is likely to be between 9 and 120 nm. This is of the same order of magnitude as the widths of the damage peaks being measured (see section 4.4.2.2). Hence it is possible that a two dimensional conduction process is occurring in some of the specimens.
<table>
<thead>
<tr>
<th>Implantation and Annealing Conditions</th>
<th>Results of Straight Line Fit</th>
<th>Effective Density of States N(E_F)</th>
<th>( \alpha ) (at 100(^\circ)K)</th>
<th>R (at 100(^\circ)K)</th>
<th>W (at 100(^\circ)K)</th>
<th>( \alpha R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion</td>
<td>Implant Temp. (^\circ)C</td>
<td>Anneal Temp. (^\circ)C</td>
<td>( T_0 ) (^\circ)K</td>
<td>( C_0 \sqrt{T} ) mhos.K(^2) per sq.</td>
<td>Sheet Value m(^{-2}) eV(^{-1})</td>
<td>Average(^1) m(^{-3}) eV(^{-1})</td>
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<tr>
<td>Te</td>
<td>20</td>
<td>-</td>
<td>NON LINEAR</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Te</td>
<td>20</td>
<td>350</td>
<td>( 9 \times 10^7 )</td>
<td>( 4 \times 10^5 )</td>
<td>( 1 \times 10^{22} )</td>
<td>( 3 \times 10^{29} )</td>
</tr>
<tr>
<td>Te</td>
<td>180</td>
<td>-</td>
<td>( 7 \times 10^7 )</td>
<td>( 2 \times 10^5 )</td>
<td>( 1 \times 10^{21} )</td>
<td>( 6 \times 10^{27} )</td>
</tr>
<tr>
<td>Te</td>
<td>250</td>
<td>-</td>
<td>( 9 \times 10^7 )</td>
<td>( 7 \times 10^7 )</td>
<td>( 7 \times 10^{28} )</td>
<td>( 3 \times 10^{35} )</td>
</tr>
<tr>
<td>Te</td>
<td>250</td>
<td>350</td>
<td>( 8 \times 10^7 )</td>
<td>( 1 \times 10^6 )</td>
<td>( 2 \times 10^{23} )</td>
<td>( 1 \times 10^{24} )</td>
</tr>
</tbody>
</table>

Notes: Average density of states was calculated assuming that the density of states was uniform with depth and that the effective thickness of the layer was the width of the conductivity versus depth peak at half the peak conductivity (from Figs. 20 and 21).

Evaluation of Mott's Parameters from the straight line fit of the resistivity versus temperature data between 80\(^\circ\)K and 150\(^\circ\)K plotted in the form of \( \log(\frac{\rho}{\sqrt{T}}) \) versus \( T^{-\frac{1}{2}} \).

**TABLE 3**
Fig. 29 shows typical plots of the resistivity data in the form \( \log \rho \) vs. \( T^{-1/3} \). The curves show extensive straight line sections with deviations at either high or low temperatures, there being no apparent correlation between these deviations and the implantation conditions or peak widths. The data from the unannealed specimens gave worse straight line fit to these plots than the annealed specimens. The data which yielded good straight line fits also apparently gave reasonable values to the slope of this line. A plot of the line slope versus line constant is shown in the inset of Fig. 29. This curve is consistent with the data of Knotek et al.66

In view of the apparent randomness of the deviations from the straight lines fitted to the \( \log \rho \) vs. \( T^{-1/3} \) plots, this analysis of the data is not satisfactory. It is interesting to note the similarities in the variation of the resistivity with \( T^{-1/4} \) between the heavy ion implanted specimens and that given by Coates and Mitchell62 for their neutron damaged GaAs specimens. For this particular case, the specimens would be uniformly damaged throughout their thickness and we would expect a true three dimensional conduction process.

D. Conductivity in Amorphous Materials with a Non-uniform Density of States

The preceding two discussions were based on the model postulated by Mott64. In that model it was assumed that the density of states in the vicinity of the Fermi energy level was a constant. This is not necessarily correct for ion implanted specimens, particularly those implanted at the higher temperatures. From the Rutherford backscattering experiments we observe that there is only a relatively small amount of residual damage for those specimens implanted at 180°C. This is consistent with other workers21 58, who have seen an essentially crystalline structure after these high temperature implantations. Intuitively one might expect that the usual band structure of the GaAs crystal to be present, but in a modified form. These modifications might take the form of band tailing or of deep levels within the energy band gap. The density of states within these deep levels may be
THE DAMAGE INDUCED CONDUCTIVITY AS A FUNCTION OF TEMPERATURE

PLOTTED AS Log (£) vs T^{-1/3};

THE INSERT SHOWING THE LINE CONSTANT AS A FUNCTION OF THE LINE SLOPE FOR THE BEST STRAIGHT LINE FITS TO THE DATA.

FIGURE 29
sufficiently high to form a broadened band of states, as described theoretically by Morgan. Pierce and Spicer using photoluminescence studies on amorphous silicon have shown that there are apparently sharp edges to the conduction and valence bands, and hence the assumption that the band structure of the crystal is destroyed by the large quantities of crystalline damage may be invalid. We should therefore consider the possibility that the electronic hopping occurs within a region in which there is a non-uniform density of states. If it is assumed that the density of states, \( N(E_F) \) in the region of the Fermi level varies as:

\[
N(E_F) = N_0 |E^p|
\]

then it has been shown by other workers that the variation of the resistivity with temperature will be of the form:

\[
\rho = \rho_0 \exp\left\{ \frac{-p+1}{p+4} AT \right\}
\]

From eqn. (5.6), we can now estimate how the resistivity is likely to vary with temperature for two specific cases. Consider a discrete energy level within the forbidden gap. Then, for a small density of states in the impurity band, the band will tend to a delta function. For this case, assuming that the centre of the density of states function resides at \( E = 0 \), the density of states will vary as \( E^p \) where \( p \) tends to infinity, and the log of the resistivity will vary as \( T^{-1} \). For much higher densities of states, the impurity band will broaden out. If the density of states is sufficiently high and the temperature is reasonably low, then the density of states in the region of the Fermi level is approximately constant. For this case, \( p \) will tend to zero and the log of the resistivity will vary as \( T^{-1/4} \). In general the approximate variation of the density of states in the region of the Fermi level will be somewhere between these two extreme limits. Hence if this model is to explain the observed variation of the resistivity with temperature we would expect the resistivity to vary as \( \exp(-AT^N) \) where \( N \) is between 0.25 and 1.
A computer programme has been written to fit the experimental data to the equation:

\[
\log[\ln(p/p_0)] = \log(A) - N \log(T) \quad \text{............(5.7)}
\]

where \( N = \frac{p+1}{p+i} \), and the other values are defined in eqn. (5.6).

Although \( p_0 \) varies with temperature it is a small change in comparison to the variation of the exponential term. Hence the assumption that \( p_0 \) is a constant may introduce small errors in the calculated values of \( A, N \) and \( p_0 \), but it will not necessarily invalidate the following argument.

The calculated values of \( p_0, \log(A), N \) and the correlation function are given in Table 4. Typical plots of the resistivity data in the form \( \log[\ln(p/p_0)] \) versus \( \log T \) are shown in Fig. 30. A plot of \( \log p_0 \) versus line slope is shown in Fig. 31. If it can be assumed that as the density of states increases, the value of \( p_0 \) increases, then Fig. 31 indicates that as the density of states increases, the power to which \( T \) is raised, \( N \), becomes closer to 0.3 and for smaller densities of states it becomes nearer 1.

By comparing the equations for \( p_0 \) and \( A \) derived by the analysis given by Hamilton\(^7\), it can be seen that \( p_0 \) is a function of \( A \). Fig. 32(a) shows the variation of \( p_0 \) as a function of \( \log(A) \). Two curves are seen, one due to the data from the room temperature implanted specimens and the other from the data of the higher temperature implanted specimens. As this was thought to be due to the differing widths of the layers being measured, the data was replotted as \( p_0 \cdot d \) versus \( \log(A) \) where \( d \) is the thickness of the conducting film at 25% of the peak in the conductivity versus depth curve of Figs. 19 and 20. The data which is illustrated in Fig. 32(b) now lies on one curve. Hence, it can be seen from Figs. 30-32 that this model could describe the temperature variation of the resistivity of all the data.
### TABLE 4

<table>
<thead>
<tr>
<th>Implantation Conditions</th>
<th>Results of Fitting Data to the Equation ( \log[\ln(\rho/\rho_0)] = \log(A) - N \log(T) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion</td>
<td>Dose ions m(^{-2})</td>
</tr>
<tr>
<td>Te</td>
<td>5\times10(^{18})</td>
</tr>
<tr>
<td>Te</td>
<td>5\times10(^{18})</td>
</tr>
<tr>
<td>Ga</td>
<td>1\times10(^{19})</td>
</tr>
<tr>
<td>Sn</td>
<td>5\times10(^{18})</td>
</tr>
<tr>
<td>Te</td>
<td>5\times10(^{18})</td>
</tr>
<tr>
<td>Te</td>
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<tr>
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</tr>
<tr>
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<td>5\times10(^{18})</td>
</tr>
<tr>
<td>Te</td>
<td>5\times10(^{18})</td>
</tr>
</tbody>
</table>

All implantations into semi-insulating GaAs (ingot No. A294).

NOTE:  
- a) After stripping 200 nm from specimen surface
- b) After stripping 304 nm from specimen surface.

The values of \(\rho_0\), \(N\), and \(\log(A)\) which give the best straight lines fit the data for the resistivity as a function of temperature to the eqn. \(\log[\ln(\rho/\rho_0)] = \log(A) - N \log(T)\).
ION - Te
ION DOSE - $5 \times 10^{18} \text{ m}^{-2}$
ION ENERGY - 150 keV.
ALL ANNEALS - 15 min.
MATERIAL - S.I. GaAs Ingot No. A294

<table>
<thead>
<tr>
<th>CURVE</th>
<th>IMPLANT TEMP</th>
<th>ANNEAL TEMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20°C</td>
<td>350°C</td>
</tr>
<tr>
<td>2</td>
<td>250°C</td>
<td>350°C</td>
</tr>
<tr>
<td>3</td>
<td>250°C</td>
<td>None</td>
</tr>
<tr>
<td>4</td>
<td>20°C</td>
<td>None</td>
</tr>
</tbody>
</table>

THE DAMAGE INDUCED CONDUCTIVITY AS A FUNCTION OF TEMPERATURE
PLOTTED AS $\log \left[ \ln \left( \frac{\rho}{\rho_0} \right) \right]$ vs $\log (T)$.

FIGURE 30
Ohms per sq.

$1 \times 10^4$

$1 \times 10^3$

$1 \times 10^2$

$1 \times 10^1$

PLOT OF $\rho_o$ AS A FUNCTION OF $N$

FIGURE 31

<table>
<thead>
<tr>
<th>ION</th>
<th>IMPLANT TEMP. °C</th>
<th>ANNEAL TEMP. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te</td>
<td>20</td>
<td>None</td>
</tr>
<tr>
<td>Sn</td>
<td>20</td>
<td>None</td>
</tr>
<tr>
<td>Te</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Te</td>
<td>20</td>
<td>130</td>
</tr>
<tr>
<td>Te</td>
<td>20</td>
<td>350</td>
</tr>
<tr>
<td>Sn</td>
<td>20</td>
<td>350</td>
</tr>
<tr>
<td>Ga</td>
<td>20</td>
<td>None</td>
</tr>
<tr>
<td>Te</td>
<td>100</td>
<td>350</td>
</tr>
<tr>
<td>Te</td>
<td>180</td>
<td>None</td>
</tr>
<tr>
<td>Te</td>
<td>180</td>
<td>350</td>
</tr>
<tr>
<td>Sn</td>
<td>180</td>
<td>None</td>
</tr>
<tr>
<td>Sn</td>
<td>180</td>
<td>None (strip)</td>
</tr>
<tr>
<td>Sn</td>
<td>180</td>
<td>350</td>
</tr>
<tr>
<td>Te</td>
<td>250</td>
<td>None</td>
</tr>
<tr>
<td>Te</td>
<td>250</td>
<td>350</td>
</tr>
</tbody>
</table>
Curves 1 - Samples implanted at 20°C
2 - Samples implanted at other temps.

$\rho_0 \times d$, Ohms m.

Curve 1 - Samples implanted at 20°C
2 - Samples implanted at other temps.

Symbol List given on Fig. 31

$\rho_0 \times d$, Ohms m.

PLOT OF $\rho_0$ AS A FUNCTION OF Log(A) AND $\rho_0 \times d$ AS A FUNCTION OF Log(A).

FIGURE 32
Hamilton\textsuperscript{70} has derived an equation similar to eqn. (5.6) for the variation of the resistivity for a thin film having a non-uniform density of conduction states. By assuming that the variation of the density of states with energy is somewhere between the extreme limits of a delta function and of a uniform density of states, as discussed above, it can be shown that, for the case of a thin film, the resistivity should vary as \( \exp(-AT^N) \) where \( N \) is between 0.33 and 1. Hence the analysis of the data as described above could also qualitatively fit this model.

Due to the variation of the resistivity with depth, further analysis of this problem is likely to be extremely complex and was not within the scope of this investigation.

**Summary**

The variation of the resistivity as a function of the analysis temperature best fits a hopping conduction model in which it is assumed that the density of states is non-uniform in the vicinity of the Fermi level. Moreover, this model may be further modified by the thinness of the conducting films and the non-uniform distribution with depth of the conduction centres.

5.3.2 Annealing of the Electrically Active Disorder

The previous section discussed the various electronic conduction mechanisms which may be occurring within these thin films. It was shown that the experimental data could be best fitted to a hopping conduction model in which the density of the conduction states in the vicinity of the Fermi energy level was non-uniform with energy and the sheet resistivity measured was further modified by the non-uniform depth distribution of the electrical activity. This section will consider the annealing behaviour of the electrical disorder and will examine the assumptions made by other experimenters. It will be shown how the data may be analysed to yield a value for the activation energy of annealing for these defects.
Kato et al. have analysed the annealing behaviour of the resistivity as a first order annealing reaction, and were able to show that:

\[
\ln\left(\frac{N_{T_1}}{N_{T_2}}\right) = tA_o \exp\left(\frac{E_a}{kT}\right) \quad \text{........................(5.8)}
\]

where \(N_T\) is the concentration of conduction centres after an annealing temperature \(T\) for \(t\) secs.

\(E_a\) is the activation energy of annealing.

\(T_1\) and \(T_2\) are two annealing temperatures such that \(T_2 > T_1\)

\(A_o\) is a constant.

The ratio \(N_{T_1}/N_{T_2}\) has to be related to the electrical conductivity of the specimen. If it is assumed (as in refs 21, 51, 63) that the conductivity near room temperature is due to holes in the valence band then:

\[
\sigma = \sigma_o \exp\left(-\frac{W}{kT}\right) \quad \text{..................(5.9)}
\]

and eqn. (5.8) can be written as:

\[
\ln\left[\ln\left(\frac{\sigma_{T_1}}{\sigma_{T_2}}\right)\right] = - \frac{E_a}{kT_2} + \text{const} \quad \text{......................(5.10)}
\]

The values of \(\sigma_{T_1}, \sigma_{T_2}\) can be measured at some convenient temperature. Fig. 33 shows a logarithmic plot of \(\ln(\rho_{T_2}/\rho_{T_1})\) versus the reciprocal anneal temperature for the resistivity data measured at room temperature. From the slope of this line, it can be estimated that the activation energy for annealing the conduction centres was 0.5 ± 0.1 eV, which is consistent with refs. 21, 51 and 63. However, this analysis assumes that eqn. (5.9) is valid in this case, i.e. there is an interband conduction process. It has been shown in section 5.3.1 that the variation of the resistivity as a function of the analysis temperature could be described theoretically by a thermally activated hopping process. For this particular case, the conductivity varies as:

\[
\sigma = \text{const}.f[N(E_F)].\exp\left\{-C/f_1[N(E_F)].T\right\}^N \quad \text{........(5.11)}
\]

where \(C\) and \(N\) are constants.
**Determination of the First Order Activation Energy of Annealing**

From a plot of $\log \left[ \frac{\ln(\frac{\rho_{T2}}{\rho_{T1}})}{\ln(\frac{\rho_{T2}}{\rho_{T1}})} \right]$ vs $T^{-1}$

**Figure 33**

**Table:**

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Temperature of Implant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>20°C</td>
</tr>
<tr>
<td>Te</td>
<td>20°C</td>
</tr>
<tr>
<td>Te</td>
<td>100°C</td>
</tr>
<tr>
<td>Sn</td>
<td>180°C</td>
</tr>
<tr>
<td>Te</td>
<td>180°C</td>
</tr>
<tr>
<td>Te</td>
<td>250°C</td>
</tr>
</tbody>
</table>

Slope gives $E_a = 0.5 \pm 0.1 \text{ eV}$
If we assume that the variation in the density of states and the analysis temperature dependence of the resistivity is as described by Pollak and Hamilton (see eqns. 5.5 and 5.6), then the pre-exponential term may be deduced along the lines suggested by Hamilton. From Mott's analysis we obtain:

\[
\sigma_0 = e^2 \nu_m N(E_F) R^2 
\] ........................(5.12)

From Hamilton we obtain:

\[
R^3 = \frac{3(p+1)}{4 \pi N_o (\Delta E)^{p+1}} 
\] ........................(5.13)

\[
\Delta E^{p+4} = \left[ \frac{3(p+1)(2\alpha)^{3/3}}{4 \pi N_o} \right]^{1/3} \frac{p+1}{3} kT 
\] ........................(5.14)

Substituting eqns. (5.13) and (5.14) into eqn. (5.12) gives:

\[
\sigma_0 = e^2 \nu_m N_o^{1/3} \left[ \frac{N_o}{(kT \alpha)^3} \right]^{2/3} \frac{p+1}{p+4} f(p) 
\] ........................(5.15)

\[
f(p) = \left\{ \frac{3}{4 \pi} \right\}^{2/3} \left\{ \frac{9 \pi}{2} \right\}^{2/3} \frac{(p+1)}{p+4} \frac{2p}{p+4} 
\]

and the conductivity will vary as:

\[
\sigma = \sigma_0 \exp \left[ \frac{1}{p+1} \left( \frac{16 \alpha^3}{N_o} \right) \frac{1}{p+4} f'(p) \right] 
\] ........................(5.16)

where

\[
f'(p) = \left[ \frac{3(p+1)}{4 \pi} \right] \frac{1}{p+4} \left( \frac{3}{p+1} \right) \frac{p+1}{p+4} + \left[ \frac{3(p+1)}{4 \pi} \right] \frac{1}{p+4} \left( \frac{p+1}{3} \right) \frac{3}{p+4} 
\]

From eqn. (5.15), if \( p = 0 \), i.e. there is a uniform density of states, then \( \sigma_0 \) is proportional to \( N_o^{3} \) and if \( p \to \infty \), i.e. the density of states function tends to a delta function then \( \sigma_0 \) is proportional to \( N_o \).
From eqns. (5.15) and (5.16) it can be seen that care must be exercised in analysing the dependence of the resistivity as a function of annealing temperature. It appears that if the conductivity is described by a model in which it is assumed that the density of states is non-uniform with energy in the vicinity of the Fermi energy level, then due to the dependence of the exponent on the density of states, it is not sufficient to determine the activation energy of annealing from the variation of the resistivity in the form described by eqn. (5.10). Instead the value of \( \sigma_0 \) and \( p \) must be determined from a least squares fit to the conductivity versus temperature data as indicated in section 5.3.1. The effective density of conduction states can then be determined from eqn. (5.15) and the activation energy of annealing should be calculated from this. Unfortunately, this was only realised after the experimental work had been completed and there was insufficient data to check whether this analysis would yield a reasonable value for the activation energy of annealing of the damage centres responsible for the electrically active conduction centres.

5.3.3 Depth Distribution of the Electrically Active Damage Centres

In section 5.3.1, it was shown that the experimental data could be fitted best to a hopping conduction model in which the density of the conduction states in the vicinity of the Fermi energy level was non-uniform with energy. The measured sheet resistivity was further modified by the non-uniform depth distribution of the electrical activity.

With this model, the conductivity is not directly proportional to the concentration of the conduction centres, but is a non-linear function of the density of conduction states (see eqn. 5.15). Hence the distribution of the conductivity with depth, shown in Figs. 20 and 21, cannot be directly interpreted in terms of the density of electrically active damage centres. However, the shape of these curves may enable us to make certain deductions concerning the behaviour of these defects. This section will discuss the additional information which can be derived from the knowledge of the depth distribution of the electrically active damage centres.
From Fig. 15 it can be seen that the sheet resistivity as a function of the implantation temperature has a minimum value at around 100°C. From the curves of the conductivity as a function of depth presented in Figs. 20 and 21 it is evident that the reason for the variation of the conductivity with implantation temperature up to 180°C is due to the differences in the depth distribution of the conductivity, and not due to changes in the peak conductivity. The peak conductivity was found to be constant for implantation temperatures up to 180°C at 100 ± 0.2 mhos m⁻¹ which is close to the saturation value given by Coates and Mitchell for neutron irradiated GaAs. For an implantation temperature of 250°C, the peak conductivity has a lower value, indicating that some of the defects are being annealed out during the implantation process.

It can be seen from Figs. 20 and 21 that the distribution of the conductivity with depth depends on the implantation temperature. For implantations of 100°C and below, the peaks in the distribution were around 100 nm and a deeply penetrating tail was not seen. For specimens implanted at temperatures of 180°C and 250°C, two peaks in the activity were seen, one peaking closer to the specimen surface than the L.S.S. distribution, the other peaking between 150 and 200 nm. The reason for the formation of this second peak is not known. However, the deeper penetration of the tail in the distribution of the conductivity with depth is probably due to the indiffusion of defects during the implantation process at these higher temperatures. This is consistent with the work of Vook and Picraux who have detected diffusion of defects into the bulk crystal during implantations conducted at temperatures as low as 275°C and with Potts and Pearson, and Aukerman and Graft who have shown that the diffusion of As vacancies is associated with a defect annealing stage at 500°C. A Ga vacancy annealing stage has been correlated with an annealing stage near 425°C.
5.4 Atomic Distribution of Sn and Te Implanted into GaAs

The data in sections 4.2.3 and 4.2.4 show the changes with the anneal temperature in the shape of the impurity profiles and in the percentages of atoms which are not on substitutional sites. This data has been reanalysed as described in section 3.3.1.2 to yield the atomic Te and Sn distributions as a function of depth. These atomic distributions are discussed in this section.

5.4.1 The Implanted Profiles Before Annealing

The dose dependence of the impurity profile is shown in Fig. 34 for the Te data and in Fig. 35 for the implanted Sn. It can be seen from these diagrams that, with the exception of the low dose Te implantation, the peaks in the distribution coincide with that predicted by the L.S.S. theory, i.e. around 40±4 nm. However, the atomic distribution with depth is broader than that predicted by this theory, and is asymmetric.

It can be seen from Fig. 34 that the shape of the Te profiles for the 20°C implanted specimens are similar to one another, but the tail of their distributions differ in shape to those samples implanted at 180°C. The differences observed in the shape of the profiles could be due either to a higher amount of channelling in the more ordered GaAs crystal for those specimens implanted at 180°C, or to an enhanced diffusion process linked with the annealing and reordering of the implantation induced crystalline damage during these higher temperature implantations. From these measurements it was not possible to differentiate between these two processes. The 180°C Sn implanted profiles shown in Fig. 35 do not show these more deeply penetrating tails seen for the 180°C Te implanted profiles.

If the atomic impurity profiles are normalised with respect to the measured implantation dose and replotted as in Fig. 36 there is clearly a dose dependence in the shape of the impurity peaks. The shift in the distribution towards the surface with
To IMPURITY PROFILES AS A FUNCTION OF DEPTH, BEFORE ANNEALING

FIGURE 34
Sn IMPURITY PROFILES AS A FUNCTION OF DEPTH, BEFORE ANNEALING

FIGURE 35
IMPURITY PROFILES WITH DEPTH, NORMALISED TO THE IMPLANTATION DOSE.

FIGURE 36
increasing dose could be a result of the sputtering of the GaAs due to the bombardment of the surface with high energy Te and Sn atoms. An estimate of the apparent sputtering rate of the GaAs can be made by measuring the shift in the front edge of the impurity distribution with dose. Estimates have yielded values of the sputtering rate for 150 keV Te as $5 \pm 2$ atoms per incident ion, and for 150 keV Sn as $10 \pm 4$ atoms per incident ion at an implantation temperature of 180°C. The sputtering yield is dependent on the target and ion species, on the ion energy and its dose. There is little information available which is directly relevant to the sputtering of GaAs for Sn and Te ions in the dose range investigated. If the information contained in Carter and Colligon is interpolated, then we might expect sputtering yields of the order of 5-25 atoms per incident ion for 150 keV Te and Sn. Hence the values of the sputtering yields obtained above are of the right order of magnitude.

5.4.2 The Atomic Profiles as a Function of Anneal Temperatures

It can be seen from Fig. 10 that for anneal temperatures up to 700°C and for the annealing conditions considered, there was no detectable change in the shape of the Te profiles from their 'as implanted' distributions. The amount of Te retained in the crystal was independent of the annealing conditions. Hence it was apparent that, for annealing temperatures up to 700°C, enhanced diffusion effects were not important when considering Te distributions implanted into GaAs at either 20°C or 180°C at these high atomic concentrations.

The atomic Sn profiles after annealing at 350°C and 450°C are shown in Fig. 37. After a 350°C anneal no movement of the Sn was observable, but after a 450°C anneal a small movement of the high dose Sn profile towards the GaAs surface was noticed. Similar profiles are shown after a 650°C and 700°C anneals in Fig. 38. These figures indicate that the movement of the impurity towards the surface is more pronounced the higher the anneal temperature and the higher the implanted dose. It was also noted that for a $1 \times 10^{19}$ m$^{-2}$ Sn dose, the dopant profiles after annealing at 700°C did not depend on whether SiO$_2$ or Si$_3$N$_4$ was used as the encapsulant.
Sn IMPURITY PROFILES AS A FUNCTION OF DEPTH AFTER ANNEALING AT TEMPERATURES OF 350°C AND 450°C.

FIGURE 37
Sn INFINITY PROFILES AS A FUNCTION OF DEPTH AFTER ANNEALING AT TEMPERATURES OF 650°C AND 700°C.

Symbols:
- No Anneal
- Implant Temp. = 180°C
- Implant Energy = 150 keV
- Nominal Dose = m-2
- Anneals

Material:
- N-Type (X2081)
- p-Type (X826)
- p-Type (X2314)

Depth Resolution = 20 nm.

ATOMIC Sn CONCENTRATION

Sn INFINITY PROFILES AS A FUNCTION OF DEPTH AFTER ANNEALING AT TEMPERATURES OF 650°C AND 700°C.

Figure 38

Depth Resolution - 20 nm
Material:
- N - Epi. (D294/4)
- S.I. (A294)
Fig. 14, which shows the Sn profiles before the encapsulant was etched off with hydrofluoric acid indicates that the Sn builds up near the GaAs/SiO<sub>2</sub> interface after annealing. Hence the surface peaks shown in the atomic profiles of Fig. 38 are not due to the etching process.

There are several possible reasons for the observed experimental results:-

(i) It is known that Sn can diffuse via an interstitial mechanism<sup>76</sup>. It was observed that the numbers of Sn atoms which were apparently displaced from the normal Ga and As lattice sites in the surface regions (less than 20 nm deep) increased with increasing anneal temperature and dose (see Figs. 10 and 11). This behaviour would be consistent with an interstitial migration process, but the reason for the apparent build up of Sn in these surface regions is unclear.

(ii) It has been shown in section 5.2 that Ga is likely to out diffuse through the SiO<sub>2</sub> encapsulant, forming Ga vacancies which are free to diffuse into the GaAs crystal. If one makes the assumption that there is negligible diffusion of the As atoms and that the diffusion processes on each sublattice are independent of one another, then one might expect a significant movement of those Sn atoms residing on the Ga sublattice in the opposite direction to the Ga vacancy motion. This will result in a net movement of the Sn atoms towards the specimen surface. As the Te atoms normally sit on the As sublattice, there will be no diffusion of the Te atoms. As the profiles of atomic Sn did not depend on whether SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> was used as the encapsulant for a 700°C anneal (ion dose 1 x 10<sup>19</sup> m<sup>-2</sup>), this model would imply that some vacancy indiffusion is occurring for Si<sub>3</sub>N<sub>4</sub> encapsulated specimens. This is consistent with the data on Fig. 13 which indicates that after a 700°C anneal Si<sub>3</sub>N<sub>4</sub> encapsulated specimens have an As rich surface.
The experimental results presented in section 4.4.1 have indicated that the maximum percentage of electrically active atoms observed for an ion dose of $5 \times 10^{18} \text{ m}^{-2}$ was about 2% for implanted Te, and was less than 1% for a similar dose of Sn. This section will consider the reasons for this low value of the electrical activity and will discuss the effects of electron degeneracy, the role of the starting material in compensating the ion implanted layer, the effects of the electrically active compensating centres on the electrical properties of the layers, and will speculate on the possibility that electrically neutral impurity complexes are formed within the ion implanted region.

5.5.1 Effects of Electron Degeneracy on the Measured Electrical Activity

The concentration of electrons in the conduction band of a semiconductor can be calculated from a knowledge of the electronic band structure using Fermi-Dirac statistics (see for example ref. 61). This part of the discussion will compare the results derived from a theoretical analysis of a simple semiconductor band structure, with the observed experimental results. Two simple models will be discussed. The first will assume that the electrons in the impurity band which is formed for large doping concentrations do not participate in the conduction process; and the second will discuss the possibility that the electrons within the impurity band are free to take part in the conduction process. In analysing these models it was assumed that there were no electrically active compensating centres, that none of the ion implanted donor atoms form stable neutral impurity complexes with other impurities, defects or host atoms; and that the effective density of states in the conduction band was independent of the donor concentration. Making these assumptions, the Fermi energy level, $E_F$; the temperature, $T$; the concentration of impurity atoms, $N_d$; and the concentration of ionised donors, $N^+_d$; are related by the eqns 61:

$$N_d = N_c \cdot F_\frac{1}{2}(E_F^d) \cdot [2 \cdot \exp(E_F^d + E_d^\ast) + 1] \quad (5.17)$$
and
\[ N_d^+ = N_d \left[ 1 + 2 \exp \left( \frac{E_F^d + E_d^*}{kT} \right) \right]^{-1} \]  \hspace{1cm} \text{(5.18)}

where \( N_d \) is the effective density of states
\( E_F^d \) is the donor ionisation energy
\( E_F^* = \frac{E_F}{kT} \)
\( E_d^* = \frac{E_d}{kT} \).

It is known that as the concentration of donor atoms is increased, the energy level due to the impurity atoms broadens out into a band of impurity levels which, for donor concentrations greater than \( 5 \times 10^{23} \text{ m}^{-3} \) in GaAs, will merge with the conduction band\(^7\). This will result in the effective donor ionisation energy becoming zero. For these high doping concentrations it is sometimes assumed that Fermi-Dirac statistics are no longer valid in determining the concentration of free electrons, and that all the donors are ionised. However, if it is assumed that the concentration of electrons in the conduction band can still be determined by Fermi-Dirac statistics and that those electrons residing in the impurity band do not participate in the conduction process, then the concentration of unbound electrons will be less than the donor concentration. Making the assumption that all the donor states reside at the conduction band minima and solving eqns. (5.17) and (5.18) we can obtain the free electron concentration as a function of the impurity concentration. This is shown in curves A and B of Fig. 39 for temperatures of 300\(^\circ\)K and 100\(^\circ\)K respectively.

It can be seen from these curves that if the electrons in the impurity band do not participate in the conduction process, then the measured donor concentration should be dependent on the analysis temperature. However, it was found that the carrier concentration deduced from the Hall effect measurements was temperature independent (see section 4.4.3.1). Hence the observed experimental results are not consistent with this model.

An alternative model which might be employed to explain the experimental results is to consider that the electrons in the impurity band have a concentration \( n_1 \) and are free to move with
ELECTRON CONCENTRATION m⁻³

Curve A - Data From Bulk Grown Samples From Refs. 81, 82

Calculated from Fermi-Dirac Statistics (see text)

Te data
Sn data

Curve A - 300⁰K
B - 100⁰K

Donor Concentration as a Function of Doping Concentration.

Figure 39
a mobility $\mu_l$. Then the Hall coefficient $R_{HE}$ will be given by:

$$R_{HE} = \frac{e(n_\perp \mu_l^2 + N_+ \mu_n^2)}{e(N_+ \mu_n + n_\perp \mu_l)^2}$$

If we assume that the electron mobility in the impurity band is of the same order of magnitude as that in the conduction band, then as $n_\perp >> N_+$,

$$R_{HE} \approx -\frac{e}{e n_\perp}$$

and $n_\perp = N_d - N_+^d$.

Now, as $N_d >> N_+^d$, the concentration of the electrons in the impurity band does not change appreciably over the temperature range 100$^\circ$K to 300$^\circ$K. Providing the scattering factor, $r$, does not change appreciably with temperature, $R_{HE}$ will be approximately constant over this temperature range, as observed. However, the measured value of $R_{HE}$ should correspond to a high electron concentration, and not to the very much lower electron concentrations measured. Hence, the above models are not sufficient in themselves to account for the low value of the measured doping concentration for our ion implanted n-type specimens, and another mechanism such as the compensation from acceptor centres or the formation of electrically neutral impurity complexes must be postulated.

5.5.2 The Role of the Starting Material in Compensating the Donor Activity

In the experiments described, an attempt was made to measure the electrical activity of ion implanted donors in three types of substrate, i.e. bulk grown semi-insulating crystals, thin low concentration Te doped epitaxial layers on semi-insulating substrates, and bulk grown p-type crystals. This section will discuss the likely effects of these different substrate materials on the measured implanted donor activity.
The semi-insulating material was heavily compensated with Cr atoms to produce a starting resistivity in excess of $10^6$ ohms m. Normally the concentration of Cr atoms is of the order of $1 \times 10^{22}$ atoms m$^{-3}$. Hunsperger and Hirsch\textsuperscript{16} have measured spreads in the doping efficiencies of sulphur implanted into GaAs with a dose of $5 \times 10^{16}$ m$^{-2}$ which could be attributed to the differences in the Cr concentration in the semi-insulating material obtained from different suppliers. However, for the high dose Te and Sn implantations investigated, the concentration of Cr atoms in the starting material is unlikely to induce sufficient compensating centres to account for the low electrical activity measured.

The epitaxially grown Te doped layers had a net donor concentration less than $1 \times 10^{22}$ m$^{-3}$. The measured Hall mobility in this material was around $0.6$ m$^2$V$^{-1}$s$^{-1}$ and was close to the theoretical value, indicating that the number of electrically active compensating centres in the starting material was small.

For the case of implantations into p-type material, the concentration of electrically active donors must be larger than the p-type concentration before any n-type electrical activity will be observed. For the p-type materials used, this will put a limit on the minimum donor concentration of around $1 \times 10^{23}$ m$^{-3}$. However, a p-n junction will be formed, and the depletion layer at zero bias will have a finite width. This will tend to reduce the width of the donor layer, and thus reduce the apparent electrical activity. If the conditions are right it is possible for the thin n-type implanted layer to become fully depleted. If we assume that the n-type layer is 50 nm wide, and that the doping concentration in this layer was uniform, then neglecting surface effects, the net donor concentration would have to be greater than $6 \times 10^{23}$ m$^{-3}$ for the layer to just be fully depleted. At this concentration no n-type activity would be observed. Hence if $1 \times 10^{23}$ m$^{-3}$ p-type material is used, the donor activity would only be observed for that portion of the peak with a donor concentration in excess of $7 \times 10^{23}$ m$^{-3}$ for an n-type layer 50 nm thick. As the measured peak electron concentration was
often less than $1 \times 10^{20}$ m$^{-3}$ in semi-insulating material, this may have been the reason why no n-type electrical activity was observed for the majority of those implantations into p-type material.

The above discussion shows that compensating centres in the starting material are not sufficient by themselves to account for the low values of the electrical activity. However, the concentration of the compensating centres may be increased by residual damage complexes. Due to the effects of the depletion layer on the measured electrical activity, care must be taken when analysing the data for thin n-type layers on p-type substrates.

5.5.3 The Effects of Electrically Active Compensating Defects on the Measured Electrical Properties

The ion implantation mechanism creates gross radiation damage to the GaAs crystal lattice. It has been shown in section 4.4 that immediately after implantation the net electrical activity is dominated by the p-type properties of the ion implantation induced defects. Although after annealing the concentration of these defects has been greatly reduced, some may still be present and form electrically active compensating centres. If the majority of the Te atoms are electrically active but are electrically compensated by acceptor-like damage centres, then the measured electron mobility would be lower than that measured on an uncompensated sample with a similar doping concentration. This is due to the additional electronic scattering by the ionised impurities. Fig. 40 shows the measured Hall mobility as a function of the net donor concentration. This figure has been constructed from the smooth curves of Figs. 23 and 24. Also shown in this diagram is the theoretical electron drift mobility from the work of Rhodes and Knight for various compensation levels, $K$, where $K$ has been defined as:

$$K = \frac{N_d^+ + N_a^-}{n}$$

The experimental points for the Te implants into epitaxial GaAs lies between the curve for $K = 1$ and $K = 5$. It will be
THE MEASURED HALL MOBILITY AS A FUNCTION OF THE NET DONOR CONCENTRATION.

FIGURE 40
noted from this figure that the measured electron mobility at a given carrier concentration for those specimens implanted into semi-insulating GaAs are lower than those obtained by implanting into epitaxial GaAs. This is probably due to the compensating centres within the bulk starting material or, in the case of the Sn implants, it may also be due to the self-compensating nature of the Sn dopant. This figure shows that the Te and Sn implants which have been annealed at 600°C have even lower mobilities than those annealed at 650°C. This is likely to be associated with some residual electrically active defects within the crystal.

The experimental points for the data for the Te implants into epitaxial GaAs lies between the curve for $K = 1$ and $K = 5$. Fig. 17 indicates that for the high doses there is only about 1% of the atoms in the crystal which are electrically active. This would mean that $K$ would have to be around 100 if carrier compensation was the dominant reason for the low activity. However, as the experimental points for the Te implants into epitaxial GaAs lie between the curves for $K = 1$ and $K = 5$ carrier compensation can not be the dominant mechanism for reducing the measured electrical activity after a 650°C anneal.

It should be noted that the mobility data in the experimental curves is the Hall effect mobility, whilst the theoretical curves of Rhodes and Knight\textsuperscript{78} are for the electron drift mobility. In practice the Hall mobility would have to be divided by a number between 1 and 2 to convert this into the electron drift mobility, and the measured electron concentration would be reduced by a similar factor. However, this does not invalidate the argument that the measured Hall mobilities are very much larger than one would expect if the material was so heavily electrically compensated. Hence one has to postulate that the impurity atoms are incorporated into the crystalline lattice in an electrically neutral form.
5.5.4 Adsorption of Ions on Dislocation Loops

Gibbons\textsuperscript{79} has discussed the possibility that implanted atoms may become adsorbed on dislocation loops. In the model he developed it was assumed that the adsorbed dopant atoms would be electrically inactive or have a much higher carrier ionisation energy than normally associated with that impurity. The probability of the impurity atom being adsorbed was proportional to \((v_s - v_a)^2\) which is the square of the differences in the atomic volumes between the implanted impurity and the host atoms. Typical values of \((v_s - v_a)^2\) for various atoms in GaAs were estimated from the definition of atomic volume given by the atomic weight divided by the density of the material\textsuperscript{80}, and are presented in Table 5.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
Element & Zn & Cd & Sn & Si & Sn & Si & Te & S & Se \\
\hline
\((v_s - v_a)^2\times10^{-60}\text{ m}^{-3}\) & 8 & 1 & 19 & 0.4 & 10 & 1 & 54 & 6 & 12 \\
\hline
\end{tabular}
\caption{Table giving the square of the atomic volume differences between the GaAs lattice atoms and the impurities atoms.}
\end{table}

It can be seen from this table that, whereas the volume difference between the Te atoms and the host lattice and hence the probability of adsorption on a dislocation loop, is very much greater than the other atoms listed, the volume differences of the donors S, Se and Si are of the same order of magnitude as the acceptors atoms Cd and Zn. This indicates that if this was the dominant mechanism for the observed reduction in the electrical activity, we would expect to measure electrical activities of Si and S doped materials as Zn and Cd doped materials. However, it has been demonstrated by other workers that whereas the percentage of active Cd\textsuperscript{7,8,9} and Zn\textsuperscript{10} implanted into GaAs is high, the activity of S\textsuperscript{20} and Si\textsuperscript{20} is relatively low. This theory also
predicts that a higher percentage of Te atoms would be adsorbed on dislocation loops than Sn, resulting in a higher percentage of electrically active Sn atoms than Te. However, the experimental points in Fig. 16 indicate that the Te activity is higher than the Sn at high doses. These differences in the dopant properties discussed above apparently indicate that adsorption of the impurity atoms onto dislocation loops is not the dominant mechanism for the observed low values for the measured electrical activity of the donor atoms.

5.5.5 Formation of Electrically Neutral Impurity Complexes

Another possible explanation is that the majority of the impurities are incorporated into the crystal lattice in such a manner that they form stable neutral impurity complexes by combining with other impurity atoms or with the lattice atoms. The ionisation energy of the conduction electrons of these neutral impurities would be much higher than would normally be associated with this impurity. The electronic scattering cross-section of these neutral impurity complexes would have to be small to account for the reasonably high values of the electron mobility. This section will discuss the results taken from the current literature relating to the formation of this type of complex and will speculate on the possibility that this form of complexing is occurring in the ion implanted films investigated.

Several workers\textsuperscript{81, 82, 83} have studied the dopant properties of bulk grown GaAs incorporating large quantities of Te in the melt, and found that the electron concentration was lower than the Te concentration. This effect has been attributed to the formation of a second phase within the melt\textsuperscript{81}, and to the formation of stable neutral complexes of the form [\textit{V}_\text{Ga} + 3.\text{Te}]\textsuperscript{82}. Kressel et al\textsuperscript{84} have pointed out that the [\textit{V}_\text{Ga} + 3.\text{Te}] complex represents a solid solution of Ga\textsubscript{2}Te\textsubscript{3} in GaAs and were able to observe directly, using the T.E.M., small precipitates in their heavily Te doped material fabricated by liquid phase epitaxy.
An estimate of the net donor carrier concentration as a function of the implanted impurity concentration for both the Sn and Te data is shown in Fig. 37 along with curves taken from refs. 81 and 82 for bulk grown GaAs. It can be seen from these curves that the net electrical activity observed during this study of the ion implanted donors into GaAs was at least an order of magnitude lower than would be expected if the impurity had been added to the melt during the growth of the GaAs. If the ion implanted Te had the same electron concentration dependence on the atomic concentration as that introduced into the melt for bulk grown GaAs, then we would expect to measure an electrical activity of about 10% for a $1 \times 10^{19}$ m$^{-2}$ Te dose. The electrical activities measured were below this value.

The concentration of the $[V_{Ga} + 3. Te]$ complexes is likely to be a function of the method used to fabricate the heavily doped material. For an ion implanted specimen the concentration of these defects is likely to be a function of the annealing and encapsulation conditions. From the discussion in section 5.2 it was indicated that Ga was likely to diffuse through the SiO$_2$ on annealing. It had been observed by Bell et al$^{35}$, using the same source of SiO$_2$ encapsulant used in this work, that for an unimplanted specimen annealed at 600°C for 15 mins. the surface was deficient in Ga to a depth of 15 nm, and that after a 750°C anneal approximately 20% of the surface Ga was oxidised in the form of Ga$_2$O$_3$. The formation of Ga$_2$O$_3$, presumably in the form of small precipitates, would encourage the formation of As$_2$Te$_3$ or Ga$_2$Te$_3$, both of which have been observed by Panish$^{85}$. This oxide formation was not observed with the Si$_3$N$_4$ encapsulants$^{35}$. It has also been shown by Harris et al$^{22}$ that the photoluminescence peak associated with a $[V_{Ga} + Te_{As}]$ complex is higher for Te implanted GaAs encapsulated with SiO$_2$ and annealed at 750°C than for a similarly implanted specimen encapsulated with Si$_3$N$_4$. They also observed a higher electrical activity with the nitride encapsulant indicating that the formation of stable vacancy impurity complexes with the SiO$_2$/GaAs system may be a reason why the electrical activity of the ion implanted Te was low.
With the Sn impurity, a similar form of complexing may occur. However, there are some important differences. From the phase diagram of Sn in GaAs\textsuperscript{86} it is apparent that Sn in pure or Ga rich GaAs forms a solid solution in GaAs. For As rich GaAs a second phase of Sn\textsubscript{2}As\textsubscript{3} may form. Nishizawa et al\textsuperscript{87} using epitaxially grown Sn doped GaAs attributed their observed decrease in \(N^+\) and \(N^-\) with increasing number of Ga vacancies to the formation of neutral \([V^+_\text{Ga} + Sn^-]_{\text{Ga}}\) complexes. Their data also indicated that \(N^+\) and \(N^-\) remained approximately constant if the numbers of As vacancies was increased.

The amphoteric nature of Sn enables other forms of defects to be produced. Sn can sit on either a Ga or As site resulting in either an n-type or p-type activity. Rytova and Fistul\textsuperscript{88} determined a relationship for the relative densities of an amphoteric impurity sitting on either a III or V lattice sites. From this it is interesting to note that the higher the anneal temperature, the higher would be the expected donor concentration. This is qualitatively consistent with the work of Kung and Spitzer\textsuperscript{89} for heavily Si doped, bulk grown GaAs. However, these workers attributed their results to the formation of neutral \([V^-_{\text{Ga}} + Si^+_{\text{Ga}}]\) complexes. Recently Wolf and Stillman\textsuperscript{90} have shown that band bending due to surface states in the surface regions in the crystal can further modify the distribution of an amphoteric impurity such as Sn in GaAs. They presented experimental data which indicated that the measured free electron concentration is greater than that which would be expected from the calculated equilibrium conditions. For our Sn implanted specimens, the majority of the Sn will be located within 100 nm of the surface. Hence the relative distribution of the atoms on Ga and As sites is likely to be controlled by the relative numbers of Ga and As vacancies, the temperature of annealing the specimen and the amount of band bending due to surface states on the GaAs. The net electrical activity may be further modified by the formation of \([V^+_\text{Ga} + Sn]\) complexes.
It was observed that although the Sn tended to move towards the GaAs crystal surface during annealing, the percentage of electrically active Sn atoms in the surface regions was higher than in the region of the L.S.S. peak. For the Te implanted material no atomic redistribution was observed and the peak in the electrical activity occurred at depths deeper than the L.S.S. peak (see section 4.4). This observation is consistent with Ga diffusion through the SiO₂ giving rise to an excess number of Ga vacancies in the surface regions, causing an increase in the concentration of \([V_{Ga} + Te]\) complexes as discussed above. For donor activity, Sn resides on a Ga site whilst Te normally sits on As sites. At high atomic concentrations, Sn tends to be amphoteric. If the concentration of Ga vacancies is increased then a higher proportion of the Sn atoms may tend to sit on Ga rather than As sites. Hence we might expect a higher donor activity in the surface regions of a Sn implanted sample when it is annealed using SiO₂ as the encapsulating film. For the Te case a higher concentration of Ga vacancies in the surface regions is likely to increase the concentration of neutral complexes reducing the net carrier concentration close to the surface.

5.5.6 Summary

The possible causes for the measured low percentage of electrically active ions have been discussed. It has been shown that the major cause of this low activity is not due to electron degeneracy or to compensation of the electrons by electrically active defect centres, or to the adsorption of ions on dislocation loops, although it is possible that each of these may have second order effects. It has been speculated that the reduction in the electrical activity was due to the formation of neutral impurity vacancy complexes and supporting evidence for this idea was obtained from the current literature. It was calculated that if the ion implanted impurity behaved in a similar manner to the bulk impurity, then for a Te dose of \(1 \times 10^{19} \text{m}^{-2}\) an electrical activity of about 10% would be expected. It was shown that the differences in the profiles of the electrical activity with depth for the Sn and Te implantations were consistent with the premise that Ga diffuses through the SiO₂ encapsulating layer during the 650°C anneal.
6. CONCLUSIONS

Some effects of implanting Te and Sn into single crystal GaAs have been investigated as a function of the ion dose, implantation temperature and the temperature of the post implantation anneal. This section states the main conclusions which can be drawn from this work.

The ion implantation process was found to create gross lattice damage in the surface layers of the crystal. This damage layer had to be annealed out in order to establish donor activity. A Te dose of $5 \times 10^{18} \text{m}^{-2}$ implanted at 20°C was found to create an amorphous surface layer. Considerable crystalline disorder was still present after annealing at 650°C using SiO$_2$ as the encapsulant. If the samples were implanted at 180°C then it was found that the defects were partially annealed out during the implantation process. Heat treating the specimens at temperatures above 450°C reduced the residual defects, but some damage was still detectable after a 700°C anneal. The residual disorder was lower after annealing at 700°C if Si$_3$N$_4$ was used, instead of SiO$_2$, as the encapsulant. Some defects were generated in the crystalline structure when the samples were heat treated at 700°C when SiO$_2$ was used as the encapsulant. Out diffusion of Ga through the SiO$_2$ layer will generate Ga vacancies in the surface layers of the GaAs when the specimens are heat treated at 650°C.

The ion implantation damage layer exhibited p-type properties with a Hall mobility less than $1 \times 10^{-5} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ for all implantation temperatures between 20°C and 250°C. On heat treating these samples, the sheet resistivity was found to increase with increasing anneal temperature to a maximum value, at 400°C, greater than $10^8$ ohms per sq. The electrical properties of the disordered layer exhibited similar electrical properties to that of an amorphous semiconductor with a non-uniform density of states in the vicinity of the Fermi energy level. The net electrical properties of these layers may be modified by the non-uniform depth distribution of the electrical activity. A method of determining
a value for the activation energy of annealing of the radiation
defects was described for this case.

It has been shown that the electrical conductivity is
confined to a shallow surface region for implantations conducted
at substrate temperatures of 20°C and 100°C, but the profiles of
the electrical conductivity with depth have a much deeper
penetration for those specimens implanted at 180°C and 250°C.
These differences have been attributed to defects diffusing into
the crystal during the ion implantation process at the higher
temperatures. The minimum value of the sheet resistivity in the
damaged layer was $1 \times 10^{-2}$ ohms m, which was similar to the
saturation value observed for the neutron damage induced
conductivity observed by Coates and Mitchell\textsuperscript{62}.

Investigation of the distribution of the Sn and Te impurity
peaks revealed that although no redistribution of the Te was seen
for anneal temperatures up to 700°C, the Sn tended to diffuse
towards the surface during the anneal at temperatures greater than
450°C. The movement of the Sn atoms was more pronounced for higher
annealing temperatures and higher doses. A build up of Sn near the
GaAs surface was observed for doses higher than $3 \times 10^{19}$ m$^{-2}$. The
Sn concentration in the region of the L.S.S. peak appeared to
saturate around $5 \times 10^{26}$ atoms m$^{-3}$ after an anneal temperature of
700°C. The concentration of Sn just below the surface of the GaAs
was higher than this value. At a dose of $1 \times 10^{19}$ m$^{-2}$ no difference
in the Sn distribution after a 700°C anneal was observed between
those specimens using SiO$_2$ and those using Si$_3$N$_4$ as the encapsulant.
No significant reduction in the number of Sn or Te atoms was
observed for anneal temperatures up to 650°C but after a 700°C
anneal approximately 30% of the Sn atoms were lost for an ion dose
of $5 \times 10^{19}$ m$^{-2}$.

Before any donor activity could be observed, the electrically
active damage defects had to be annealed out. It was observed that
n-type activity could be obtained at 500°C if the specimens were
implanted at 180°C, but no donor activity was seen for anneal
temperatures up to 700°C for those samples implanted at 20°C. The percentage of electrically active atoms reached a maximum value at 650°C. It was found that this percentage for a 1 × 10¹⁷ m⁻² Sn implant annealed at 650°C was 15%, and that for a similarly implanted Te specimen it was 10%. This dropped to about 1% for a dose of 1 × 10¹⁹ m⁻². It was calculated that if the ion implanted Te behaved similarly to the bulk grown Te doped GaAs, then we would expect an electrical activity of about 10% for a dose of 1 × 10¹⁹ m⁻². It was concluded that the low values for the electrical activity were not due to electron degeneracy, or due to electrically active compensating centres. Measurements on the Hall mobility indicated that the scattering cross-section of the electrically inactive dopant was small. It was therefore speculated that the majority of the dopant atoms were incorporated in the form of stable electrically inactive complexes formed between the dopant atoms and damage centres, Ga or As vacancies, or between other dopant atoms. The differences in the shapes of the profiles of the electrical activity with depth between the Te and Sn implanted specimens were consistent with Ga outdiffusion through the SiO₂ and the subsequent indiffusion of Ga vacancies.
A.1 The Fourier Transform

A.1.1 Basic Concepts

The Fourier transform of a non-periodic waveform is analogous to the Fourier series of a periodic waveform. According to a theorem by Fourier, any periodic function may be represented as the sum of a number (possibly infinite) of sine and cosine functions. In the case of a non-periodic waveform, this representation cannot be made. Instead recourse is usually made to the Fourier Integral, in which the component waves differ only by infinitesimal increments of wavelength. By suitably distributing the amplitudes of the various components, any arbitrary waveform may be expressed by such an integral, which is known as the Fourier Transform or Fourier Integral.

The Fourier Integral permits the representation of an arbitrary function \( f(t) \), which might consist of a number of completely different analytic pieces of information in various parts of the \( t \) axis, by a single expression:

\[
f(t) = \left( \frac{1}{2\pi} \right) \int_{-\infty}^{\infty} F(w)e^{jwt} \, dw \quad \text{(A.1)}
\]

which is valid for all \( t \). The quantity \( F(w) \) is given by:

\[
F(w) = \left( \frac{1}{2\pi} \right) \int_{-\infty}^{\infty} f(t)e^{-jwt} \, dt \quad \text{(A.2)}
\]

and is known as the Fourier Integral or Fourier Transform of \( f(t) \). For a proof of the validity of these equations, see for example Papoulis\(^9\).
A.1.2 Numerical Fourier Transforms

For the numerical calculation of the Fourier Transform it is assumed that the data points $f(t)$ are equally spaced with time intervals $\Delta t$. The data cannot contain significant information about the Fourier components with periods less than $2\Delta t$. Therefore it is not possible to compute the numerical Fourier transform for frequencies higher than about $(2\Delta t)^{-1}$. If frequencies higher than this are taken, it will be observed that the high frequency spectrum will be a mirror image of the low frequency spectrum, rising to a maximum at a frequency of $(\Delta t)^{-1}$. This phenomenon is known as aliasing, and results when too high a frequency is taken in the discrete Fourier transform. The resulting spectrum is obviously not a true representation of the Fourier transform.

In addition, observational data are given for a finite length of $t$, e.g. $-t_{1} < t < t_{1}$. By a corresponding argument, the Fourier transform need not be calculated for values of $w/2\pi$ more closely spaced than $(2t)^{-1}$. If there were any significant fine detail in $F(w)$ that required a finer tabulation interval than $(2t)^{-1}$ for its description, then the measurements of $f(t)$ would have to be extended beyond $t = t_{1}$ to reveal it.

Hence the discrete Fourier transforms may be written as:

$$F(w) = \sum_{-t}^{t} f(t)e^{-jwt} \, dt \quad \text{...............(A.3)}$$

for $w = 0, \frac{2\pi}{2t}, \frac{2\pi}{t}, \ldots, \frac{\pi}{\Delta t}$

A.1.3 Accuracy of the Numerical Fourier Transform

The numerical Fourier transform (as defined in eqn. A.3) was calculated on the Hewlett Packard calculator (type 9100) for the case of the Gaussian curve.

$$f(t) = \frac{1}{\sigma\sqrt{2\pi}} \, e^{-t^2/2^2} \quad \text{...............(A.4)}$$
The value of \( f(t) \) in the summation of eqn. (A.3) was calculated at each instant, and to make the calculation more realistic the value of \( f(t) \) was rounded off so as to limit the accuracy to which \( f(t) \) is known to 1 part in \( 10^8 \), 1 part in \( 10^9 \). The standard deviation of the Gaussian curve was 4.5, and the interval between each data point in the \( t \) direction was 1. The Fourier transform frequencies, \( f \), calculated were:

\[
f = \frac{k}{40} \quad \text{where} \quad k = 0, 1, 2, \ldots, 20
\]

A comparison of this numerical Fourier transform was made with the theoretical Fourier transform of a Gaussian curve defined by:

\[
F(w) = e^{-\frac{w^2\sigma^2}{2}} \quad \text{...............}(A.5)
\]

The results for the first twelve transform points are summarised in Fig. A.1. The deviation of the numerical Fourier transform from the theoretical curve at the high frequency end of the spectrum is due to a form of noise introduced onto the original data points by the rounding off process described above. In general some form of statistical error (noise) in the data will always be present which will tend to mask the true shape of the Fourier transform curve at high frequencies.

**A.2 Deconvolution Theory**

The effect of any detection system is to transform a delta function at the input to the system into a curve \( R(t) \) at the output of the system. In our case the curve \( R(t) \) approximates to a Gaussian curve. In general the detection system will transform a curve \( V_1(t) \) into a different curve \( V_2(t) \). It can be shown from the convolution theorem (see for example Papoulis\(^{91} \)) that:

\[
V_2(w) = R(w) \times V_1(w) \quad \text{...............}(A.6)
\]
and that the inverse also holds

\[ V_1(w) = \frac{V_2(w)}{R(w)} \]  \hspace{1cm} \text{(A.7)}

where \( R(w) \), \( V_1(w) \) and \( V_2(w) \) are the Fourier transforms of \( R(t) \), \( V_1(t) \) and \( V_2(t) \).

Eqn. (A.6) is the result of the convolution theorem, and eqn. (A.7) describes the reverse process, which is known as deconvolution.

Taking the inverse transform of eqn. (A.7) we have the result:

\[ V_1(t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \frac{V_2(w)}{R(w)} \exp(-jwt) \, dw \]  \hspace{1cm} \text{(A.8)}

This is an expression for the corrected data \( V_1 \) in terms of the Fourier transforms of the two experimental results \( V_2 \) and \( R \).

### A.3 Computational Details

The numerical Fourier transforms were calculated using a procedure written by Mason, which was based on the fast algorithm of Cooley and Tukey. After the Fourier transforms of the data and resolution functions had been obtained, the numerical deconvoluted Fourier transform \( V_1(w) \) as defined by eqn. (A.7) was obtained by successive complex divisions at every frequency point calculated.

The numerical Fourier transforms calculated can be considered as approximations to the Fourier transform of the smooth curve defined by the data points. It has been seen before (for the case of a Gaussian curve) that the numerical Fourier transform deviates markedly from the theoretical Fourier transform at high transform frequencies (see Fig. A.1). This deviation was attributed to a form of noise. The effect of these deviations from the Fourier transform on the calculated numerical Fourier transform of the deconvoluted spectra is illustrated in Fig. A.2. This figure illustrates that the magnitude...
Fourier Transform of a Gaussian Curve with a standard deviation of 4.5

Numerical Fourier Transform when the data points are known to an accuracy of:
- ⬜ 1 part in $10^4$
- ⬜ 1 part in $10^6$
- ⬜ 1 part in $10^8$

(see text).

Accuracy of the Numerical Fourier Transform

Figure A1
The effect on the deconvoluted points of the deviations of the numerical Fourier transform from the true Fourier transform for the case of Gaussian convoluted data points and resolution functions generated as in Figure A1.

Figure A2
of the deconvoluted Fourier transform at high transform frequencies may reach a value several orders of magnitude greater than the transform at low frequencies. The resulting transform is obviously a poor approximation to the real deconvoluted transform.

If one assumes that the idealised output spectra are relatively slowly varying functions (i.e. do not contain step functions), then it can be assumed that the high frequency components of the Fourier transform will be small compared to the low frequency components. In the programme we obtained a better approximation to the numerical deconvoluted Fourier transform by reducing the magnitude of the high frequency components of the original Fourier transform of the data function to zero. This truncation point occurs at frequency, \( F \), on Fig. A.2. It should be noted that this truncation of the Fourier transform will limit the resolution that one can obtain using this programme. The maximum resolution \( R_{\text{max}} \) of the deconvoluted transform will be given by:

\[
R_{\text{max}} = \frac{F_{\text{max}}}{F}
\]  

(A.10)

where \( F_{\text{max}} \) is the maximum transform frequency.

A.4 The Deconvolution Programme in Practice

The deconvolution programme was tested using the following procedure. Two known curves were convoluted to form a third curve. This third convoluted curve was called the data function, and one of the original curves was called the resolution function. These curves were then fed into the deconvolution programme. The resulting output was then compared with the other known curve.

The convolution was formed by a numerical technique using a Hewlett Packard calculator. Two cases were tried:
1. A data function consisting of a Gaussian curve of standard deviation of 5 was convoluted with a resolution function consisting of a Gaussian curve of standard deviation of 4.5. The convoluted function together with the original data function and the deconvoluted points are shown in Fig. A.3.

2. A resolution function consisting of a Gaussian curve of standard deviation of 4.5 was convoluted with a data function with a curve equation of:

\[ \begin{align*}
  x < 0, \quad y &= 0 \\
  x > 0, \quad y &= \frac{100}{\sqrt{2\pi}} \exp\left[ -\frac{(x-5)^2}{50} \right]
\end{align*} \]

The convoluted function together with the original data function and the deconvoluted points are shown in Fig. A.4.

In both cases the convoluted data was fed into the deconvolution programme with a step rate, (Δx) of +1.

As can be seen from these figures good agreement between the shape of the deconvoluted curve and the original unconvoluted curve is obtained except at the very rapidly varying step edge of Fig. A.4. However, the resulting deconvoluted points are a better approximation to the true curve than the convoluted data points. The deconvolution of a practical Te peak is illustrated in Fig. A.5. For this case, the initial detector resolution was 17 keV, and after deconvolution the resolution was apparently reduced to 12 keV. This residual resolution is a direct result of the frequency limiting of the deconvoluted Fourier transform as was discussed in section A.3. Also shown in Fig. A.5 is a similarly implanted specimen which has been analysed using a high resolution detector (approximately 12 keV). It can be seen that good agreement between the shapes of the two peaks is obtained.
COMPARISON OF CONVOLUTED 'DATA' WITH DECONVOLUTED 'DATA'
AND ORIGINAL THEORETICAL 'DATA'
FOR THE CASE OF TWO GAUSSIAN FUNCTIONS.

FIGURE A3
COMPARISON OF CONVOLUTED 'DATA' WITH DECONVOLUTED 'DATA'
AND THE ORIGINAL THEORETICAL 'DATA' FUNCTION
FOR THE CASE OF A TRUNCATED GAUSSIAN THEORETICAL 'DATA' FUNCTION

FIGURE A4
ATOMIC CONCENTRATION

Smoothed curve from the backscattered Te peak using a detector with a resolution of 17 keV.

Deconvoluted points, with an effective resolution of 12 keV.

Data points and smoothed curve from the backscattered Te peak using a detector with a resolution of 12 keV.

Implantation Conditions:
- Energy - 150 keV.
- Temp. - 20°C
- Dose - $1 \times 10^{19}$ m$^{-2}$

COMPARISON OF THE ORIGINAL CURVE WITH THE DECONVOLUTED CURVE FOR A PRACTICAL Te IMPURITY SPECTRA

FIGURE A5
APPENDIX B - DETERMINATION OF THE STOPPING POWER OF 1.5 MeV He IONS IN ION IMPLANTED GALLIUM ARSENIIDE

The energy of a light ion reaching the detector after being backscattered from an atom at a depth, t, below the surface is given by (from eqn. 3.10):

\[ E_2(t) = kE_1 - T \cdot S(E_1) \] ........................(B.1)

If a uniform layer of thickness, d, is removed from the substrate surface, then the energy of the backscattered ion from the new depth, (t-d) can be written as:

\[ E_2(t-d) = k \times E_1 - T' \times S(E_1) \] ........................(B.2)

where \( T \) is the effective path length of the ion when backscattered from a depth, (t-d).

Subtracting eqn. (B.2) from (B.1) gives:

\[ E_2(t) - E_2(t-d) = (T-T') \times S(E_1) \] ........................(B.3)

Hence if a known thickness is removed from the substrate surface and a plot is made of the change in the backscattered energy from a known point against the change in the effective path length, we can determine a value for the stopping power for the analysing ion beam.

A plot of the energy shift of the rear edge of a 5 \times 10^{19} \text{ m}^{-2} implanted Te peak with an energy of 150 keV as a function of the change in effective path length of the He ion beam shown in Fig. B.1. The Te samples were etched in a solution of \( \text{H}_2\text{SO}_4 \), \( \text{H}_2\text{O}_2 \), and \( \text{H}_2\text{O} \) in the ratio 1:1:100 as described in section 3.1.4. The error bars on Fig. B.1 indicate the maximum error in each experimental point. These relatively large errors are due to:

(a) the difficulties in measuring accurately the step heights on certain specimens.

(b) the small changes in energy involved.
Implantation Conditions :

- Energy - 150 keV
- Temp. - 20°C and 180°C
- Dose - 5 x 10^11 m^2
- No Anneal & Annealed at 600°C 15 min.
- Implanted Ion - Te
- Material - N-type (X2081) [110] GaAs
- S.I. (A294) [110] GaAs

Line representing constant energy of 360 keV μm.
From Fig. B.1 a mean value of the stopping power of 360 ± 40 keV μm⁻¹ has been determined, which agrees well with the value of 350 keV μm⁻¹ for the electronic stopping power of 1.6 MeV He ions from the data of Northcliffe and Schilling⁹⁹, but is very much smaller than that predicted from the Johnson and Gibbons tables⁹⁵.
The theories of amorphous conduction mechanisms are based on the assumption that electrons in an amorphous material are localised in potential wells such that at \( T = 0^\circ K \) they will not diffuse away from these wells. At temperatures greater than \( T = 0^\circ K \) they may hop from one such well to another by the adsorption and emission of a phonon. If the temperature is high enough the electrons may no longer be localised but free to diffuse throughout the crystal.

The simplest forms of the theory have been determined with the assumption that the density of states in the region of the Fermi energy level is uniform. The results from these calculations will be considered first.

The condition for localisation gives:

\[
\alpha R \gg 1 \tag{C.1}
\]

where \( R \) is the mean distance between one potential well and its nearest neighbour; and

\( \alpha \) is the rate at which the atomic wave function falls off with distance.

Mott\(^4\) has shown that if the condition for localisation is not met, i.e. the electrons are free to diffuse throughout the crystal, then the conduction shows an activated temperature dependence with the resistivity \( \rho \) given by:

\[
\rho = [e^2 \cdot \alpha^2 \cdot \nu_{ph} \cdot \phi \cdot N(E_F)]^{-1} \exp(W/kT) \tag{C.2}
\]

where \( \nu_{ph} \) is a phonon frequency

\( \phi \) is a number depending on the overlap between wave functions and contains a factor \( \exp(-2\alpha R) \)

\( N(E_F) \) is the density of states in the region of the Fermi energy level.

\( W \) is the hopping energy
If the electrons are localised, then the conductivity is assumed to be due to electrons hopping from one potential well to another, the distance between each site being large in comparison to \( \alpha \). In this case, the resistivity will have the form\(^{66, 96, 97} \):

\[
\rho = \rho_0 \exp\left[ \frac{C}{N(E_F)kT} \right] \quad \text{..................(C.3)}
\]

The value of \( C \) has been determined by Mott\(^{64} \) as 2.06, Pollak\(^{69} \) as 1.84 and Ambegoaker et al\(^{97} \) as 2. The pre-exponential term has been calculated by Mott\(^{71} \) to be:

\[
\rho_0 = \left[ 9. \frac{N(E_F)}{8 \pi \alpha kT} \right]^{-\frac{1}{2}} \frac{1}{e^2} \quad \text{..................(C.4)}
\]

and by Pollak\(^{69} \):

\[
\rho_0 = 78 \text{ Ca}[kT\alpha^3 N(E_F)]^\frac{1}{4} \quad \text{..................(C.5)}
\]

where \( C \) is a constant for a given material.

Knotek et al\(^{66} \) have used similar considerations to those used for the 3-D treatment of hopping and extended the calculations to thin samples. They showed that for two dimensional hopping conductivity, the resistivity should vary as:

\[
\rho = \rho_0 \exp\left( B/T^{1/3} \right) \quad \text{..................(C.6)}
\]

for film thicknesses less than 3 to 4 times the characteristic hopping distance.

More recently, Pollak\(^{69} \) and Hamilton\(^{70} \) have investigated the expected temperature dependence of the resistivity if the density of states is non-uniform in the vicinity of the Fermi energy level. Both of these workers have shown that if:

\[
N(E_F) = N_0 E^p, \quad \text{where} \quad p > 0, \quad \text{and} \quad E > 0,
\]

then
\[ \ln(p/p_o) \text{ is proportional to } -1/\left[ \frac{p^p}{p^{p+4}} \right] \] ............(C.7)

This temperature dependence reduces to eqn. (C.3) if \( p = 0 \) (i.e. for a uniform density of states), and to a 1/T dependence if the density of states tends to a delta function. Hamilton\(^7\) also derived a similar equation to eqn. (C.7) for the case of a thin specimen with a non-uniform density of states.

Croitura et al.\(^{66}\) have pointed out that the presence of a \( \log(\sigma) \text{ vs } T^{-\frac{1}{4}} \) law or something similar does not necessarily imply a variable range hopping mechanism. Lewis\(^6\) has stated that although a \( \log(\sigma) \text{ versus } T^{-\frac{1}{4}} \) straight line fit is obtainable, a true test of the model can only be made by the calculation of physically realisable quantities from the proposed model. He has shown that reasonable values for \( N(E_F) \) and can be determined using eqns. (C.3) and (C.4) for the case of amorphous silicon. He showed that:

\[ N(E_F) = (\sigma_o \sqrt{T})^3 \sqrt{T_o} \times (2.04 \times 10^{-3}) \text{ cm}^{-3} \text{ eV}^{-1} \] (C.8)

\[ \alpha = (\sigma_o \sqrt{T}) \sqrt{T_o} \times (2.16 \times 10^{-3}) \text{ cm}^{-1} \] .......(C.9)

\[ R = \left[ \frac{9}{8\pi k T_o N(E_F)} \right]^{\frac{3}{4}} \text{ cm} \] ...................(C.10)

\[ W = \left[ \frac{3}{4\pi R^2 N(E_F)} \right] \text{ eV} \] ...................(C.11)

where \( T_o \) is the slope, and \( \sigma_o \sqrt{T} \) is the intercept at \( T = 0 \) of the straight line fit to the curve obtained when the data is plotted in the form \( \ln(\sigma \sqrt{T}) \text{ against } T^{-\frac{1}{4}} \).

Using these equations Lewis\(^6\) was able to show that an estimate could be made for the product \( \alpha R \), and for the average hopping energy.
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