CARRIER REMOVAL IN ION IMPLANTED GALLIUM ARSENIDE

by

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This work is concerned with the determination of some of the properties of GaAs after bombardment with $H^+_1$, $H^+_2$, $H^+_3$, $O^+$ and $Ar^+$ ions. The capacitance-voltage, Copeland, Hall-effect and resistivity measurement methods have been employed as diagnostic techniques.

The carrier removal rate, i.e. number of charge carriers removed per incident ion, has been determined as a function of the ion, ion energy, ion dose, implant temperature and annealing temperature in order to characterize the electrical effects of the radiation damage caused by the ions.

It was demonstrated that the carrier removal caused by implanting equivalent doses of $H^+_1$, $H^+_2$ and $H^+_3$ ions into GaAs was identical and approximately independent of the ion energy in the range 300-500 keV. Carrier removal profiles have been measured in annealed, oxygen implanted GaAs. A dose of $10^{15}$ $O^+$/cm$^2$ produced a resistivity of about $10^8$ $\Omega$/sq over a layer 0.5 - 0.6 micron thick, but no significant electrical compensation was observed from doses less than $10^{13}$ $O^+$/cm$^2$. However, doses of $10^{11}$ to $5 \times 10^{12}$ $O^+$/cm$^2$ produced resistivities of $10^8 - 10^9$ $\Omega$/sq without subsequent annealing. It has been observed that the implants performed at 200°C resulted in less radiation damage than for room temperature implantations.
Compared with unimplanted GaAs, there was an increase in resistivity of about 30% and 100% for doses of $3 \times 10^{13}$ and $10^{14}$ $\text{Ar}^+/	ext{cm}^2$ respectively, after annealing at 700°C.
ACKNOWLEDGEMENTS

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This thesis is dedicated to my parents and my aunt.
Contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>I. Introduction</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I.1. Aims of the work</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>I.2. GaAs as a device material</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>I.3. Ion Implantation</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter</th>
<th>II. Radiation Damage</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>II.1. Introduction</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>II.2. Proton bombarded GaAs</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>II.2.1. Basic properties</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>II.2.2. Carrier removal</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>II.2.3. Proton ranges in GaAs</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>II.2.4. Thermal stability of proton bombarded layers</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>II.2.5. Applications of proton bombardment</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>II.3. $H_2^+$ and $H_3^+$ Bombardments in GaAs</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>II.4. Oxygen Bombardment</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>II.4.1. Optical Measurements</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>II.4.2. Electrical Measurements</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>II.4.3. Applications of oxygen bombardment</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>II.5. Compensation in GaAs by heavy ions</td>
<td>35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter</th>
<th>III. Experimental Technique</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>III.1. Specimen preparation</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>III.2. Implantation method</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>III.3. Encapsulation and annealing</td>
<td>41</td>
</tr>
<tr>
<td>Chapter</td>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>III.4.</td>
<td></td>
<td>Electrical contacts</td>
</tr>
<tr>
<td>III.4.1.</td>
<td></td>
<td>Ohmic contacts</td>
</tr>
<tr>
<td>III.4.2.</td>
<td></td>
<td>Schottky contacts</td>
</tr>
<tr>
<td>III.5.</td>
<td></td>
<td>Measurement techniques</td>
</tr>
<tr>
<td>III.5.1.</td>
<td></td>
<td>Capacitance-voltage measurements</td>
</tr>
<tr>
<td>III.5.2.</td>
<td></td>
<td>Copeland technique</td>
</tr>
<tr>
<td>III.5.3.</td>
<td></td>
<td>Hall measurements</td>
</tr>
<tr>
<td>III.5.4.</td>
<td></td>
<td>Specimen preparation and Hall measurements</td>
</tr>
<tr>
<td>IV.</td>
<td></td>
<td>Results</td>
</tr>
<tr>
<td>IV.1.</td>
<td></td>
<td>Preparation of Schottky contacts</td>
</tr>
<tr>
<td>IV.2.</td>
<td></td>
<td>Proton bombardment</td>
</tr>
<tr>
<td>IV.2.1.</td>
<td></td>
<td>Isolation depth</td>
</tr>
<tr>
<td>IV.2.2.</td>
<td></td>
<td>Dose dependence of the profiles</td>
</tr>
<tr>
<td>IV.2.3.</td>
<td></td>
<td>Carrier removal rate</td>
</tr>
<tr>
<td>IV.2.4.</td>
<td></td>
<td>C-V characteristics</td>
</tr>
<tr>
<td>IV.2.5.</td>
<td></td>
<td>$H_2^+$ and $H_3^+$ bombardments</td>
</tr>
<tr>
<td>IV.2.6.</td>
<td></td>
<td>Thermal stability of proton bombarded layers</td>
</tr>
<tr>
<td>IV.3.</td>
<td></td>
<td>Oxygen Bombardment</td>
</tr>
<tr>
<td>IV.3.1.</td>
<td></td>
<td>Resistivity</td>
</tr>
<tr>
<td>IV.3.2.</td>
<td></td>
<td>Profiles</td>
</tr>
<tr>
<td>IV.4.</td>
<td></td>
<td>Argon bombardment</td>
</tr>
<tr>
<td>IV.4.1.</td>
<td></td>
<td>Resistivity</td>
</tr>
<tr>
<td>IV.4.2.</td>
<td></td>
<td>Carrier removal</td>
</tr>
<tr>
<td>IV.4.3.</td>
<td></td>
<td>Profiles after 700°C annealing</td>
</tr>
<tr>
<td>V.</td>
<td></td>
<td>Discussion</td>
</tr>
<tr>
<td>Chapter</td>
<td>Section</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>V.1.</td>
<td>V.1.1.</td>
<td>Isolation depth</td>
</tr>
<tr>
<td></td>
<td>V.1.2.</td>
<td>Carrier removal and profiles</td>
</tr>
<tr>
<td></td>
<td>V.1.3.</td>
<td>Thermal stability of proton bombarded GaAs</td>
</tr>
<tr>
<td></td>
<td>V.1.4.</td>
<td>H$_2^+$ and H$_3^+$ Implants</td>
</tr>
<tr>
<td>V.2.</td>
<td>V.2.1.</td>
<td>Dose dependence of resistivity</td>
</tr>
<tr>
<td></td>
<td>V.2.2.</td>
<td>Resistivity versus dose after 700°C annealing</td>
</tr>
<tr>
<td></td>
<td>V.2.3.</td>
<td>Temperature dependence of resistivity</td>
</tr>
<tr>
<td></td>
<td>V.2.4.</td>
<td>Profiles and carrier removal after 700°C annealing</td>
</tr>
<tr>
<td>V.3.</td>
<td>V.3.1.</td>
<td>Effect of dose on residual damage</td>
</tr>
<tr>
<td></td>
<td>V.3.2.</td>
<td>Recovery of damage</td>
</tr>
<tr>
<td></td>
<td>V.3.3.</td>
<td>Carrier removal</td>
</tr>
<tr>
<td></td>
<td>V.3.4.</td>
<td>Profiles</td>
</tr>
<tr>
<td>VI.</td>
<td>VI.1.</td>
<td>Conclusions</td>
</tr>
<tr>
<td></td>
<td>VI.1.1.</td>
<td>General conclusions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Future work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Appendix I (List of publications)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Appendix II</td>
</tr>
<tr>
<td></td>
<td></td>
<td>References</td>
</tr>
</tbody>
</table>
CHAPTER I

1. Introduction

1.1. Aim of the project

This investigation is concerned with the examination of some of the properties of GaAs after bombardment with $\text{H}_1^+$, $\text{H}_2^+$, $\text{H}_3^+$, $\text{O}^+$ and $\text{Ar}^+$ ions.

The main aim has been to determine the electrical effects of radiation damage (which reflected itself in carrier removal) as a function of several parameters such as ion, implant energy, dose, implant temperature and annealing temperature. The Copeland, capacitance-voltage and the Hall coefficient measurements have been employed as the diagnostic techniques, and yielded carrier concentration, mobility and resistivity profiles as a function of depth. It was thought that the study of carrier removal might produce useful information concerning high resistivity layer formation, since this is one of the important applications of ion implantation to device fabrication.

In addition, investigation of the effects of implant temperature and annealing temperature on carrier removal may also provide information which will help to explain the low electrical activity of dopant ion implantations. Activity is defined as the ratio of the sheet carrier concentration to the implanted ion dose. This low activity is believed to be due, in part, to residual carrier removal resulting from incomplete annealing.
1.2. GaAs as a device material

Gallium arsenide and silicon or germanium have the same basic crystal structure, zinc-blende and diamond. Because of this common property there are certain similarities in their semiconducting properties. However, the place of gallium arsenide as one of the most important semiconductor materials lies in the following:

(i) A gallium arsenide p-n junction is an efficient light emitter whereas silicon and germanium diodes are not.

(ii) For germanium and silicon, the conduction band minimum occurs at a momentum different from that of the maximum of the valence band. But in gallium arsenide, the minimum and the maximum occur at the same momentum - a feature that is the basis for the injection laser and the light emitting diode. Thus, gallium arsenide is a direct gap material in which an electron can make the transition directly from the conduction band to the valence band without changing momentum and can give up its energy in the form of a quantum of light.

(iii) The greater band gap and greater mobility of electrons in its conduction band minima give GaAs a higher operating temperature and higher frequency capabilities than silicon and germanium.

(iv) Because there are two valleys in its conduction band, one of which is at a slightly higher energy level,
about 0.36 eV above the other, GaAs exhibits a negative resistance effect (i.e. the Gunn effect). Electrons in the lower valley have a much higher mobility than those in the other valley, but the energy difference between the two levels is so small that strong electric fields give the electrons enough energy to move from one minimum to the other. When the upper valley is more densely populated than the lower, the material exhibits a differential negative resistance; as the voltage increases, more electrons transfer to the lower-mobility band and the current decreases, causing bulk instabilities such as the Gunn effect.

One of the problems with GaAs as a device material is the decomposition of the surface region\(^{(1,2,3)}\) during high temperature heat treatment which is an inevitable device fabrication step. An effective encapsulant for implanted GaAs should be able to protect the implanted GaAs surface from decomposition. It should also be able to prevent outdiffusion of the implanted species. A poor encapsulant can result in low activation of implanted ions and anomalous carrier concentration changes in the substrate. The encapsulation requirements appear to be more severe for samples implanted with n-type dopants than for samples implanted with p-type dopants.

The first encapsulant reported for protecting gallium arsenide was silicon dioxide. However, gallium outdiffusion occurs into such a layer\(^{(4)}\). This led to an intensive search for other possible encapsulants.
Among the ones reported to date are $\text{Al}_2\text{O}_3$, $\text{AlN}$, $\text{Si}_3\text{N}_4$, $\text{Ga}_2\text{O}_3$ etc. $\text{Si}_3\text{N}_4$ has been demonstrated to be the best for high temperature ($>700^\circ\text{C}$) annealing. \(^{(8,9)}\)

1.3. Ion Implantation

Ion implantation is a process whereby controlled amounts of chosen ion species can be introduced into the surface regions of a material in the form of accelerated ions. Although, it is not as well established as the alternative methods of doping such as diffusion, epitaxy and growth from the melt, it offers certain advantages over the other methods. The main advantages of ion implantation as a device fabrication step can be summarized as follows:

(i) The total amount and purity of ions implanted can be accurately controlled and monitored. This is not possible in the case of diffusion where surface conditions and parameters of the gas modify the amount which diffuses in.

(ii) The concentration of implanted species, as a function of depth, can be controlled by varying the implant energy and ion dose. This is evidently very difficult in the case of diffusion.

(iii) Implantation and subsequent annealing are comparatively low temperature processes and therefore diffusion of unwanted impurities through the surface is eliminated.
(iv) It is a non-equilibrium process, so that solubility limits can be exceeded. Therefore, it is possible to introduce a material which does not readily diffuse.

(v) Implanted ions enter the surface usually as a well-directed beam so that high definition of the implanted region can be achieved using conventional masking techniques.

(vi) The process is highly versatile and, in principle, a single implantation facility can be used for many different ion species and for ion bombardments aimed at a number of useful non-doping processes in device fabrication.

(vii) The process can be automatically controlled almost completely. So, some of the manual operations are eliminated and possible contamination during implantation can be minimized.

The major disadvantage of any ion implantation process is that energy deposition produces displacement of the original atoms from their lattice sites (i.e. radiation damage) in the solid. It also produces significant changes in surface properties of the material. In most cases, it is necessary to remove the radiation damage by heat treatment but this may cause undesirable effects such as decomposition of surface regions, undesirable diffusion of implanted species etc.
Irrespective of the disadvantages, the most striking benefit of ion implantation, deriving from its reproducibility, is the improvement in yield of silicon LSI circuits, typically by an order of magnitude. The same advantages have also been shown to benefit GaAs\(^{(10)}\). In addition to the present, the future applications are likely to be in the field of integrated logic and integrated optical circuits where the advantages of ion implantation will play an important role\(^{(11)}\).
CHAPTER II
RADIATION DAMAGE.

11.1. Introduction

Ions travelling in a solid medium lose their energy in two ways, (1) electronic stopping, i.e. excitation and ionization of electrons, including charge exchange mechanisms, (2) nuclear stopping, i.e. elastic collisions with the nuclei. These may be regarded as two independent processes, so that the linear rate of energy loss is given by the sum of two contributions. Nuclear collisions can involve large energy losses and significant angular deflections of the projectile ions. It is also the mechanism responsible for displacements of lattice atoms. In general, radiation damage occurs when a lattice atom receives an energy greater than about 25 eV - the displacement energy. (12) The electronic collisions involve much smaller energy losses per collision, negligible angular deflection and comparatively less lattice damage. The relative importance of the two mechanisms changes rapidly with the energy, \( E \), and atomic number, \( Z \), of the ion. Nuclear stopping predominates for low \( E \) and high \( Z \), whereas electronic stopping becomes dominant for high \( E \) and low \( Z \).

Accelerated atomic projectiles introduced into materials create disorder which modifies to some extent the electrical and optical properties of the material. Physical changes induced in the target material arise either from the radiation damage or from the chemical
properties of the projectile dopant or in some cases, a combination of both. The distribution of damage along an ion track varies considerably with the mass of the ion. If the size of the implanted species is such as to allow substitutional occupation of lattice sites, the resulting physical properties of the implanted material will be determined mainly by the charge state of the implanted ion and any residual damage remaining after heat treatment. On the other hand if the particle is very small, as is the case with protons (or neutrons and electrons) no substitutional occupation occurs and any physical changes will be the result of how much disorder the projectile ion generated in the process of expending its energy.

During the course of our investigation, we will refer to two damage regimes which have been separately identified as (a) heavy ion damage, neutrons can also be classified in this category, (b) light ion damage. In the case of heavy ions, the stopping cross section is so large that the individual collision cascades are essentially indistinguishable and the damage is contained within one large defect cascade, (figure II.1.a). For light ions, a large fraction of the ion energy is dissipated in inelastic collisions and because of the smaller collision cross-section, their penetration is significantly greater. The majority of defects formed are essentially isolated defects along the ion track (figure II.1.b).
FIGURE (II.1): (a) COLLISION CASCADE IN SILICON BY A HEAVY ION.
(b) COLLISION CASCADE IN SILICON BY A LIGHT ION.
II. 2. PROTON BOMBARDED GaAs

II.2.1. Basic Properties

The depth distribution of defects in proton bombarded GaAs suggests that the stopping mechanism is mainly electronic rather than nuclear. In this situation, the primary encounters occur through essentially unscreened Coulomb collisions and the number of large energy transfers is very much reduced and therefore the formation of amorphous material is unlikely.

The first attempt to investigate the density of defects and electrical properties of proton bombarded GaAs was made in 1966 by Wohlleben and Beck. They bombarded a number of n-type and p-type specimens with 3 MeV protons which are estimated to have a range of 60 microns in GaAs. According to the scattering theory, the effective cross-section for the scattering of protons at the nuclei of lattice atoms is, to a good approximation, inversely proportional to the proton energy. Therefore, the density of lattice defects produced by the protons increases with increasing proton penetration reaching a maximum at the projected range. By choosing the average specimen thickness to be about 45 micron, they eliminated, to some extent, the non-uniform distribution of defects in their specimens. Therefore, the protons had enough energy to transmit through the whole specimen emerging from the back face with 1.1 MeV residual energy.
According to their findings, several basic conclusions can be drawn by examining the carrier removal curves. The results obtained from Hall effect measurements are shown in Figure (II.2). By calculating the integral carrier removal rates and extrapolating to the case of infinite $N_p$ (proton dose), they found that the smallest measurable electron and hole concentrations were about $10^9$ and $10^{10}$ cm$^{-3}$ respectively, corresponding to a resistivity value of $10^7$ $\Omega$cm. Extrapolation of their results leads one to expect that under continuous irradiation, the carrier concentration of p-type GaAs approaches a limiting value of $10^9$ cm$^{-3}$ and n-type GaAs is converted to p-type GaAs reaching the same limiting value. Correspondingly, the Fermi level adjusts to a new value $E_F = E_V + 0.85$ eV. In fact, the carrier removal rate was found to be very dependent on the position of the Fermi level. As seen from figure II.3, in order to reduce the carrier concentration to a given value, the specimen must be irradiated with a given dose of protons which increases as the initial carrier concentration increases. In addition, they also computed the differential removal rates by differentiating the integral carrier removal curves (figure II.4). The similarity between the differential removal rates for n-type and p-type GaAs suggests that the distribution of bombardment induced damage centres in both types are nearly identical. In other words, both donors and acceptors must be generated.
FIGURE (II.2): INTEGRAL CARRIER REMOVAL RATES, \( \frac{n_0 - n}{N_p} \) AND \( \frac{p_0 - p}{N_p} \), FOR n- AND p- TYPE GaAs OF DIFFERENT INITIAL DOPING, \( n_0 \) AND \( p_0 \). (AFTER WOHLLEBEN AND BECK\(^{(13)}\)).

FIGURE (II.3): ELECTRON AND HOLE CONCENTRATION OF p- AND n- TYPE GaAs WITH DIFFERENT INITIAL DOPING, \( n_0 \) AND \( p_0 \), AS A FUNCTION OF PROTON DOSE FOR 3 MeV PROTONS. (AFTER WOHLLEBEN AND BECK\(^{(13)}\)).

SEE FOLLOWING PAGE FOR KEY TO FIGURES (II.2) AND (II.3).
FIGURE (II.4): DIFFERENTIAL CARRIER REMOVAL RATES, $dn/dN_p$ AND $dp/dN_p$, FOR $n$- AND $p$- TYPE GaAs OF DIFFERENT INITIAL DOPING, $n_o$ AND $p_o$. (AFTER WOHLLEBEN AND BECK (13)).

KEY FOR FIGURES (II.2), (II.3) AND (II.4).

<table>
<thead>
<tr>
<th>n-TYPE GaAs: curve</th>
<th>$n_o$ (cm$^{-3}$)</th>
</tr>
</thead>
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II.2.2. Carrier Removal

Early work to determine the carrier removal in proton bombarded GaAs has been briefly summarized in the previous section. We have defined the carrier removal, $\Delta n$, as the difference between the sheet carrier concentration measured after bombardment and the initial sheet carrier concentration. The integral carrier removal rate, $K_{\text{int}}$, is defined as the carrier removal per incident ion, $\Delta n/dose$. In addition, the carrier removal rate, $K_x$, measured at a depth, $x$, is also meaningful. For convenience, during the course of our work, $K_p$, corresponding to the maximum carrier removal rate measured at the minimum of the carrier concentration profile of a bombarded sample, is determined in most cases.

Pruniaux et al. investigated the carrier removal rates as a function of the proton dose at three depths in the crystal. The 1.1 $\mu$m depth corresponds to the projected range or profile minimum of 150 keV protons (figure II.5) incident on GaAs. Similarly, 0.3 $\mu$m corresponds approximately to the zero bias depletion depth and is therefore the smallest depth at which data were obtained. They found the removal rate at 1.1 $\mu$m was $7 \times 10^4$ electrons per incident proton. The removal rate at 0.3 $\mu$m was, as expected, less at $1.2 \times 10^4$ electrons per proton. They also reported that the removal rate at the profile minimum has been observed to decrease rapidly after the samples were more than 60% compensated. The ratio of the removal rate at the profile minimum of 150 keV proton bombarded GaAs to that near the surface (at 0.3 $\mu$m) increases at higher
Figure (II.5): Reciprocal carrier concentration versus depth of proton-implanted GaAs. Incident proton energy was 150 keV. The n-type epitaxial GaAs had an initial carrier concentration, $N_o$, of $1.3 \times 10^{16}$ cm$^{-3}$. Each incremental proton dose was $\sim 10^{10}$ cm$^{-2}$. (After Pruniaux, North, and Miller [14].)
incident energies and was observed to be about ten for an energy of about 300 keV. The integral removal rate over the whole profile was computed to be $4 \times 10^4$ electrons per incident proton.

Harada et.al. have performed similar experiments with protons in the energy range 60 to 400 keV. They reported that the carrier removal was energy dependent up to 150 keV and remained constant up to 400 keV. For 60 keV protons the removal rate $K_p$ appeared to be $8 \times 10^4$ electrons/proton, whereas, for 150 keV it was half that value—$4 \times 10^4$ electrons/proton. Beyond 150 keV, judging by the shape of their profiles, removal rate, $K_p$, remained almost constant. In other words, the peak heights of the profiles of 150 to 400 keV bombardments appeared to be almost identical.

II.2.3. Proton Ranges in GaAs

In order to apply the technique of proton isolation to the fabrication of devices based on GaAs it is essential to know the range of the protons. There have been several calculations of the ranges of ions in solids. However, there is no complete theory of the electronic stopping power of protons in GaAs. Consequently, precise data of proton ranges in GaAs is not available, since L.S.S. theory is not applicable to light ions, such as protons. Tsurishima et.al. calculated the projected range by means of some extended electronic stopping power derived on the basis of both the L.S.S. and Bethe-Bloch theory.
Recently, Northcliffe et al.\(^{(16)}\) reported semi-empirical values of the electronic stopping power of protons in Ge. Since Ge is between gallium and arsenic in the periodic table, the electronic energy loss for two germanium atoms is expected to be nearly equal to the electronic energy loss for one GaAs molecule. Thus, the stopping power of protons in GaAs can be approximately calculated.

Using Northcliffe's data\(^{(16)}\), Matsumura et al.\(^{(17)}\) computed the proton ranges in GaAs up to 1 MeV. They also verified experimentally the validity of their calculated results, assuming that the depth of the damage peak was very nearly equal to the range of the implanted protons. They finally concluded that the range of protons in GaAs increased by about 0.85 microns for every 100 keV of the proton energy up to 600 keV above which, the range per 100 keV increased. Recent experimental studies by Speight et al.\(^{(22)}\) are in good agreement with Matsumura\(^{(17)}\) within the energy range 0.2 to 1 MeV. Experimental results of Sakurai et al.\(^{(20)}\) over the energy range 75 to 700 keV and theoretical calculations of Tsurishima et al.\(^{(19)}\) are also in good agreement with Matsumura\(^{(17)}\).

In apparent contrast to the above results, Foyt et al.\(^{(21)}\) found that the "isolation depth" was 1 micron per 100 keV. They defined the term "isolation depth" as the depth at which a so-called donor peak occurred at the end of the profile (figure II.6). These donor peaks are
FIGURE (11.6): CARRIER CONCENTRATION PROFILE
CREATED BY THE PROTON BOMBARDMENT
OF n-GaAs (n=2 x 10^{16} \text{cm}^{-3}) WITH A
100 keV BEAM OF DOSE 10^{13} \text{cm}^{-2}.
(AFTER FOYT, LINDLEY, WOLFE AND DONNELLY^{21}).
only observed\(^{(15,20,21)}\) on profiles obtained from C-V techniques and do not represent the free electron concentration with depth. The reason for their existence is believed to be due to electron emission from the deep donor or compensating acceptor centres produced by proton bombardment.

Okunev et al\(^{(23)}\) employed a different method to investigate the range-energy relationship of protons in GaAs. Knowing the distribution of the intensity of the edge luminescence across the thickness of the crystal, they determined the depth of penetration of 2 to 5 MeV protons. The experimental data were also compared with the results calculated using the Bethe-Bloch equation for the stopping power expression. The experimental and theoretical results seem to match satisfactorily. To characterize the results, they reported that the proton range can be related to the proton energy by the following expression:

\[
R = CE^\gamma
\]

where \(R\) and \(E\) are the proton range and energy and \(C\) and \(\gamma\) are constants which were experimentally determined to be 5 and 1.5 respectively.
II. 2.4. Thermal stability of proton bombarded layers

a) Electrical properties

Although proton isolation has been demonstrated to be a useful step in device fabrication, unless its thermal stability is thoroughly established its use in device technology would be limited, since bombarded layers degrade at high operating temperatures. After the bombardment is completed, even contact alloying at an elevated temperature of 300 to 400°C can cause some recovery of the radiation damage. Therefore, a study of annealing characteristics is necessary.

As mentioned earlier (section II.1.1) most of the proton damage is concentrated around the projected range. Pruniaux's observations\(^{(14)}\) on "lightly" bombarded \((10^{10}-10^{11} \text{ H}^+/\text{cm}^2)\) samples annealed at 250°C for several hours show that, around the projected range, recovery tends to be more rapid than the region nearer to the surface. He also emphasized that semi-insulating properties of the lightly bombarded layers disappear after annealing in excess of 350°C.

In the case of heavily bombarded samples, the annealing temperature necessary to restore the electrical properties of the material is higher than that for lightly bombarded samples\(^{(20)}\).

Foyt et al.\(^{(21)}\) found that profiles obtained from samples bombarded with \(10^{13} \text{ ions/cm}^2\) of 100 keV protons were not affected by annealing at 300°C for 16 hours.
However, there was a decrease in the magnitude of the donor peak at 400°C. But even at this temperature the low carrier concentration region remained semi-insulating and the carrier concentration in this region was estimated to be less than $10^{11}$ cm$^{-3}$. Annealing at 700°C overnight resulted in complete recovery of the resistivity. Foyt also stated that it was possible to carry out contact alloying at 500°C without removing the high resistivity layers.

For IMPATT diodes, Speight et al. showed that the process of contact making at 450–500°C may be safely carried out after the high dose ($4 \times 10^{14}$ proton/cm$^2$) bombardment necessary for electrical isolation of devices.

Sakurai et al. observed a significant amount of recovery on lightly bombarded specimens at 435°C for 10 minutes. Above a proton dose of $6 \times 10^{12}$ H$^+_1$/cm$^2$, no recovery of carriers was observed even after 35 hours of annealing at the same temperature, (435°C), although the "isolation depth" moved slightly towards the surface. Similar results have been achieved by Harada et al. who realised that the lightly bombarded specimens (60 keV, $10^{12}$ H$^+_1$/cm$^2$) were affected by an anneal at 300°C for 10 minutes and complete recovery occurred at 500°C for the same annealing period.
b) **Optical Properties**

As will be described in the next section, proton bombardment is an attractive method used in the fabrication of optical devices. It is therefore worthwhile to review the effects of heat treatment on the optical properties of proton bombarded GaAs. Dyment et al.\(^{(24)}\) found that optical absorption increased almost linearly with proton dose up to \(10^{17}\) proton/cm\(^2\) in p-type bulk GaAs. They also found that the damage responsible for high optical absorption could be completely annealed out at 450°C for 15 minutes or at 500°C for 5 minutes. Either of these heat treatments may be used for the fabrication of stripe-geometry lasers\(^{(24)}\) and result in complete recovery of optical absorption but leave a sufficient average resistivity in the bombarded region to confine the current within the stripe. Since the damage responsible for high optical absorption can be annealed out more easily than that causing carrier compensation, the defects causing the high resistivity must have comparatively higher activation energies.

c) **Multiple Energy Bombardment**

Recently, Donnelly et al.\(^{(73)}\) showed that multiple energy bombardment was superior to single energy bombardment in producing high resistivity layers in n\(^+\) GaAs \((n = 4 \times 10^{18} \text{ cm}^{-3})\). At first, they attempted to use 400 keV protons for the purpose of creating a semi-insulating layer of about 4 \(\mu\)m thick. However, the layer could not be effectively compensated by single
energy (400 keV) protons. To overcome this problem, they used a multiple energy bombardment (50 keV - 400 keV) which effectively compensated the whole layer. The compensated layers produced by such a multiple energy bombardment showed a better i.e. higher, temperature stability than those for single energy bombardments. With no annealing, there was an optimum multiple energy bombardment dose, $D_o$, which maximized the average resistivity ($10^7 - 10^8 \ \Omega\cdot\text{cm}$). With annealing, larger doses, i.e. larger than the optimum dose, $D_o$, were needed to achieve the same resistivity. In other words, the resistivity of multiple energy bombarded material increases at first then goes through a maximum with increasing annealing temperature. There is also an optimum dose, $D_T$, for any specific annealing temperature. The optimum dose, $D_T$, needs to be increased with increasing annealing temperature. To achieve the highest resistivity, Donnelly et.al\(^{(73)}\) have employed multiple energy bombardment and an anneal at a temperature as high as 500°C.

For IMPATT diodes, Speight et.al\(^{(22)}\) showed that the process of contact making at 450-500°C could safely be carried out after the high dose ($4 \times 10^{14}$ protons/cm\(^2\)) multiple energy (0.1 to 1 MeV in steps of 0.1 MeV) bombardment was accomplished. This arrangement resulted in a 12 $\mu$m thick high resistivity ($10^8 \ \Omega\cdot\text{cm}$) layer necessary for electrical isolation of devices. According to Speight's experimental results\(^{(22)}\), high resistivity
layers produced by the above mentioned multiple energy bombardment were stable at 400°C for 10^3 hours. At a temperature of 470 to 500°C the resistivity was still as high as 10^8 \( \Omega \cdot \text{cm} \) up to 10^2 hours and then it dropped to a value of 10^3 \( \Omega \cdot \text{cm} \).

II.2.5. Applications of Proton Bombardment

In recent years the simple process of proton bombardment has been the most attractive aspect of ion implantation because of its wide application in device fabrication. It has been mainly used to produce high resistivity layers for isolation purposes.

a) GaAs

Lindley\(^{(26)}\) and Stillman et al.\(^{(27)}\) have employed the technique to guard photodiodes, whilst another type of device which utilizes proton isolation is the IMPATT diode. Murphy et al.\(^{(28)}\) and Speight et al.\(^{(29)}\) have fabricated IMPATT diodes using proton isolation to define the active device areas and also to suppress edge breakdown. It seems that the devices made in this way have several advantages over the mesa-etched devices. Using proton isolation, device performance and uniformity of breakdown voltage over a slice was considerably improved\(^{(22)}\). After intensive annealing studies, Speight et al.\(^{(22)}\) found that proton isolation was not a limiting factor in determining the device lifetime. The mechanism responsible for failure at elevated operating temperatures (>200°C) was believed to be the indiffusion of metal from contacts to the active device junction, thus, causing
a short circuit. Speight et al.\(^{(22)}\) also observed that the Mean Time To Failure (MTTF) was 250 hours at 350°C and estimated the MTTF at 200°C to be \(5 \times 10^6\) hours.

Another important application of proton bombardment is in the fabrication of GaAs field effect transistors. The most straightforward case is the isolation of single transistors on a chip which eliminates the need for mesa etching\(^{(34)}\). Pruniaux et al.\(^{(30)}\) have also exploited the proton damage to make a semi-insulated gate gallium arsenide field effect transistor. The advantage of having a semi-insulating layer between the gate and the channel enables the transistor to be operated with either polarity of the gate bias. Also, high concentration material can be used in the channel because the leakage current through the semi-insulating layer does not depend on the carrier concentration of the channel region, in contrast to the Schottky barrier gate FET.

It has been shown by several groups that surface waveguides can be formed in GaAs by proton bombardment. Garmire et al.\(^{(31)}\) produced optical waveguides in n-type GaAs by bombarding with 300 keV protons. The guiding was thought to be due to the refractive index difference resulting from carrier removal in the bombarded region. Somekh et al.\(^{(32)}\) fabricated optical waveguides and directional couplers in GaAs by 300 keV proton bombardment. Stoll et al.\(^{(33)}\) have also exploited the same idea to fabricate optical waveguide detectors based on the
principle of bombarding a small volume of an epitaxial GaAs waveguide to create an optically highly lossy depletion region of a reverse-biased Schottky contact deposited on the bombarded area. Electron-hole pairs generated by optical stimulation in the depletion region result in an external current flow indicating the measure of the stimulation.

b) Other materials

The concept of high resistivity formation by proton bombardment has also been applied to other materials as well as GaAs. Dyment et al.\(^{(35)}\) used proton bombardment to guard Ga\(_{1-x}\)Al\(_x\)As LEDs. According to their findings, proton bombardment provided precise control over the light emitting area but caused a large reduction in overall device efficiency. This reduction was thought to be due to the bombardment induced defect centres functioning as carrier traps and optical absorption centres. However, the efficiency improved by changing the isolation depth (bombardment energy) from deep to shallow, but diodes in which oxide-masking was used still showed highest efficiency due to an enhanced reflection at SiO\(_2\) metal interface. Thus a combination of both techniques - proton bombardment for a better control over the light-emitting area and oxide masking for high efficiency were employed in the fabrication process. In addition, thermal stability tests performed at 100\(^\circ\)C for 1.0\(^3\) hours at a current density of 3 kA/cm\(^2\) showed that
LEDs utilizing proton bombardment guarding had a reliability equal to, or better than LEDs with oxide-masking. Favennec et al.\(^{25}\) also investigated the thermal behaviour of proton bombarded Ga\(_{1-x}\)Al\(_x\)As in an attempt to produce integrated arrays of electroluminescent diodes. They found that no modification in the average resistivity was observed below 180\(^\circ\)C. At higher temperatures, two annealing stages were observed at 220 and 240\(^\circ\)C. After annealing at 550\(^\circ\)C the resistivity recovered its initial value.

The proton bombardment technique has also found application in producing high-resistivity layers in other compound semiconductors such as GaP, ZnTe and InP, but on the other hand proton bombardment in InAs or ZnO increases the free carrier concentration.

**II.3. H\(^+\)\(_2\) and H\(^+\)\(_3\) Bombardments in GaAs**

An ion travelling with high speed through matter can lose or capture electrons in collisions with the atoms of the medium traversed. If collisions are considered to be between the ion and the outer loosely bound electrons of the atom, and also if the binding energy of outer electrons is neglected the ion may be regarded as being bombarded by electrons with relative velocity, \(v\), equal to the velocity of the moving ion. Electron(s) of the ion can be stripped off by a collision with the electrons of the medium\(^{43}\). This picture has
been suggested by Lamb\textsuperscript{(14)} and used in discussing the charge state of the energetic fragments produced in the slow neutron fission of uranium when passing through matter.

We used the criterion suggested by Lamb\textsuperscript{(14)} to explain the dissociation of $H^+_2$ and $H^+_3$ ions. When the ions $H^+_2$ or $H^+_3$ strike the specimen (GaAs), the bond is broken by collisions in the first few atomic layers of the specimen. In other words, immediately after the bombardment, $H^+_2$ and $H^+_3$ ions split up into two and three protons respectively. The energy of the incident $H^+_2$ or $H^+_3$ ions is shared equally by the dissociation product protons\textsuperscript{(45,46)}. It has been reported that this process of dissociation, takes place in a very short time of the order of about $10^{-16} - 10^{-17}$ seconds\textsuperscript{(45)}.

Dissociation of $H^+_2$ and $H^+_3$ ions and the cross-sections of the dissociation products have been extensively studied in gas media, but comparatively little data are available on the dissociation of $H^+_2$ and $H^+_3$ ions in solid media. It is worthwhile to review some of the complementary work published so far.

Golovchenko et al.\textsuperscript{(46)} observed 1 MeV protons transmitted through thin self-supporting carbon foils when the energy of incident $H^+_2$ ions were 2 MeV. The idea was to study the physical phenomena behind the joint energy and angular distribution of dissociation product protons.
Caywood et al. (45) obtained backscattering data of 0.8 MeV H<sup>+</sup>, 1.6 MeV H<sup>+</sup><sub>2</sub> and 2.4 MeV H<sup>+</sup><sub>3</sub> ions incident on silicon. Since electrons are stripped off in a very short time ($10^{-16}$ - $10^{-17}$) seconds, the situation can be considered as one in which 1, 2 or 3 protons are introduced in the crystal simultaneously at essentially the same location. The back-scattering yield of H<sup>+</sup><sub>1</sub> and H<sup>+</sup><sub>2</sub> ions were found to be the same within the experimental error. The H<sup>+</sup><sub>3</sub> spectrum appeared to be somewhat different than those obtained from H<sup>+</sup><sub>1</sub> and H<sup>+</sup><sub>2</sub>. The number of protons back-scattered, when the beam was aligned along a channel, was greater in the case of an H<sup>+</sup><sub>3</sub> beam. When several protons enter a channel simultaneously, the effect is to narrow the channel and increase the probability of dechannelling with resultant large angle scattering.

Recently, Mitchell et al. (83) investigated the damage caused by protons and deuterons. For some high dose implants, a diatomic beam of twice the energy was employed instead of a monoatomic beam. Using the Rutherford backscattering technique, they concluded that the effect of equivalent implants of mono- and diatomic implants of H<sup>+</sup><sub>1</sub> and D<sup>+</sup><sub>1</sub> are identical in terms of damage production.

In plasma forming experiments, Sweetman (37) obtained 30 keV H<sup>+</sup> atoms by accelerating 90 keV H<sup>+</sup><sub>3</sub> ions which entered a dissociation chamber and exchanged charges with
a water vapour atmosphere. This method of forming a neutral beam from $\text{H}_3^+$ ions had the advantage over formation by charge exchange from $\text{H}_1^+$ by yielding three times the neutral intensity per charged particle accelerated.

Finally, we employed $\text{H}_2^+$ and $\text{H}_3^+$ ions for the purpose of providing an equivalent proton implant in GaAs. Our results indicated that the amount of radiation damage and consequently the carrier removal rate caused by a proton implant with a particular energy $E$ and dose $D$ was equal to $\text{H}_2^+$ or $\text{H}_3^+$ implants of energy $2E$ and dose $\frac{3}{2}D$ (in case of $\text{H}_2^+$ ions) or $3E$ and $3D$ (in case of $\text{H}_3^+$ ions) respectively (see reference 47).

II.4. Oxygen Bombardment.

In 1959, Weisberg et al. (36) demonstrated the possibility of forming high resistivity layers in n-type GaAs. Since then, Favennec et al. (37) made the first attempt to form actual semi-insulating layers in n-type and p-type GaAs by oxygen implantation. According to Favennec's findings, the carrier compensation was due to two mechanisms; (a) bombardment-induced defects and (b) the chemical doping effect of oxygen. In order to prove the existence of a doping effect, Favennec et al. (37) implanted carbon (1 MeV, $5 \times 10^{13} \text{C}^+/\text{cm}^2$) into GaAs. This implant was thought to produce about the same damage as a 1 MeV, $5 \times 10^{11}$ oxygen implant. After annealing at $750^\circ \text{C}$,
a complete recovery of mobility which reached the value given by Sze and Irvin\textsuperscript{(38)} was observed. The electrical activity was found to be 40\% which is the maximum solubility of carbon in GaAs\textsuperscript{(36)}. This simple experiment leads one to conclude that there is no significant amount of radiation damage remaining at a temperature as high as 750°C, therefore the mechanism responsible for the carrier compensation for oxygen implanted samples is a doping effect of oxygen. To characterize the compensation phenomena, the properties of oxygen bombarded layers have been optically and electrically examined.

II.4.1. Optical Measurements

Using scanning electron microscopy Favennec et al.\textsuperscript{(37)} found the existence of a high-resistivity layer on samples that had been subjected to multi-energy oxygen bombardment which provided a flat oxygen distribution over the whole epitaxial layer. After multiple energy bombardment and 800°C annealing, they observed that the whole epitaxial layer was converted to a high resistivity layer. Favennec\textsuperscript{(39)} also showed the existence of two types of non-radiative recombination centres in the oxygen bombarded regions. One of them was detected at the implanted ion range and also participated in compensation, the other, which did not participate in electrical compensation, existed deeper than the projected range and showed a tendency to diffuse. The diffusion of non-
participating defects was observed during hot (360°C) implantations as well as during an anneal at 360°C. From this work, one could not distinguish if the non-participating defects were bombardment induced defect centres or oxygen ions.

II.4.2. Electrical Measurements

Favennec et al.\(^{37}\) investigated the temperature dependence of the resistivity of multi-energy oxygen bombarded layers and found that the high value of the resistivity measured on as-implanted samples was not affected by annealing temperatures up to 800°C. To characterize the properties of the semi-insulating layer, Hall measurements were performed on samples implanted with a dose of \(5 \times 10^{11} \; \text{O}^+ / \text{cm}^2\) at 1 MeV. The resulting profiles indicated that the semi-insulating layer was buried between two undamaged, surface and background, regions. For the same implant energy (1 MeV) and for unannealed samples, Copeland measurements indicated that the thickness of two semi-insulating layers increased from 0.6 to 1.8 \(\mu\)m as the ion dose increased from \(10^{12}\) to \(10^{14}\) ions/cm\(^2\).

In their recent work, Favennec\(^{39}\) reported that the carrier compensation in oxygen bombarded layers was not dependent on the doping species of the material. The carrier compensation was successfully realised on Si, Te, Sn and Se doped GaAs. In addition, since some carrier compensation was observed for oxygen doses as
low as $10^{15} \text{cm}^{-2}$ they suggested that the formation of oxide compounds $\text{Ga}_x\text{O}_y$ and $\text{As}_x\text{O}_y$ might be the possible mechanism producing the high resistance in the bombarded layers. Further work is needed to evaluate this suggestion. On the other hand, Itoh et al. from photoluminescence studies, found that in silicon doped GaAs an oxygen atom occupied an arsenic site if it was empty, otherwise the oxygen atom stayed at an interstitial site and formed a silicon-oxygen complex.

II.4.3. Application of oxygen bombardment.

As mentioned earlier (section 2.2), compensated layers in GaAs have been utilized to form waveguides. For the same purpose, Favennec et al. have carried out low and high dose oxygen implantations in order to investigate the guiding properties of oxygen bombarded layers. In the case of low dose ($10^{10}-10^{12} \text{cm}^{-2}$) bombardment, no waveguiding was observed even after annealing at $450\degree\text{C}$. This was due to the light being absorbed by the remaining radiation damage centres. In the case of high dose ($10^{14} - 5 \times 10^{14} \text{cm}^{-2}$) implants, the guiding properties of the bombarded layers exhibited somewhat different behaviour. After annealing at $500\degree\text{C}$, weak guiding was observed. Annealing at higher temperatures to increase the efficiency was not satisfactory because of the failure of the silicon dioxide encapsulant i.e. the SiO$_2$ layer was reported to create a number of diffusing centres which resulted in further absorption of the light. So, their work was directed to find a non-reactive encapsulant.
Blum et al. have employed oxygen bombardment to form stripe-geometry double heterostructure GaAs/GaAlAs injection lasers. This method had several advantages over the alternative methods. By employing \( O^+ \) bombardment, techniques such as mesa etching, diffusion and annealing of optical damage after proton bombardment were eliminated. The radiation damage caused by oxygen ions was annealed out during the junction formation process therefore no post-annealing was needed. Annealing and ageing studies indicated that residual damage in the oxygen-bombarded layers did not cause any detrimental effects on the lifetime of the device.

Blum et al. also found that oxygen bombardment resulted in relatively better lateral spread confinement over the mask edge. The sharp profile was thought to be due to diffusion of oxygen into the active device area which blocked the carrier outdiffusion from the stripe region. In fact, the actual mechanism causing the lateral confinement and also, why the sharp lateral confinement was not obtained in all such cases is not known. When the mechanism of lateral confinement is thoroughly understood, oxygen bombardment may become a very useful method in device fabrication.
II.5. Compensation in GaAs by heavy ions

One of the problems in the application of ion implantation to GaAs is the difficulty of forming heavily doped n$^+$ layers. Dopant ions usually produce low electrical activity in the bombarded region which is believed to be due to the residual damage remaining after inadequate annealing. Investigation of the nature of the recovery of the implantation-induced damage would be expected to contribute to our understanding of the problem of forming n$^+$ layers. The investigation of compensation is also of interest in semi-insulating layer formation. Recently, to obtain higher electrical activity, the importance of hot implants has been emphasized by several research groups.

Foyt et.al\(^{14,8}\) found that implants performed at 500$^\circ$C resulted in more efficient doping for selenium in GaAs than, when implants were carried out at room temperature.

Harris et.al\(^{14,9}\) observed higher electrical activity when implants were made at 150$^\circ$C as opposed to room temperature.

It is believed that, hot-implants produce less lattice disorder. According to Whitton et.al\(^{50}\), the lattice damage caused by room temperature S$^+$ implants was almost completely eliminated by performing the implant at 150$^\circ$C. Similarly, for Te$^+$ ions, Eisen et.al\(^{51}\) observed a large reduction in the amount of lattice
disorder when implanting at 150°C rather than room temperature.

Using Rutherford backscattering and electron microscopy, Bicknell et al.\textsuperscript{(52)} examined Ar\textsuperscript{+} and Te\textsuperscript{+} bombarded GaAs. In the case of argon implants at room temperature, the damage increased with increasing dose. The lowest dose 6 x 10\textsuperscript{11} Ar\textsuperscript{+}/cm\textsuperscript{2} resulted in insignificant damage which was not detectable by electron microscopy. A densely populated damage region was observed in samples implanted with 6 x 10\textsuperscript{13} Ar\textsuperscript{+}/cm\textsuperscript{2} and also the highest argon dose, 6 x 10\textsuperscript{14} Ar\textsuperscript{+}/cm\textsuperscript{2}, resulted in a continuous non-crystalline layer at the sample surface. Similar results were also obtained for Te implants, where, again a dose of 10\textsuperscript{13} Te\textsuperscript{+}/cm\textsuperscript{2} created a small number of defects and little non-crystalline material while high doses created non-crystalline material.

Consequently, to reduce the amount of ion damage, Ar\textsuperscript{+} or Te\textsuperscript{+} implants were carried out at 100°C. In this case, only the 6 x 10\textsuperscript{14} Ar\textsuperscript{+}/cm\textsuperscript{2} implanted sample showed visible signs of damage which was in the form of small defects about 100\textgreek{A} in diameter. For Te\textsuperscript{+} implants at 100°C, the 10\textsuperscript{15} Te\textsuperscript{+}/cm\textsuperscript{2} dose created many small defects similar to the 6 x 10\textsuperscript{14} argon implant at the same temperature. Surprisingly, the two smaller doses of Te\textsuperscript{+} (10\textsuperscript{13} and 5 x 10\textsuperscript{14} Te\textsuperscript{+}/cm\textsuperscript{2}) both produced small amounts of non-crystalline material. This anomaly was overcome by increasing the implant temperature from 100
to 180°C. In this case, only one sample implanted with \(10^{15} \text{Te}^+/\text{cm}^2\) showed visible defects which were smaller in number than the ones seen in the case of a room temperature \(6 \times 10^{12} \text{Ar}^+/\text{cm}^2\) implant. Bicknell's backscattering measurements also indicated a decrease in damage, when implants were carried out hot rather than cold.

In the light of the above brief discussion, we attempted to determine the nature of recovery and consequently, the amount of residual damage in GaAs bombarded at 20°C with argon. The results of our study will be given in the next chapter.

So far, there has been only one report of the use of argon ion implantation to make devices. This was by Macksey et al. who employed 30 keV argon ions to create a region of high resistivity GaAs which was used as the semi-insulating gate of a power FET.
CHAPTER III

111. Experimental Technique

111.1. Specimen preparation

In most of the experimental work the material used was either epitaxial n/n^+ or n/Si. Bulk chromium doped gallium arsenide was also used for some preliminary experiments. The properties of the materials used are shown in table III.1.

Bulk material was normally received in the form of ingots which were cut into slices by means of a slow speed circular diamond saw. This cutting process has been reported to cause mechanical surface damage extending to several microns in depth\(^{54}\). Therefore, chemical polishing and etching had to be undertaken.

The sawn slices were cleaned in warm trichloroethylene and methanol, then mounted on quartz discs. Polishing was carried out by hand on a Hyprocel Pellon Pan - W pad which was continuously wetted by a 5% bromine-methanol solution. After a certain time (about 30 minutes) when 10-20 micron had been removed, the surface was smooth and shiny. These slices were then transferred to a rotating beaker assembly for free etching in 0.5% bromine-methanol solution. The process of polishing and free etching was believed to remove in total about a few hundred microns of material.
<table>
<thead>
<tr>
<th>Slice Number</th>
<th>Carrier Concentration (cm(^{-3}))</th>
<th>Thickness of epitaxial layer (micron)</th>
<th>Type *</th>
<th>Experiments for which the specimens used</th>
</tr>
</thead>
<tbody>
<tr>
<td>US4</td>
<td>4.0.10(^{15})</td>
<td>10.5</td>
<td>n/n(^+)</td>
<td>(H_1^+), (H_2^+), (H_3^+) bombardments.</td>
</tr>
<tr>
<td>US5</td>
<td>1.5.10(^{15})</td>
<td>9.5</td>
<td>n/n(^+)</td>
<td>&quot;</td>
</tr>
<tr>
<td>US15</td>
<td>2.5.10(^{15})</td>
<td>7.5</td>
<td>n/n(^+)</td>
<td>&quot;</td>
</tr>
<tr>
<td>US27</td>
<td>2.2.10(^{15})</td>
<td>7.0</td>
<td>n/n(^+)</td>
<td>&quot;</td>
</tr>
<tr>
<td>US36</td>
<td>1.3.10(^{17})</td>
<td>1.4</td>
<td>n/SI</td>
<td>Oxygen bombardments</td>
</tr>
<tr>
<td>MS1877A</td>
<td>7.6.10(^{16})</td>
<td>0.9</td>
<td>n/SI</td>
<td>Oxygen and Argon bombardments</td>
</tr>
</tbody>
</table>

* n/n\(^+\) = n layer grown on low resistivity n\(^+\) layer
n/SI = n layer grown on semi-insulating layer
Although smooth and shiny surfaces can also be produced by mechanical polishing, this process has been found to cause lattice damage extending to several microns in depth.\(^{(55)}\) Therefore, chemical polishing and etching have been used since this process is known to produce damage-free surfaces\(^{(56,57)}\).

Having completed the surface treatments, slices were diced into 4 or 5 mm squares by means of a diamond impregnated wire saw. Following the dicing, the square shaped samples were degreased in trichlorethylene and rinsed in hydrochloric acid and methanol to remove any native oxides that may have formed.\(^{(58)}\)

In the case of epitaxial material, the dicing and the following chemical treatment was carried out in the same way as for bulk material.

111.2. Implantation method.

\(H_1^+, H_2^+, H_3^+,\) and \(O^+, \text{Ar}^+\) implants have been carried out on the 2 MeV van de Graaff and 600 keV heavy ion accelerators, respectively.

Prior to the implantations, all the specimens were rinsed in HCl and methanol to remove any native oxides that may have formed in air.\(^{(58)}\)

Implants were performed at energies ranging from 200 to 1500 keV depending on the ion. \(H_1^+, H_2^+, \text{and } H_3^+\) ions were implanted at very low doses, \((10^{10} - 10^{11} \text{ ion cm}^{-2})\) because of the nature of the investigation. In this case,
to achieve the required dose, beam currents had to be maintained at a very low level, usually less than 10\text{nA/cm}^2. Comparatively higher beam currents of about 0.5 \text{\mu A/cm}^2 were used when implanting with oxygen or argon ions where the doses ranged from \(10^{12}\) to \(10^{15}\) ions cm\(^{-2}\).

To minimize the possibility of channelling effects, the sample holder was machined in such a way that the specimens were exposed to the beam at about 8° off the \(\langle 110 \rangle\) or \(\langle 100 \rangle\) directions.

Most of the argon implantations were performed at a temperature of 200°C. To obtain this temperature, a heater placed beneath the sample holder plate was provided and the implant temperature was measured by a thermo-couple connected to the middle of the sample holder plate.

III. 3. Encapsulation and annealing.

Aluminium encapsulation layers, 3000-15000\text{Å} thick, were deposited by evaporating aluminium from a tungsten filament in a vacuum which was maintained better than 5 \times 10^{-6} torr. It was found that the actual film thickness was not crucial to the encapsulation efficiency. Thin films (\(<1000\text{Å}\)) were avoided because of the possibility of the film being discontinuous and also because of the formation of aluminium oxide, which may consume most of the aluminium layer leaving the GaAs surface unprotected during annealing.
After annealing, the aluminium layer was dissolved by soaking in hot concentrated HF for about 1 minute followed by a rinse in distilled water and then in methanol.

After encapsulation the specimens were placed, passivated face downwards, on a quartz boat which was then placed in the annealing furnace. Before each run, the position and temperature of the hot-zone was carefully measured. Most specimens were annealed in hydrogen + nitrogen or nitrogen atmosphere. In addition, some specimens were also annealed in an evacuated (<5 x 10⁻⁶ torr) glass tube.

III.4. Electrical contacts

III.4.1. Ohmic contacts

Most of the $H^+_1$, $H^+_2$ and $H^+_3$ bombarded specimens were annealed during the ohmic contact making. As will be shown in Chapter IV.2.7, the effect of this annealing was found to be considerable. Since this process is also part of the annealing experiments, it was thought that a detailed description of the system should be given.

The apparatus used for the contacting process is shown in figure III.1. A large slice of bulk GaAs was placed on the hot plate and the specimen was placed, implanted face downwards on to this slice. A small
piece of tin was put on top of the specimen. Hydrogen was passed through concentrated HCl to create an atmosphere of hydrogen chloride in the chamber, which acted as a flux to aid the formation of the contact. The system was flushed out thoroughly with hydrogen chloride before starting to heat the specimen. The heat was applied until the tin melted and formed an alloyed tin-dot. The specimen was then allowed to cool in a flowing hydrogen atmosphere. During this heat treatment, the temperature rose to about 300°C in about 10 seconds. By taking the average temperature for a number of runs it was found that the tin-dotting process was reproducible and took place at about 300 ± 20°C.

III.4.2. Schottky contacts

Schottky barrier contacts were prepared by the evaporation of gold or aluminium. Initially, gold was used as the contact metal for the Schottky barrier. However, it is well-known that Au-GaAs contacts are degraded at high temperatures 400°C (59,60). Considering this degradation obstacle, aluminium was chosen as an alternative metal because of the known thermal stability of the Al-GaAs Schottky contacts up to about 500°C (59).

A stainless-steel mask was used to define the contact areas which were 1 mm in diameter.
The experimental technique employed to prepare the Schottky barrier contacts was as follows:—

(a) Au-GaAs Schottky barriers.
Prior to deposition, by evaporation of gold, each bulk specimen was etched in $\text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{H}_2\text{O}_2$ followed by a rinse in methanol. Then the deposition was carried out at a pressure below $5 \times 10^{-6}$ Torr.

(b) Al-GaAs Schottky barriers.
A different surface preparation method was used prior to deposition of the aluminium. The method was:—

(i) to boil the specimens in an HCl bath for a few minutes.
(ii) Rinse in methanol.
(iii) Etch in 0.5% bromine-methanol for about one minute, followed by a final rinse in pure methanol.

The barrier formation was carried out at a pressure below $5 \times 10^{-6}$ torr using either of the following methods:—

(i) Al deposition at room temperature
(ii) Al deposition at room temperature followed by annealing at 300 to 500°C
(iii) Al deposition at an elevated temperature (150°C)

Annealing of the Schottky barriers deposited at room temperature was carried out at 350, 450 and 550°C for 15 minutes in flowing nitrogen + hydrogen or nitrogen atmosphere. Some of the specimens were also annealed in an evacuated glass tube.
The results of the experiments carried out on Al-GaAs Schottky barriers will be given in Chapter IV.1.

The ohmic contacts were made on the back face of the specimens as described in the previous section either before or after the Schottky barrier contacts were formed.

Having made the contacts, specimens were mounted onto a piece of aluminium sheet using conducting silver paste to make the electrical contact with the back electrode.

III.5. Measurement techniques

III.5.1. Capacitance - voltage measurements.

A Schottky barrier is formed when a metal and a semiconductor of different work functions are placed in intimate contact. An electrostatic barrier then occurs between the two media. Electrons flow from semiconductor to metal which causes the Fermi levels to coincide. The resulting uncompensated donors on the semiconductor surface region are balanced by holes from the metal causing band bending in the interface region (figure III.2.). The electron affinity of the semiconductor $\chi_s$ and the work function of the metal $\phi_m$ remain unaltered. This is shown diagramatically in figure III.2.

In the case of a perfect contact:

$$\phi_B = \phi_m - \chi_s \quad (III.5.1.)$$

This is the Schottky relationship.
FIGURE (III.2): BAND ENERGY DIAGRAMS OF A METAL–SEMICONDUCTOR CONTACT (N-TYPE).

(a) BEFORE THE CONTACT.
(b) AFTER THE CONTACT.
The theoretical analysis of Schottky capacitance is similar to that of a p-n junction in which one side is much more heavily doped than the other.

For any junction, the width of the depletion region can be calculated by solving Poisson's equation:

\[
\frac{d^2V}{dx^2} = -\frac{qN}{\varepsilon}
\]

(III.5.2)

where;

\( q \) = electronic charge
\( N \) = carrier concentration
\( \varepsilon \) = permittivity of semiconductor
\( V \) = voltage
\( x \) = distance

from the junction to the extremities, when \( \frac{dV}{dx} = 0 \), For charge neutrality \( \frac{dV}{dx} \) must be continuous at the junction, which leads to the expressions

\[
x^n^2 = \frac{2ev_D}{qN_D} \cdot \frac{N_a}{N_a + N_d}
\]

(III.5.3)

\[
x^p^2 = \frac{2ev_D}{qN_a} \cdot \frac{N_d}{N_a + N_d}
\]

(III.5.4)

where;

\( x_p \) = depletion layer width into metal side
\( x_n \) = " " " " semiconductor side
\( N_a \) = acceptor concentration
\( N_d \) = donor concentration
When \( N_a \gg N_d \), such as the case of a metal - (n type) semiconductor junction, then;

\[
x_n^2 + \frac{2eV_D}{qN_D} = x_p + 0 \tag{III.5.5}
\]

Hence, the depletion region can be considered to extend entirely into the n-type semiconductor.

When a reverse bias voltage, \( V \), is applied to the diode, this adds to the "built in diffusion voltage \( V_D \)" resulting in a depletion depth formula:-

\[
x_n = \left( \frac{2e(V+V_D)}{qN_D} \right)^{\frac{1}{2}} \tag{III.5.6}
\]

Using the expression for a simple parallel plate capacitor:-

\[
C = \frac{\varepsilon A}{x} \tag{III.5.7}
\]

we find that:-

\[
C^2 = \frac{q\varepsilon A^2N_D}{2(V + V_D)} \tag{III.5.8}
\]

This is the so-called Schottky capacitance law\(^{61}\).

Superimposing a small modulating A.C. voltage upon the applied D.C. reverse bias will cause a small modulation in the depletion depth. This results in an incremental change in the capacitance. If \( N(x) \) is the concentration in the depletion region, then:-
\[ \frac{\Delta V}{\Delta \left( \frac{1}{C^2} \right)} = \frac{eG^2N_(D)(x)}{2} \]  

(III.5.9)

Hence, when the applied reverse bias voltage is changed the capacitance will change according to equation III.5.9. If a plot is then made of \(1/C^2\) versus \(V\), the slope of this at any point is proportional to the ionized impurity concentration. As a function of depth.

If the semiconductor is homogenous, that is, if there is no variation in concentration with depth, then a plot of \(1/C^2\) versus \(V\) will be a straight line. If the material is inhomogenous, a simple computation of the \(C-V\) results will yield the profile of the ionized impurity concentration with depth.

\(C-V\) measurements were mainly employed to investigate the thermal stability of Al-GaAs Schottky barrier diodes.

III.5.2. Copeland Technique

If a Schottky barrier junction is reverse biased, the voltage across the depletion region, \(V\), as a function of charge per unit area, \(Q\), is given as:-

\[ V(Q) = \int_0^{x(Q)} E(x,Q)dx \]  

(III.5.10)

where \(x(Q)\) is the depletion layer width. The charge associated with this depletion layer, \(x(Q)\), is given by

\[ Q = q \int_0^{x(Q)} n(x)dx \]  

(III.5.11)
where, $q$ is the electronic charge and $n(x)$ is the free carrier concentration. The electric field at a point $x$ in the depletion region is:

$$E(x, Q) = \frac{Q}{\varepsilon} - \frac{q}{\varepsilon} \int_0^x n(x) \, dx$$  \hspace{1cm} (III.5.12)

where, $\varepsilon$ is the permittivity of the semiconductor.

If the charge per unit area $Q$ is increased by a small increment $\Delta Q$, then the voltage changes by an increment $\Delta V$. Using equation III.5.10 and III.5.11, $\Delta V$ is expressed as:

$$\Delta V = \int_0^{X(Q)} [E(x, Q + \Delta Q) - E(x, Q)] \, dx + \int_{X(Q)}^{X(Q + \Delta Q)} E(x, Q + \Delta Q) \, dx$$  \hspace{1cm} (III.5.13)

$$\Delta V = \frac{\Delta Q \cdot X(Q)}{\varepsilon} + \frac{q}{\varepsilon} \int_{X(Q)}^{X(Q + \Delta Q)} n(x') \, dx' \, dx$$  \hspace{1cm} (III.5.14)

If $\Delta Q$ is small enough so that $n(x)$ may be considered equal to $n(X)$ between $X(Q)$ and $X(Q + \Delta Q)$, then III.5.14 can be expressed as:

$$\Delta V = \frac{\Delta Q \cdot X(Q)}{\varepsilon} + \frac{n(x)q}{2\varepsilon} \left[X(Q + \Delta Q) - X(Q)\right]^2$$  \hspace{1cm} (III.5.15)
From equation III.5.12:-

\[ \Delta Q = q \int_{X(Q)}^{X(Q + \Delta Q)} n(x) \, dx \]  

(III.5.16)

\[ = n(X)q \{X(Q + \Delta Q) - X(Q)\} \]  

(III.5.17)

therefore, (III.5.15) becomes:-

\[ \Delta V = \frac{\Delta Q \cdot X}{\varepsilon} + \frac{\Delta Q^2}{2qen(X)} \]  

(III.5.18)

when an A.C. current \( I \sin \omega t \) injected into the junction, \( \Delta Q \) can be written as

\[ \Delta Q = \frac{I \cos \omega t}{\omega A} \]  

(III.5.19)

where \( \omega \) is the angular frequency of the driving current and \( A \) is the contact area. By substituting III.5.19 into III.5.18:

\[ \Delta V = \frac{I \cos \omega t}{\omega A} \cdot X + \frac{I^2 (\cos 2\omega t + 1)}{4\omega^2 q \varepsilon A^2} \cdot \frac{1}{n(X)} \]  

(III.5.20)

As seen from the final equation (III.5.20), it is concluded that, when an A.C. current is injected into a diode, the fundamental voltage produced across the diode is proportional to the junction depletion layer width and the second harmonic voltage is proportional to the
reciprocal of the free carrier concentration. Thus, by measuring the fundamental and second harmonic voltages as a function of reverse bias, a free carrier concentration profile can be obtained (70).

In practice, output voltages of the first and second harmonics of the Copeland profiler were electronically processed to obtain a direct plot of carrier concentration versus depth. In order to make the numerical analysis of the profiles, it was essential to calibrate the depth and the carrier concentration scales.

Two methods were used for calibrating the profiles:

(a) The fundamental and second harmonic voltages were measured and using the Copeland equation (III.5.20) the depth and the carrier concentration at a certain d.c. reverse bias could be evaluated. Since this is a tedious procedure, a simpler comparative method was adopted and has been used throughout the course of this work.

(b) Calibration of the depth scale, corresponding to the fundamental frequency channel, could be achieved by using at least two known capacitors in place of the Schottky diode. Then the points on the depth scale corresponding to each capacitance were converted to a depth scale using the expression:

\[ C = \varepsilon A / \lambda \]

where \( A \) is the contact area of the unknown diode.
Similarly, to calibrate the carrier concentration scale a known Schottky diode having a constant carrier concentration similar to the unknown diode can be used in place of the unknown diode. Once a known point is determined, the carrier concentration corresponding to this point can be changed (multiplied or divided) by an order of magnitude using the scale selection switch provided on the Copeland profiler, so the second known point can be determined.

The use of a standard capacitor and a Schottky diode enables the analysis of the unknown profile to be made by simple comparison.

III.5.3. Hall Measurements

Consider orthogonal coordinates x, y, z then, when a magnetic field is applied in the x direction and an electrical current flows in the y direction, then for a semiconductor material an electric field is created in the z direction. This phenomenon is known as the Hall effect and is widely used as a useful diagnostic technique in semiconductor technology.

Hall effect and resistivity measurements were carried out using the technique developed by van der Pauw\(^{62}\) who has shown that the Hall coefficient and resistivity of the semiconductor may be obtained for any arbitrary shaped specimen without knowing the current distribution within the specimen. Van der Pauw\(^{62}\) made the assumptions that the semiconductor specimen is
homogeneous in thickness and has four small contacts arranged around the perimeter (see figure III.3).

The Hall coefficient can be obtained by measuring the change in resistance caused by the applied magnetic field $B$ and is given by:

$$R_H = \frac{d \Delta R_{BD,AC}}{B}$$

where:

- $d$ = thickness of the specimen $R_{BD,AC}$ is defined as the potential difference between the contacts A and C per unit current through contacts B and D i.e. $V_{AC}/I_{BD}$.

In general, the sheet Hall coefficient $R_{HS}$ is measured:

$$R_{HS} = \frac{R_H}{d} = \frac{\Delta R_{BD,AC}}{B}$$

If the resistivity, $\rho$, is measured then the Hall mobility may be obtained from:

$$\mu_H = \frac{R_H}{\rho}$$

It should be noticed that the Hall mobility $\mu_H$ is different from the conductivity mobility

$$\mu = \frac{1}{n e \rho}$$
FIGURE (III.3): ILLUSTRATION OF ARBITRARY SHAPED SPECIMEN WITH CONTACTS, A, B, C, D.
The Hall and conductivity mobilities are related by the Hall constant
\[ r = \frac{\mu_H}{\mu} \]

Under the conditions mentioned above, the resistivity is given by:
\[ \rho = \frac{\pi d}{\ln 2} \cdot \frac{R_{AB, CD} + R_{BC, DA}}{2} \cdot f \]

where:
\[ R_{AB, CD} = \text{the potential difference between contacts C and D per unit current through contact A and B i.e. } V_{CD}/I_{AB} \]

Similarly,
\[ R_{BC, DA} = V_{DA}/I_{BC} \text{ and } f \text{ is a function of the ratio } R_{AB, CD}/R_{BC, DA} \text{ which satisfies the relationship:} \]
\[ \frac{R_{AB, CD} - R_{BC, DA}}{R_{AB, CD} + R_{BC, DA}} = f \cdot \text{arc sinh} \left( \frac{\exp \frac{\ln 2}{f}}{2} \right) \]

In the ideal case (for a perfect sample geometry)
\[ R_{AB, CD} = R_{BC, DA}; \quad f \text{ is unity.} \]

In general, the sheet resistivity is measured:
\[ \rho_s = \rho = \frac{\pi}{\ln 2} \cdot \frac{R_{AB, CD} + R_{BC, DA}}{2} \cdot f \]
The Hall constant is a function of the magnitude of the applied magnetic field, the temperature, degeneracy and the carrier scattering mechanism. According to the reported work (63, 64, 65) on determining the value of $r$ for various scattering mechanisms, it seems difficult to decide on a suitable value of $r$ for our measurements. For simplicity, since $r$ has the value close to one, we chose it to be unity. This assumption may cause, at most, about 15% error in the determination of $n$ under our experimental conditions, i.e. room temperature measurements with a 5KG applied magnetic field. (66)

If a thin layer is removed from the surface of the specimen following a set of Hall measurements and, if this process is repeated until most of the implanted layer has been removed, then a profile of the implanted layer can be obtained. If $\left[ R_{HS} \right]_i$ and $\left[ \rho_s \right]_i$ are the measured values following the removal of $i$th layer of thickness $d_i$, the carrier concentration $n_i$ and mobility $\mu_i$ in the $i$th layer can be evaluated from (67, 68)

$$\frac{\left[ R_{HS} \right]_i - \left[ R_{HS} \right]_{i+1}}{\left[ \rho_s \right]_i^2 - \left[ \rho_s \right]_{i+1}^2} = qn_i \mu_i d_i$$

and

$$\frac{1}{\left[ \rho_s \right]_i} - \frac{1}{\left[ \rho_s \right]_{i+1}} = qn_i \mu_i d_i$$
from these,

\[ \mu_i = \frac{\Delta \left( \frac{R_{Hi}}{\rho_s} \right)}{\Delta \left( \frac{1}{\rho_s} \right)} \]

and

\[ n_i = \frac{\Delta \left( \frac{1}{\rho_s} \right)}{q d_1 \mu_i} \]

**III.5.4. Specimen preparation and Hall measurements**

Van der Pauw (69) has shown that the error introduced by the finite dimensions of the ohmic contacts may be eliminated substantially by cutting the specimen into a clover leaf shape. Therefore, this method has been employed in the course of this work.

Each specimen was mounted on a glass slide using white wax and a stainless steel clover leaf shaped mask was affixed to the surface. The cutting was carried out using a microblaster which provided a nitrogen gas jet carrying alumina particles as the abrasive. After the cutting, the mask was removed in warm trichloroethylene. The specimen was also thoroughly cleaned in warm trichloroethylene to remove any traces of wax and finally rinsed in methanol.

As the next step in the preparation procedure, four ohmic contacts (tin-dots) were alloyed to specimens near the edge of each leaf. The contact making process has been described in the section III.4.1.
The contacted sample was then mounted on a microscope slide with apiezon w black wax. The other end of the glass slide was stuck to a printed circuit board having four contact terminals which were later connected to the ohmic contacts of the specimen by silver-dag.

Ohmic contacts and the silver conducting paths were painted with liquid apiezon w black wax to protect them from the etchant. Having completed this process, specimens were left to dry overnight. They were then ready for measurements.

To obtain the sheet resistivity of a specimen using the Van der Pauw equation, voltage and current were measured in two different configurations with a third one necessary to determine the sheet Hall coefficient. The method used was to maintain the current through the specimen at a constant value and only measure the voltage developed between the required pair of contacts. The current was supplied by a commercially available constant current source (Keithley instruments model 225) which allowed the current to be selected and maintained within ± 0.5%.

The voltages between the various contacts were measured with an accuracy of ± 0.01% using a DVM with an input impedance greater than 10^10 ohms. The measured voltages were small, typically of the order of 1–100mV. Therefore, coaxial cables were used for all the connections to avoid undesirable pick-up.
For higher accuracy, instead of the three basic measurements mentioned above, readings were also taken with the constant current reversed to compensate for slightly non-linear contacts and also with the magnetic field reversed to reduce the effect of misalignment of the ohmic contacts with the field.

The etching solution used was concentrated sulphuric acid + hydrogen peroxide + water in the volume ratio 1:1:125. This etchant was found to produce an etch rate of 200 - 400Å per minute with uniform layer removal over the specimen surface up to about 10,000Å. After each etching step the specimen was rinsed in distilled water.

Having completed the required number of etch steps, the mask made with the black wax over the contact areas was removed using warm trichloroethylene and samples were rinsed in methanol. The step heights were measured using a Rank-Taylor-Hobson Talystep. Each step height was measured twice, so an average of 8 measurements were taken and the etch rate calculated from these values. The maximum error in talystep measurements was estimated to be about ± 10 - 15%.

Using the calculated sheet data, after each etch step, and the calculated average etch rate, the depth profiles of carrier concentration, resistivity and mobility were computed.
CHAPTER IV
RESULTS

Introduction

In this chapter, the experimental results obtained from various measurements are presented. The discussion of the results will be given in Chapter V. Presentation of the results consists of four parts. The first part deals with the results of the preliminary experiments, the next part shows a comparison of $H_1^+$, $H_2^+$ and $H_3^+$ implants into GaAs and the third and fourth describe the results of the investigation of $O^+$ and $Ar^+$ bombarded GaAs.

The properties of the material used for each experiment have been given in Chapter III.1.

IV.1. Preparation of Schottky contacts

Schottky barrier contacts were prepared by the evaporation of gold or aluminium. Initially, gold was used as the contact metal for the Schottky barrier. However, it is well known that Au - GaAs contacts are degraded at temperatures greater than $400^\circ C$. Because of this, aluminium was chosen as an alternative metal. The results associated with this preliminary work are as follows:

a). Etching

Two solutions, $H_2SO_4$,$H_2O$,$H_2O_2$ and Bromine-methanol (0.5% Bromine in methanol) were used to clean the GaAs specimens. Bromine-methanol was found to be the best.
It was observed that some of the diodes etched in $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$ had larger forward breakdown voltages. This was thought to be due to an interfacial layer, probably a thin layer of native oxide, since a thin layer of oxide was found by other workers after etching in $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$ solution. This suspected oxidation has not been encountered when a solution of bromine-methanol was used.

b). **Au-GaAs Schottky barriers**

The optimum temperature for Au-GaAs Schottky barrier formation was found to be about $100^\circ$C. The diodes formed at this temperature had forward and reverse breakdown voltages of about +0.5 and -60V respectively ($n \approx 10^{15}\text{cm}^{-3}$). The temperature range in which these experiments were carried out was 70-200°C. The I-V measurements showed that the quality of the diodes was good enough for a meaningful C-V measurement to be made. Diodes made at higher temperatures (180-200°C) usually had smaller (<0.5V) forward breakdown voltages which might be due to indiffusion of gold.

c). **Al-GaAs Schottky barrier contacts**

As mentioned earlier in section III.4.2, three separate methods of making Al-GaAs diodes were studied. It was found that all three methods produced good quality schottky barriers (as estimated from I-V measurements) provided that the necessary surface preparation and heat treatment were applied.
The diodes produced at the elevated temperature (150°C) had larger reverse breakdown voltages, -60 to -80 volts, \( n = 10^{15} \text{cm}^{-3} \) whereas the room temperature deposited diodes had values between -50 and -60 volts. In both cases, the forward breakdown voltage was about +0.5 volts. It was also noted that the surface treatment prior to the room temperature deposition was crucial. However, chemical treatment was less important for elevated temperature depositions.

d). **Annealing of Al-GaAs Schottky diodes.**

Annealing over the temperature range 350 to 450°C slightly improved the quality of the contacts as estimated from I-V measurements. Capacitance-voltage measurements performed before and after annealing cycles indicated that there was no significant change in either the zero bias Schottky capacitance or in the carrier concentration of the semiconductor. The results of C-V measurements are shown in table (IV.1)

Initially, when annealing was carried out in a flowing nitrogen atmosphere, a slight increase in the Schottky capacitance was sometimes recorded. This was thought to be due to slight oxidation of the metal contact resulting from the possible existence of oxygen in the nitrogen gas. To overcome this undesirable oxidation, annealing was carried out in either flowing hydrogen/nitrogen or in an evacuated glass tube.

Annealing at 550°C for 15 minutes caused degradation of the contacts so that they became leaky and almost ohmic in character (Figure IV.1).
FIGURE (IV.1): I-V CHARACTERISTICS OF A :-
(a) GOOD QUALITY, (b) DEGRADED CONTACT
TABLE (IV.1)

Electron concentration before and after annealing Al-Schottky barriers.

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Contact Number</th>
<th>Electron Conc. Before annealing (x10^{17}cm^{-3})</th>
<th>Annealing Temperature (°C)</th>
<th>Electron Conc. After annealing (x10^{17}cm^{-3})</th>
<th>Frequency (kHz)</th>
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</thead>
<tbody>
<tr>
<td>B2</td>
<td>1</td>
<td>2.75</td>
<td>350</td>
<td>2.75</td>
<td>1</td>
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<tr>
<td></td>
<td>2</td>
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<td>&quot;</td>
<td>2.80</td>
<td>&quot;</td>
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<tr>
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<td>3</td>
<td>3.00</td>
<td>&quot;</td>
<td>2.83</td>
<td>&quot;</td>
</tr>
<tr>
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<td>&quot;</td>
<td>2.90</td>
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</tr>
<tr>
<td></td>
<td>1</td>
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<td>&quot;</td>
<td>2.80</td>
<td>500</td>
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<tr>
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<td>&quot;</td>
<td>2.83</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.81</td>
<td>&quot;</td>
<td>2.93</td>
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<td>&quot;</td>
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<td>-</td>
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</tr>
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<td>1.09</td>
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<td>&quot;</td>
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<td>&quot;</td>
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<td>1</td>
<td>1.44</td>
<td>&quot;</td>
<td>-</td>
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<td>1.10</td>
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<tr>
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IV. 2. Proton Bombardment.

Introduction

The importance of proton bombardment in device fabrication has been emphasized in Chaper II. In this section, results associated with some of the properties of the proton bombarded GaAs are described.

IV. 2. 1. Isolation Depth

The term isolation depth "l" (=R_p) is generally defined as the point at which the maximum carrier removal occurs (figure IV.2). The zero bias depletion depth "d_{ZB}" is also shown on the same diagram. The thickness of the isolated layer, "l", can be varied by altering the bombardment energy. Most of the bombardments were carried out at 300, 400 and 500 keV. Also, in order to obtain a better understanding of the range-energy relationship, some lower energy (150-300 keV) bombardments were performed. Figure IV.3 shows the relationship between the proton energy and the isolation depth within 150-500 keV range. The mean range values obtained from Copeland measurements are plotted together with reported data in Figure IV.3, whilst the standard deviations on each range value are presented in table (IV.2).
FIGURE (IV.2): MODEL PROFILE OBTAINED FROM A PROTON BOMBARDED GaAs.
The theoretical (Rp) range-energy relationship of protons in GaAs.

FIGURE (IV.3): RANGE - ENERGY RELATIONSHIP OF PROTONS IN GaAs.
TABLE (IV.2)

Range - Energy relationship of protons in GaAs

<table>
<thead>
<tr>
<th>Number of Specimens</th>
<th>Energy (keV)</th>
<th>( R_p (\mu m) ) (Mean Value)</th>
<th>( \bar{R} (\mu m) ) Standard Dev^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>1.6</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>300</td>
<td>2.3</td>
<td>0.1</td>
</tr>
<tr>
<td>17</td>
<td>400</td>
<td>3.4</td>
<td>0.1</td>
</tr>
<tr>
<td>11</td>
<td>500</td>
<td>4.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

In the case of low dose bombardments \( (\approx 10^{10} \text{ proton/cm}^2) \), a precise control of the dose is usually difficult. Because of this problem, all the specimens were bombarded with higher doses \( (\approx 10^{11} \text{ proton/cm}^2) \) and annealed during the ohmic contact alloying process at \( 300^\circ \pm 20^\circ \text{C} \) for about 10-15 seconds. This treatment caused some of the damage to anneal and that remaining allowed us to observe the complete profile (see section IV.2.6). Figure IV.4 shows the electron concentration profiles for samples bombarded with \( 1.5 \times 10^{11} \text{ H}^+_1/\text{cm}^2 \) at energies of 300, 400 and 500 keV. Ohmic contacts were made to these samples after the bombardment. The background carrier concentration
FIGURE (IV.4): PROFILES OF 300, 400 AND 500 kev PROTON BOMBARDED SPECIMENS.

Dose: $1.5 \times 10^{11} \text{ H}_2^+/\text{cm}^2$
of each specimen was the same \( n = 3 \times 10^{15}\text{cm}^{-3} \). As seen
from the figure IV.4, the profile minima occur
at 2.3, 3.4 and 4.3 \( \mu \text{m} \) for 300, 400 and 500 keV
bombardments respectively. Also, at the front part of
the profiles, the damage and hence the removal rate
decreases with increasing energy.

IV.2.2. Dose Dependence of the Profiles

Figure IV.5 shows some of the typical Copeland
profiles measured on 180 keV bombarded samples
\( (n = 3 \times 10^{15}\text{cm}^{-3}) \). After annealing at 300\(^\circ\text{C}\) for one
minute, complete Gaussian shaped profiles were not
observed for a dose above \( 5 \times 10^{11}\text{H}^+/\text{cm}^2 \).

The electron concentrations in the bombarded regions
for doses of \( 10^{12} \) and \( 5 \times 10^{12}\text{H}^+/\text{cm}^2 \) were unmeasurable
because of a large zero-bias depletion width \( d_{ZB} \).
In a similar way, the front part of the \( 5 \times 10^{11}\text{H}^+/\text{cm}^2 \)
bombarded sample up to 0.9 \( \mu \text{m} \) from the surface was also
unmeasurable. The zero-bias depletion width \( d_{ZB} \)
increased at about 2.1 microns for an increase in proton
dose of one order of magnitude (table IV.3).

Table IV.3.
Variation of \( d_{ZB} \) with dose for 180 keV proton
bombardment

| Dose \( \text{H}^+/\text{cm}^2 \) | \( d_{ZB} \) (micron) | Average carrier concentration in the
deprecated region \( \text{cm}^{-3} \) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( 5 \times 10^{11} )</td>
<td>0.9</td>
<td>( 10^{15} )</td>
</tr>
<tr>
<td>( 10^{12} )</td>
<td>2.0</td>
<td>( 2.7 \times 10^{14} )</td>
</tr>
<tr>
<td>( 5 \times 10^{12} )</td>
<td>3.1</td>
<td>( 1.1 \times 10^{14} )</td>
</tr>
</tbody>
</table>
Figure IV.5: Profiles of 180 keV bombarded specimens.
The profiles measured on 500 keV bombarded samples are shown in figure IV.6. The carrier concentrations at the profile minima decreased linearly up to the dose of $2 \times 10^{11} \text{H}^+/\text{cm}^2$. A similar family of profiles were obtained also for 300 and 400 keV bombardments.

As in the case of 180 keV bombardments, here again, large doses, greater than $2 \times 10^{11} \text{H}^+/\text{cm}^2$, resulted in high carrier removal, in other words low carrier concentration in the bombarded regions, which could not be measured by the Copeland technique.

IV.2.3. Carrier Removal Rate

a) Annealed GaAs.

Our results indicated that significant annealing takes place during the contacting, tin-dotting, process. As will be revealed in section IV.2.6, the heights ($\Delta n$) of the profiles vary with annealing. For example, the carrier removal rate $K_p$ ($= \Delta n$/dose) was computed to be $0.6 \times 10^4$ electron/proton for a dose of $5 \times 10^{11} \text{H}^+/\text{cm}^2$ implanted at 180 keV (figure IV.5). This relatively low value of $K_p$ was the result of (i) one minute annealing at $300^\circ\text{C}$ during the tin dotting process and (ii) the comparatively high proton dose. The discussion of (i) and (ii) will be given in Chapter V. The integral removal rate $K_{\text{int}}$ for the same bombardment was computed to be about 1 electron/proton.

Table IV.4 shows the removal rates ($K_p$) measured at the profile minima. All the results presented in Table IV.4 were obtained from annealed/tin-dotted specimens.
ENERGY: 500 kev
DOSE: $6 \times 10^{10} - 2 \times 10^{11}$ $H^+_1$/cm$^2$

FIGURE (IV.6): PROFILES OF 500 kev PROTON BOMBARDED SPECIMENS
The list of experimental data obtained on annealed (during tin-dotting) specimens.

<table>
<thead>
<tr>
<th>Slice Number</th>
<th>Dose (ion/cm²)</th>
<th>Range (μ) (Micron)</th>
<th>Kp (x10⁴ e/p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US4</td>
<td>6 x 10¹⁰</td>
<td>2.3 2.2</td>
<td>1.4 1.2</td>
</tr>
<tr>
<td>US4</td>
<td>8 x 10¹¹</td>
<td>2.2 2.2</td>
<td>1.6 1.5</td>
</tr>
<tr>
<td>US5</td>
<td>1 x 10¹¹</td>
<td>2.4 2.4</td>
<td>1.3 1.4</td>
</tr>
<tr>
<td>US5</td>
<td>1 x 10¹¹</td>
<td>2.3 2.3</td>
<td>1.4 1.3</td>
</tr>
<tr>
<td>US5</td>
<td>1.5 x 10¹¹</td>
<td>2.4 2.3</td>
<td>1.5</td>
</tr>
<tr>
<td>US5</td>
<td>1.8 x 10¹¹</td>
<td>2.3 2.3</td>
<td>1.4</td>
</tr>
<tr>
<td>US5</td>
<td>1.8 x 10¹¹</td>
<td>2.1</td>
<td>1.3 1.3</td>
</tr>
<tr>
<td>US5</td>
<td>1.9 x 10¹¹</td>
<td>2.1 2.1</td>
<td>1.2 1.0</td>
</tr>
<tr>
<td>US15</td>
<td>2 x 10¹¹</td>
<td>2.4 2.3</td>
<td>1.2 1.2</td>
</tr>
<tr>
<td>US5</td>
<td>2.5 x 10¹¹</td>
<td>2.3</td>
<td>1.0</td>
</tr>
<tr>
<td>US5</td>
<td>3 x 10¹¹</td>
<td>2.2 2.3</td>
<td>1.0 1.1</td>
</tr>
<tr>
<td>US5</td>
<td>4 x 10¹¹</td>
<td>2.3 2.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Slice Number</th>
<th>Dose (ion/cm²)</th>
<th>Range (μ) (Micron)</th>
<th>Kp (x10⁴ e/p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US4</td>
<td>6 x 10¹⁰</td>
<td>3.5 3.4</td>
<td>1.3</td>
</tr>
<tr>
<td>US4</td>
<td>8 x 10¹⁰</td>
<td>3.5 3.2</td>
<td>1.2 1.3</td>
</tr>
<tr>
<td>US15</td>
<td>9 x 10¹⁰</td>
<td>3.6 3.6</td>
<td>1.0, 1.0</td>
</tr>
<tr>
<td>US15</td>
<td>1 x 10¹¹</td>
<td>3.4 3.2</td>
<td>1.3, 1.4</td>
</tr>
<tr>
<td>US4</td>
<td>1.5 x 10¹¹</td>
<td>3.4 3.2</td>
<td>1.2, 1.2</td>
</tr>
<tr>
<td>US15</td>
<td>2 x 10¹¹</td>
<td>3.3 3.3</td>
<td>1.2, 1.2</td>
</tr>
<tr>
<td>US5</td>
<td>4 x 10¹¹</td>
<td>3.6 3.6</td>
<td>0.8, 0.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Slice Number</th>
<th>Dose (ion/cm²)</th>
<th>Range (μ) (Micron)</th>
<th>Kp (x10⁴ e/p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US15</td>
<td>6 x 10¹⁰</td>
<td>4.2 4.5</td>
<td>1.2 1.3</td>
</tr>
<tr>
<td>US15</td>
<td>8 x 10¹⁰</td>
<td>4.1 4.1</td>
<td>1.2, 1.2</td>
</tr>
<tr>
<td>US15</td>
<td>1 x 10¹¹</td>
<td>4.3 4.3</td>
<td>1.1 1.1</td>
</tr>
<tr>
<td>US15</td>
<td>1.5 x 10¹¹</td>
<td>4.2 4.2</td>
<td>1.0 1.1</td>
</tr>
<tr>
<td>US15</td>
<td>2 x 10¹¹</td>
<td>4.3 4.3</td>
<td>0.8 0.8</td>
</tr>
</tbody>
</table>

Estimated error in range measurements: 11%
"""" carrier removal rate Kp: 15%
As seen from this table, $K_p$ lies between $1.1$ and $1.5 \times 10^4$ electrons/proton up to doses of $2-3 \times 10^{11} \text{H}_1^+ / \text{cm}^2$. The higher doses resulted in a lower carrier removal rate ($K_p$) of about $0.8 \times 10^4$ electrons/proton. A detailed discussion of this point will be given in Chapter V.

The value of $K_{\text{int}}$ was computed to be about $2$ electrons/proton being independent of proton energy within the energy range $300$ to $500$ keV. The calculated integral removal rates together with the results of equivalent $\text{H}_2^+$ and $\text{H}_3^+$ bombardments are presented in Table IV.7 (section IV.2).

b) Unannealed GaAs.

In order to measure carrier removal on unannealed GaAs, ohmic contacts were alloyed to a number of specimens prior to bombardments. Copeland measurements performed on these specimens indicated that the carrier removal rates $K_p$ were $6.1$, $6.2$ and $6.2 \times 10^4$ for $300$, $400$ and $500$ keV bombardments respectively, which are much higher than the values for annealed samples. The dose was $2 \times 10^{10} \text{H}_1^+ / \text{cm}^2$ for all three bombardments. The integral removal rates $K_{\text{int}}$ for these specimens were computed to be about $9$ electrons/proton. Thus $K_p$ and $K_{\text{int}}$ do not depend on proton energy for a dose of $2 \times 10^{10} \text{H}_1^+ / \text{cm}^2$.

The carrier removal profiles of $400$ keV bombardments obtained from the Copeland profiles are shown in figure IV.7. To eliminate the effect of the materials having different initial carrier concentrations, carrier
FIGURE (IV.7): CARRIER REMOVAL PROFILES OF 400 keV PROTON BOMBARDED (AS - IMPLANTED) SPECIMENS.
removal $\Delta n$, instead of free carrier concentration $n$, versus dose has been calculated and plotted. From these profiles (table IV.5) $K_p (= \Delta n$/dose) appeared to be constant, having a value of about $6 \times 10^{11}$ electrons/proton, up to proton doses of $3 \times 10^{10} H_1^*/cm^2$. It decreased to $4.8 \times 10^{11}$ electrons/proton for a dose of $5 \times 10^{10} H_1^*/cm^2$ (table IV.5). From the same set of profiles in figure IV.7, the integral removal rate $K_{int}$ was found to be independent of proton dose up to $3 \times 10^{10} H_1^*/cm^2$. $K_{int}$ had a value of about 9 electrons/proton, it then decreased to 8.3 electrons/proton for the largest dose $5 \times 10^{10} H_1^*/cm^2$ (table IV.5).

IV.2.4. C-V Characteristics

Pruniaux et al. (14) measured the C-V characteristics of samples bombarded with $10^{14}$ protons/cm$^2$ and found that the C-V characteristics closely resembled that of an MIS structure.

At the early stage of our work, the C-V technique was used as a check on the semi-insulating character of the proton bombarded samples.

A typical example of capacitance-voltage characteristic of proton bombarded samples is shown in figure IV.8. The bombardment conditions of the sample is also shown on the figure.

When the positive bias on the metal electrode is increased, current leakage occurs through the partly conducting semi-insulating layer, apparently due to the high number of non-compensated carriers. Also, large
### TABLE (IV.5)

List of experimental data obtained on unannealed samples.

<table>
<thead>
<tr>
<th>Slice Number</th>
<th>Energy (keV)</th>
<th>Ion</th>
<th>Dose (ion/cm²)</th>
<th>Range (Micron)</th>
<th>K_p \times 10^4 e/p</th>
<th>K_{(int)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>US15</td>
<td>300</td>
<td>H_1^+</td>
<td>2 \times 10^{10}</td>
<td>2.3</td>
<td>6.1</td>
<td>8.7</td>
</tr>
<tr>
<td>US15</td>
<td>400</td>
<td>H_1^+</td>
<td>2 \times 10^{10}</td>
<td>3.3</td>
<td>6.2</td>
<td>8.2</td>
</tr>
<tr>
<td>US15</td>
<td>500</td>
<td>H_1^+</td>
<td>2 \times 10^{10}</td>
<td>4.3</td>
<td>6.2</td>
<td>9.0</td>
</tr>
<tr>
<td>US36</td>
<td>400</td>
<td>H_1^+</td>
<td>1 \times 10^{10}</td>
<td>3.3</td>
<td>6.0</td>
<td>8.7</td>
</tr>
<tr>
<td>US27</td>
<td>400</td>
<td>H_1^+</td>
<td>2 \times 10^{10}</td>
<td>3.3</td>
<td>6.2</td>
<td>9.0</td>
</tr>
<tr>
<td>US27</td>
<td>400</td>
<td>H_1^+</td>
<td>3 \times 10^{10}</td>
<td>3.3</td>
<td>6.0</td>
<td>9.0</td>
</tr>
<tr>
<td>US27</td>
<td>400</td>
<td>H_1^+</td>
<td>4 \times 10^{10}</td>
<td>3.3</td>
<td>5.5</td>
<td>9.0</td>
</tr>
<tr>
<td>US27</td>
<td>400</td>
<td>H_1^+</td>
<td>5 \times 10^{10}</td>
<td>3.3</td>
<td>4.8</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Estimated error in range: 11% in K_p: 15% and in K_{(int)}: 20%
FIGURE (IV.8): C-V CHARACTERISTIC OF A LIGHTLY PROTON
BOMBARDED SPECIMEN

ENERGY: 400 kev
DOSE: $1.5 \times 10^{11} \text{ H}^+ / \text{cm}^2$
forward breakdown voltages were not observed. In this case, it is concluded that the doses chosen here were not high enough to render the material semi-insulating.

**IV.2.5. \( H_2^+ \) and \( H_3^+ \) Bombardments**

The removal of carriers in GaAs by proton bombardment is well known. We assumed that for the energies used, which are in excess of 100 keV, the \( H_2^+ \) and \( H_3^+ \) ions dissociate on hitting the GaAs surface, with the total energy being shared equally by the product H nuclei. To prove the point, the investigation of the relative effect of the dissociation product H nuclei on GaAs was undertaken.

Implants were carried out at about 8° to the surface normal of (100) oriented n/n+ GaAs (\( n = 1 - 3 \times 10^{15} \text{ cm}^{-3} \)). The implant energies were a) 300, 400 and 500, b) 600, 800, 1000 and c) 900, 1200, 1500 keV for \( H_1^+(a) \), \( H_2^+(b) \) and \( H_3^+(c) \) ions, respectively. Equivalent implants were accomplished by arranging that the ion energies were twice (for \( H_2^+ \)) and three times (for \( H_3^+ \)) that of the \( H_1^+ \) ions. The proton dose was between \( 5 \times 10^{10} \) and \( 4 \times 10^{11} \text{ H}_1^+/\text{cm}^2 \). The dose of \( H_2^+ \) and \( H_3^+ \) bombardments were half and a third of the proton dose.

All the \( H_1^+, H_2^+ \) and \( H_3^+ \) bombarded samples were subjected to an annealing during tin-dooting at 300 °C for 10-15 seconds.
The two parameters $K_p (\propto \Delta n\text{/dose})$ and $\ell$ (figure IV.2) have been measured using the Copeland technique and after equivalent $H_1^+$, $H_2^+$, $H_3^+$ implants at each of the three energy groups mentioned above, a comparison was made. Measurements indicated that the electron concentration profiles and consequently the carrier removal rates, $K_p$ and $K_{int}$ obtained from equivalent implants of $H_1^+$, $H_2^+$ or $H_3^+$ ions were identical within experimental error. Table IV.6 shows the list of data obtained from $H_2^+$ and $H_3^+$ bombardments. The data for $H_1^+$ bombardments was previously given in section IV.2.3. Table IV.7 demonstrates the degree of similarity of equivalent implants of $H_1^+$, $H_2^+$ and $H_3^+$ ions.

As an example, a typical set of Copeland profiles of equivalent $H_1^+$, $H_2^+$ and $H_3^+$ bombarded samples are shown in figure IV.9.

IV.2.6. Thermal Stability of Proton Bombarded Layers

Having investigated the thermal stability of Al-GaAs schottky barrier contacts, some of the $H_1^+$ implanted specimens were annealed in a hydrogen + nitrogen atmosphere without removing the aluminium contacts.

As a preliminary experiment, to demonstrate the degree of recovery during the tin-dotting/annealing process, two samples, having the same background carrier concentration, were bombarded with $6 \times 10^{10}$ $H_1^+$/cm$^2$ at 300 keV. The first specimen (a) was tin-dotted (at 280°C for about 20 seconds) before the
### TABLE IV.6

Experimental data obtained from annealed/tin-dotted H$_2^+$ and H$_3^+$ implanted specimens

<table>
<thead>
<tr>
<th>Slice Number</th>
<th>Energy (keV)</th>
<th>Dose (ion/cm$^2$)</th>
<th>Range (μm)</th>
<th>K$_p$ (x10$^4$ e/p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US5</td>
<td>600</td>
<td>5 x 10$^{10}$</td>
<td>2.3</td>
<td>1.5</td>
</tr>
<tr>
<td>US5</td>
<td>600</td>
<td>9 x 10$^{10}$</td>
<td>2.3</td>
<td>1.3, 1.3</td>
</tr>
<tr>
<td>US15</td>
<td>600</td>
<td>1 x 10$^{11}$</td>
<td>2.3</td>
<td>1.0, 1.1</td>
</tr>
<tr>
<td>US5</td>
<td>600</td>
<td>2 x 10$^{11}$</td>
<td>2.3</td>
<td>0.8</td>
</tr>
<tr>
<td>US5</td>
<td>800</td>
<td>5 x 10$^{10}$</td>
<td>3.2</td>
<td>1.2, 1.2</td>
</tr>
<tr>
<td>US4</td>
<td>800</td>
<td>7.5 x 10$^{10}$</td>
<td>3.4</td>
<td>1.2</td>
</tr>
<tr>
<td>US15</td>
<td>800</td>
<td>1 x 10$^{11}$</td>
<td>3.3</td>
<td>1.2, 1.2</td>
</tr>
<tr>
<td>US5</td>
<td>800</td>
<td>2 x 10$^{11}$</td>
<td>3.2</td>
<td>0.8, 0.8</td>
</tr>
<tr>
<td>US15</td>
<td>1000</td>
<td>4 x 10$^{10}$</td>
<td>4.3</td>
<td>1.3</td>
</tr>
<tr>
<td>US15</td>
<td>1000</td>
<td>7.5 x 10$^{10}$</td>
<td>4.3</td>
<td>1.1, 1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H$_3^+$</th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>US5</td>
<td>900</td>
<td>3.3 x 10$^{10}$</td>
<td>2.3</td>
<td>1.4</td>
</tr>
<tr>
<td>US4</td>
<td>900</td>
<td>4 x 10$^{10}$</td>
<td>2.3</td>
<td>1.3</td>
</tr>
<tr>
<td>US5</td>
<td>900</td>
<td>6 x 10$^{10}$</td>
<td>2.1</td>
<td>1.4, 1.3</td>
</tr>
<tr>
<td>US5</td>
<td>900</td>
<td>6.6 x 10$^{10}$</td>
<td>2.4</td>
<td>1.0, 1.0</td>
</tr>
<tr>
<td>US4</td>
<td>900</td>
<td>7.5 x 10$^{10}$</td>
<td>2.3</td>
<td>1.0, 1.1</td>
</tr>
<tr>
<td>US5</td>
<td>900</td>
<td>1 x 10$^{11}$</td>
<td>2.2</td>
<td>1.0, 1.1</td>
</tr>
<tr>
<td>US5</td>
<td>1200</td>
<td>3.3 x 10$^{10}$</td>
<td>3.3</td>
<td>1.4, 1.5</td>
</tr>
<tr>
<td>US15</td>
<td>1200</td>
<td>5 x 10$^{10}$</td>
<td>3.4</td>
<td>1.2, 1.2</td>
</tr>
<tr>
<td>US15</td>
<td>1200</td>
<td>6.6 x 10$^{10}$</td>
<td>3.3</td>
<td>1.2, 1.2</td>
</tr>
<tr>
<td>US5</td>
<td>1200</td>
<td>1.3 x 10$^{11}$</td>
<td>3.2</td>
<td>0.8, 0.8</td>
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<tr>
<td>US15</td>
<td>1500</td>
<td>3.3 x 10$^{10}$</td>
<td>4.3</td>
<td>1.0, 1.0</td>
</tr>
<tr>
<td>US15</td>
<td>1500</td>
<td>5 x 10$^{10}$</td>
<td>4.3</td>
<td>1.0, 1.1</td>
</tr>
</tbody>
</table>

Estimated error in range: 11% and in K$_p$: 15%
<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Ion ( \text{H}_1^+ )</th>
<th>Dose (Ion/cm(^2))</th>
<th>Range (Micron)</th>
<th>( \mathcal{E}(p) ) (Micron)</th>
<th>( K(\text{int}) ) (e/p)</th>
<th>( T_\alpha ) (C(^\circ))</th>
<th>Time (Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>( \text{H}_1^+ )</td>
<td>( 1.8 \times 10^{11} )</td>
<td>2.3</td>
<td>0.09</td>
<td>1.8</td>
<td>300(^\pm)</td>
<td>10-15</td>
</tr>
<tr>
<td>400</td>
<td>( \text{H}_1^+ )</td>
<td>( 1.5 \times 10^{11} )</td>
<td>3.4</td>
<td>0.13</td>
<td>2.0</td>
<td>20</td>
<td>n</td>
</tr>
<tr>
<td>500</td>
<td>( \text{H}_1^+ )</td>
<td>( 1.5 \times 10^{11} )</td>
<td>4.3</td>
<td>0.08</td>
<td>1.8</td>
<td>1.9</td>
<td>n</td>
</tr>
<tr>
<td>600</td>
<td>( \text{H}_2^+ )</td>
<td>( 9 \times 10^{10} )</td>
<td>2.3</td>
<td>0.11</td>
<td>1.8</td>
<td>20</td>
<td>n</td>
</tr>
<tr>
<td>800</td>
<td>( \text{H}_2^+ )</td>
<td>( 5 \times 10^{10} )</td>
<td>3.3</td>
<td>0.07</td>
<td>2.10</td>
<td>2.10</td>
<td>n</td>
</tr>
<tr>
<td>900</td>
<td>( \text{H}_3^+ )</td>
<td>( 6 \times 10^{10} )</td>
<td>2.3</td>
<td>0.09</td>
<td>2.0, 2.0</td>
<td>n</td>
<td>n</td>
</tr>
<tr>
<td>1000</td>
<td>( \text{H}_2^+ )</td>
<td>( 7.5 \times 10^{10} )</td>
<td>4.3</td>
<td>0.02</td>
<td>2.10</td>
<td>n</td>
<td>n</td>
</tr>
<tr>
<td>1200</td>
<td>( \text{H}_3^+ )</td>
<td>( 3.3 \times 10^{10} )</td>
<td>3.4</td>
<td>0.08</td>
<td>2.10</td>
<td>n</td>
<td>n</td>
</tr>
<tr>
<td>1500</td>
<td>( \text{H}_3^+ )</td>
<td>( 5 \times 10^{10} )</td>
<td>4.3</td>
<td>0.01</td>
<td>2.0</td>
<td>n</td>
<td>n</td>
</tr>
</tbody>
</table>

* Estimated maximum error in range: 11% and in \( K(\text{int}) \): 20%.
Figure (IV.9): Profiles of equivalently $H_1^+$, $H_2^+$, $H_3^+$ implanted specimens.
bombardment. The second specimen (b) was also subjected to the same heat treatment after the bombardment. Copeland profiles measured on these two specimens indicated that a large amount of recovery takes place during the tin-dotting/annealing process (Figure IV.10).

The carrier removal rates calculated from the profiles were $1.10^4$ and $6.10^4$ electrons/proton for samples (a) and (b) respectively.

To investigate the actual thermal behaviour of proton bombarded layers a number of as-implanted, unannealed, 400 keV specimens were prepared. Figure IV.11 shows how the carrier removal concentration $\Delta n$ recovers during annealing for different doses of 400 keV protons. As mentioned earlier in section IV.2.3 the carrier removal rate, $(K_p = \Delta n/dose)$ of as-implanted GaAs is constant at $6 \times 10^4$ electrons/proton up to proton doses of $3 \times 10^{10}$ ions/cm$^2$. Figure IV.11 also illustrates this fact since the shape of the curves (i.e. $K_p$) is a constant after annealing up to doses of about $3 \times 10^{10}$ $H_1^+/cm^2$. One can also conclude that there is a fast annealing stage between 225 and 300°C. This can be considered as an indication of the degree of annealing during the tin-dotting process.

Figure IV.12 shows the profiles measured on 400 keV, $3 \times 10^{10}$ $H_1^+/cm^2$ bombarded specimens after each annealing cycle. The shapes of the profiles have not been affected by annealing. The recovery ratios of these specimens were calculated and shown in figure IV.13 which indicates that about 75% recovery occurred after annealing at 385°C.
(A): AFTER TIN DOTTING
(B): BEFORE TIN DOTTING

ENERGY: 300 kev
DOSE: $6 \times 10^{10} \text{H}^+/\text{cm}^2$

FIGURE (IV.10): ILLUSTRATION OF DEGREE OF DAMAGE RECOVERY BY TIN-DOTTING PROCESS
FIGURE (IV.11): VARIATION OF MAXIMUM CARRIER REMOVAL (AT PROFILE MINIMA) WITH DOSE DURING ANNEALING
FIGURE (IV.12): CARRIER REMOVAL PROFILES AS A FUNCTION OF ANNEALING TEMPERATURE

ENERGY: 400 kev
DOSE: $3 \times 10^{10} \text{ H}^+ / \text{cm}^2$
FIGURE (IV.13): CARRIER RECOVERY RATIOS AS A FUNCTION OF ANNEALING TEMPERATURE, MEASURED AT DEPTHS A, B, C (SEE ALSO FIGURE (IV.12)).
IV.3. Oxygen Bombardment

Introduction

The carrier removal mechanism caused by oxygen bombardment is not as well established as proton bombardment, but the oxygen implantation as a method of forming high resistivity layers has several advantages over proton bombardment. The main success is the thermal stability of the bombarded layers up to at least 800°C.\(^{(37)}\)

In this part, results associated with the properties of 400 keV oxygen bombarded (n/SI type) GaAs are given. All the implants were carried out at room temperature. In most cases, implants were followed by high temperature (700 - 800°C) annealing.

The aim of the study was to confirm the results of Favennec et al.\(^{(37)}\), that high resistivity layers could be formed in oxygen bombarded GaAs annealed at 700 to 800°C.

IV.3.1. Resistivity

a) Dose dependence of resistivity.

The dose dependence of the resistivity of oxygen implanted GaAs was investigated on n/SI GaAs \((n = 1.3 \times 10^{17} \text{ cm}^{-3})\), the epitaxial layer being 0.9 micron thick. The measurements were carried out by means of an electrometer having an input resistance of \(10^{14} \Omega\). Hall effect measurements were only performed on samples with resistivities less than about \(10^5 \Omega/\square\).
The resistance values have been converted to sheet resistivities $R_s = R \left( \frac{w}{L} \right) \frac{\Omega}{\square}$ using the measured aspect ratio of $L/w = 3$, where, $L = 3\, \text{mm}$ and $w = 1\, \text{mm}$. $R_s$ is plotted versus dose in figure IV.14. The resistivity value of unimplanted material was about $150 \, \Omega/\square$. After the implant, this value increased to about $5 \times 10^8 \, \Omega/\square$ for a dose of $10^{11} \, \text{O}^+/\text{cm}^2$. A gradual increase in resistivity was observed up to an oxygen dose of $5 \times 10^{12} \, \text{O}^+/\text{cm}^2$ (figure IV.14). For higher doses, greater than $5 \times 10^{12} \, \text{O}^+/\text{cm}^2$, the sheet resistivity decreased sharply tending towards the value of about $10^4 \, \Omega/\square$ which is the value measured for an implant of $10^{15} \, \text{O}^+/\text{cm}^2$.

b) Dose dependence of resistivity after $700^\circ\text{C}$ annealing.

Following heat treatment at $700^\circ\text{C}$, the net increase in resistivity as a result of implantation plus annealing was $30 - 40\%$ of that of the unimplanted samples for doses of $10^{12}$ to $10^{13} \, \text{O}^+/\text{cm}^2$. For higher doses the resistivity after annealing increased with increasing dose. However, for a dose of $1.10^{15} \, \text{O}^+/\text{cm}^2$ the measured sheet resistivity of about $10^3 \, \Omega/\square$ was not that of the implanted region but corresponded to the resistivity of the thin partially conducting layer near the epitaxial layer-substrate interface (figure IV.14). This was proved by profiling experiments which showed that no change occurred in the sheet Hall coefficient and sheet resistivity up to about $0.5\, \mu\text{m}$ from the surface. The detailed calculation to estimate the actual value of
FIGURE (IV.14): SHEET RESISTIVITY AS A FUNCTION OF DOSE FOR "AS IMPLANTED" SAMPLES AND FOR SAMPLES ANNEALED AT 700°C FOR 15 MINUTES.
the resistivity is given in appendix II. Thus the region up to 0.5 \( \mu \text{m} \) is of high resistivity which we estimate to be of the order of \( 10^8 \ \Omega/\square \). Such a high resistivity layer would still be conducting enough in the direction of the film thickness that about 0.5 \( \mu \text{m} \) would represent a short circuit path to the more conducting interface region. This analysis does not apply to the specimens implanted with doses less than \( 10^{15} \ O^+/\text{cm}^2 \) because these samples are appreciably conducting throughout after annealing at 700°C (See figure IV.16).

c) Temperature dependence of resistivity

The change in sheet resistivity with annealing temperature was studied for a dose of \( 10^{15} \ O^+/\text{cm}^2 \) (figure IV.15). After implantation, the resistivity increased with increasing annealing temperature up to about 500°C. Above 500°C the resistivity apparently decreased but this is due to the shorting effect described above (see IV.3.1(b)). Thus the resistivity for this dose increases with increasing annealing temperature up to 700 to 800°C where it reaches a constant value of about \( 10^8 \ \Omega/\square \), (see appendix II).

IV.3.2. Profiles

a) Dose dependence of carrier concentration

Figure IV.16 shows the variation of carrier concentration and mobility profiles with oxygen dose. Following an anneal at 700°C for 15 minutes, the sheet carrier concentration, \( N_s \), decreased to a value of
ENERGY: 400 kev  
DOSE: \(10^{15} \text{ O}^+ / \text{cm}^2\)  
ANNEALING TIME: 15 min.

FIGURE (IV.15): SHEET RESISTIVITY AS A FUNCTION OF ANNEALING TEMPERATURE FOR A SAMPLE IMPLANTED WITH \(10^{15} \text{ O}^+ / \text{cm}^2\)
FIGURE (IV.16): ELECTRON CONCENTRATION AND MOBILITY PROFILES AS A FUNCTION OF OXYGEN DOSE FOLLOWING ANNEALING AT 700°C FOR 15 MINUTES WITH ALUMINIUM ENCAPSULATION. THE UNIMPLANTED GaAs HAD AN ELECTRON CONCENTRATION OF $1.3 \times 10^{17}$ ($10^{12}$, $10^{13}$ O$^+$/cm$^2$) OR $7.5 \times 10^{16}$ cm$^{-3}$ ($5 \times 10^{13}$, $10^{14}$, $10^{15}$ O$^+$/cm$^2$).
about $10^{13}$ cm$^{-2}$ and remained approximately constant up to the dose of $10^{13}$ O$^+/cm^2$. The material used for the $10^{12}$ and $10^{13}$ O$^+/cm^2$ implants had an initial sheet carrier concentration of about $10^{13}$ cm$^{-2}$. For higher doses, $N_s$ steeply decreased having a value which is estimated to be less than $10^{11}$ cm$^{-2}$ for $10^{15}$ O$^+/cm^2$. The initial sheet carrier concentration of unimplanted material was measured to be about $7.5 \times 10^{12}$ cm$^{-2}$. Very similar values of sheet carrier concentrations were also found after annealing at 800°C which are shown on Table IV.8.

b) Carrier removal

Carrier concentration profiles obtained after annealing at 700 and 800°C are shown in figure IV.16 and 17. From these profiles, the carrier removal rates calculated at depths of 1000, 3000, 5000 and 8000Å are shown in Table IV.8, together with the calculated values of the integral removal rates.

Ion doses in excess of $10^{13}$ O$^+/cm^2$ produced significant carrier removal in the region of the projected range 0.55 - 0.6 μm, (figure IV.16). In this region, for doses above $10^{13}$ O$^+/cm^2$, carrier removal increased with dose, but the carrier removal rate (carrier removal/dose) decreased with increasing dose. The value of $K$ (= Δn/Dose) at a depth of 5000 Å was computed to be about $3 \times 10^3$ electrons/oxygen ion for $10^{13}$ O$^+/cm^2$, but for the highest dose, $10^{15}$ O$^+/cm^2$, it
TABLE (IV.6)
Experimental and calculated data of oxygen bombarded GaAs

<table>
<thead>
<tr>
<th>Material</th>
<th>Dose $^{o+}$/cm$^2$</th>
<th>$\mu_s$ *</th>
<th>$\rho_s$ *</th>
<th>$N_s$ *</th>
<th>$T_a$ (°C)</th>
<th>Carrier removal rate (e/o$^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(cm$^2$/v.sec)</td>
<td>(Ωcm)</td>
<td>(cm$^{-2}$)</td>
<td>(°C)</td>
<td>$K_{5000}$</td>
</tr>
<tr>
<td>US36</td>
<td>$10^{12}$</td>
<td>4260</td>
<td>109</td>
<td>$1.2 \times 10^{13}$</td>
<td>700</td>
<td>-</td>
</tr>
<tr>
<td>US36</td>
<td>$10^{13}$</td>
<td>5077</td>
<td>113</td>
<td>$1.0 \times 10^{13}$</td>
<td>700</td>
<td>3$\times 10^3$</td>
</tr>
<tr>
<td>MS1877A</td>
<td>$5.10^{13}$</td>
<td>5380</td>
<td>385</td>
<td>$3.0 \times 10^{12}$</td>
<td>700</td>
<td>1.2$\times 10^3$</td>
</tr>
<tr>
<td>MS1877A</td>
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<td>6260</td>
<td>606</td>
<td>$1.6 \times 10^{12}$</td>
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<td>670</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>700</td>
<td>75</td>
</tr>
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<td>5223</td>
<td>$1\times 10^3$</td>
<td>$1.1 \times 10^{12}$</td>
<td>800</td>
<td>-</td>
</tr>
<tr>
<td>MS1877A</td>
<td>$10^{15}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>800</td>
<td>-</td>
</tr>
</tbody>
</table>

* $\mu_s$ = Sheet mobility.
* $\rho_s$ = Sheet resistivity.
* $N_s$ = Sheet electron concentration.
* $T_a$ = Annealing temperature.

Estimated error in $N_s$: 7%
Estimated error in $K$: 12%
Estimated error in $K_{int}$: 7%
FIGURE (IV.18): VARIATION OF SHEET CARRIER CONCENTRATION, Ns, AND CARRIER REMOVAL RATE, $K_{5000}$, WITH OXYGEN DOSE AFTER ANNEALING AT 700°C FOR 15 MINUTES
decreased to an estimated value of about 75 electrons/oxygen (figure IV.18).

In addition to carrier removal near the projected range a significant decrease in carrier concentration was observed near the surface, which was most apparent at doses of $5 \times 10^{13}$ and $10^{14}$ $\text{O}^+/\text{cm}^2$ (figure IV.16). The same effect also occurred when chemically grown Si$_3$N$_4$ layers were used as encapsulants rather than the usual encapsulant of evaporated aluminium, (figure IV.17). This effect may be attributed to the encapsulant failing partially or to defect migration. The detailed discussion of the carrier removal near the surface will be given in the next chapter. The carrier removal rate calculated at about $3000\text{Å}^0$ was comparatively small. It thus seems that the recovery rate in this region is largest (figure IV.16, table IV.8).

c) Mobility

The mobility was measured as a function of depth (figure IV.16 and 17) and it was found to be degraded over the whole profile for doses equal to or greater than $5 \times 10^{13}$ $\text{O}^+/\text{cm}^2$. The measured mobility profiles for doses of $10^{12}$ and $10^{13}$ $\text{O}^+/\text{cm}^2$ were in good agreement with the data of Sze and Irvin$^{(38)}$. The sheet mobility values measured after each implant for the dose range of $10^{12} - 10^{13}$ $\text{O}^+/\text{cm}^2$ are shown in table IV.8.
Figure (IV.17): Carrier concentration and mobility profiles as a function of oxygen dose following annealing at 800°C for 15 minutes with Si₃N₄ encapsulation. The unimplanted GaAs had an electron concentration of $7.5 \times 10^{16}$ cm$^{-3}$. 
IV.4. Argon Bombardment

Introduction

In this part, results associated with hot (200°C) and room temperature argon implants are described.

Most of the implants were carried out at 200°C with the aim of investigating the residual damage after annealing at 700°C or above. Since most active ion implants are usually carried out at elevated temperatures (about 200°C) followed by high temperature annealing, it was thought that an investigation of residual damage after annealing could provide useful information to help in explaining the results of dopant ion implants.

In addition, a number of specimens were also implanted at room temperature to characterize the recovery nature of argon bombarded layers. The argon bombarded specimens have been measured using Hall effect and resistivity measurements in conjunction with layer removal.

IV.4.1. Resistivity

The resistivity of argon bombarded layers was studied as a function of implant temperature, dose and annealing temperature. The material used was an epitaxial n/Sl layer, having a thickness of 0.9 micron and a resistivity of 155 $\Omega \cdot \text{cm}$

a) 200°C Implants

The variation of sheet resistivity with dose was studied after annealing at 700°C for 15 minutes, (figure IV.19). The sheet resistivity was found to be
ENERGY: 200 keV
DOSE: $5 \times 10^{11} - 10^{14} \text{ Ar}^+ / \text{cm}^2$

$T_i$: 200°C
$T_a$: 700°C

FIGURE (IV.19): SHEET CARRIER CONCENTRATION, $N_s$, AND RESISTIVITY AS A FUNCTION OF DOSE FOR SPECIMENS IMPLANTED AT 200°C AND ANNEALED AT 700°C FOR 15 MINUTES WITH ALUMINIUM ENCAPSULATION.
about 200 $\Omega/\square$ for the dose range of $5 \times 10^{11}$ to $3 \times 10^{13}$ ions/cm$^2$ then it increased to about 320 $\Omega/\square$ for the highest dose ($10^{14}$ Ar$^+/\text{cm}^2$). For this dose the measured resistivity was about twice as high as the resistivity of the unimplanted material.

The change in sheet resistivity was also investigated as a function of annealing temperature, (figure IV.20) for samples implanted at 400 keV with a dose of $5 \times 10^{12}$ Ar$^+/\text{cm}^2$. The annealing time was 15 minutes except at 800°C when the time was limited to 5 minutes because of possible failure of aluminium as the encapsulant. The resistivity was probably maximum around 400°C above which it sharply decreased tending towards a value of 200 $\Omega/\square$ at 800°C, giving an indication of the amount of residual damage.

b) Room Temperature implants.

The dependence of resistivity on annealing temperature was studied for specimens implanted at 200 keV, with a dose of $10^{14}$ Ar$^+/\text{cm}^2$. The resistivity gradually decreased, with increasing temperature, within the temperature range 500 to 800°C, reaching the value of about 275 $\Omega/\square$, (figure IV.20). This value was found to be about the same after 700 or 800°C anneals, but the annealing time for 800°C annealing was 5 minutes (see section IV.4.1.(a)). Considering the initial resistivity value (155 $\Omega/\square$), it is evident that there is still considerable damage remaining even after annealing at 800°C.
Figure (IV.20): Sheet resistivity as a function of annealing temperature for specimens implanted at 200°C and room temperature.
IV.4.2. Carrier Removal

The sheet carrier concentration was measured as a function of dose and temperature and allowed the calculation of carrier removal rates. The implant and annealing conditions were as described in the previous section (IV.4.1.)

a) 200°C Implants

Figure IV 19 shows the variation of sheet carrier concentration with dose after 700°C annealing. The carrier concentration remained at a value of about $6 \times 10^{12}$ cm$^{-2}$ up to a dose of $10^{13}$ Ar$^+/\text{cm}^2$, then it decreased to about $3.5 \times 10^{12}$ cm$^{-2}$ for a dose of $10^{14}$ Ar$^+/\text{cm}^2$. The initial carrier concentration of unimplanted material and also the implant conditions have been described in the previous section (IV.4.1). The integral carrier removal rates were computed for each implant dose (see table IV.9).

Table IV.9: Variation of carrier removal rate $K(\text{int})$ with dose.

<table>
<thead>
<tr>
<th>Dose (Ar$^+/\text{cm}^2$)</th>
<th>$5 \times 10^{11}$</th>
<th>$10^{12}$</th>
<th>$5 \times 10^{12}$</th>
<th>$3 \times 10^{13}$</th>
<th>$10^{14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K(\text{int})$ (e/Ar$^+$)</td>
<td>3</td>
<td>1.5</td>
<td>0.3</td>
<td>$7.6 \times 10^{-1}$</td>
<td>$4 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
The annealing temperature dependence of carrier concentration is shown in figure IV.21. Following the 400°C anneal, the carrier concentration could not be measured due to lack of sensitivity of the measurement system. Above 400°C, a rapid increase in carrier concentration was observed and this was followed by a plateau region corresponding to the temperature range of 700 - 800°C. The integral carrier removal rates for each temperature were calculated (See table IV.10).

Table IV.10. Variation of carrier removal rate $K(\text{int})$ with the annealing temperature for samples implanted at 200°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K(\text{int})$ e/Ar$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>1.5*</td>
</tr>
<tr>
<td>500</td>
<td>1.2</td>
</tr>
<tr>
<td>600</td>
<td>0.7</td>
</tr>
<tr>
<td>700</td>
<td>0.46</td>
</tr>
<tr>
<td>800</td>
<td>0.28</td>
</tr>
</tbody>
</table>

* Assuming that, $N_s$ (at 400°C) is very small compared with the unimplanted value.

Therefore the $K(\text{int}) = \frac{7.5 \times 10^{12}}{5 \times 10^{12}} = 1.5 \text{e/Ar}$

where, $7.5 \times 10^{12} \text{cm}^{-2}$ is the background carrier concentration.
FIGURE (IV.21): SHEET CARRIER CONCENTRATION AS A FUNCTION OF ANNEALING TEMPERATURE FOR SPECIMENS IMPLANTED AT 200°C AND ROOM TEMPERATURE
b) Room Temperature implants

The sheet carrier concentration increased monotonically with increasing temperature, reaching a value of about $4 \times 10^{12} \text{ cm}^{-2}$ for 700 or 800°C anneals (figure IV.21). This value ($4 \times 10^{12} \text{ cm}^{-2}$) indicated that the carrier removal, $\Delta n$, was still significant but since the implant dose was comparatively high ($10^{14} \text{ Ar}^+ / \text{cm}^2$), the carrier removal rates were found to be low. The calculated values of integral removal rates $K_{(\text{int})}$ are presented in table IV.11.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$K_{(\text{int})}$ ($\times 10^{-2}$) $e/\text{Ar}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>4.9</td>
</tr>
<tr>
<td>700</td>
<td>3.6</td>
</tr>
<tr>
<td>800</td>
<td>3.4</td>
</tr>
</tbody>
</table>
IV.4.3. Profiles after 700°C annealing.

Hall coefficient and resistivity measurements were carried out in conjunction with layer removal in order to obtain carrier concentration and mobility profiles. The measurements were performed on samples implanted at 200°C with 200, 400 and 500 keV ions.

The profiles presented in this section are the average of 2 to 4 specimens. The theoretical atomic profiles are also plotted on each figure.

In the case of 200 and 400 keV implants, Gaussian-shaped profiles were not observed for doses above $5 \times 10^{12} \text{ Ar}^+ / \text{cm}^2$ (figure IV.22 and 23). This may be due to unannealed damage (i.e. higher carrier removal); it could also be the result of a process like damage enhanced arsenic/gallium outdiffusion which occurs in the early annealing stages.

As the implant energy increased, the profiles became broader (figure IV.24). The carrier removal measured at the tail region (defined as the region beyond 5000 Å in depth) was still high. In other words the complete recovery expected at the tail region did not occur (Table IV.12).

The profile minima of 200, 400 and 500 keV implants occurred at about 900, 1600 and 2700 Å respectively (figure IV.24). These values are lower than those of the theoretically calculated ranges of 200, 400 and 500 keV argon ions in germanium. Theoretical data for germanium
FIGURE (IV.22): ELECTRON CONCENTRATION AND MOBILITY PROFILES OF 200 keV ARGON BOMBARDED (AT 200°C) SPECIMENS FOLLOWING ANNEALING AT 700°C FOR 15 MINUTES WITH ALUMINIUM ENCAPSULATION
FIGURE (IV.22): ELECTRON CONCENTRATION AND MOBILITY PROFILES OF 400 keV ARGON BOMBARDED (AT 200°C) SPECIMENS FOLLOWING ANNEALING AT 700°C FOR 15 MINUTES WITH ALUMINIUM ENCAPSULATION
DOSE: \(5 \times 10^{12} \text{ At/cm}^2\)

\(T_i: 200^\circ C\) \(T_a: 700^\circ C\)

**Figure (IV.24):** Carrier concentration profiles of 200, 400 and 500 keV argon bombarded (at 200°C) specimens following annealing at 700°C for 15 minutes with aluminium encapsulation.
was used because there is none available for argon implants into GaAs. The ratios of experimental and theoretical ranges were found to be 0.6, 0.6 and 0.7 for 200, 400 and 500 keV implants, respectively.
Calculated data of carrier removal rate $K_x$ as a function of depth.

<table>
<thead>
<tr>
<th>Ion Energy (keV)</th>
<th>Dose ($\text{Ar}^+/\text{cm}^2$)</th>
<th>Depth (Å)</th>
<th>$K_x$ ($\text{e}/\text{Ar}^+$)</th>
</tr>
</thead>
<tbody>
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TABLE (IV.13) Continued.

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Estimated error in $K_x$: ± 7%
This chapter consists of three parts, (a) proton bombardment, (b) oxygen bombardment and (c) argon bombardment. In these parts, a detailed discussion of the results and also, to some extent, a comparison with published data is made.

V.1. Proton Bombardment
V.1.1. Isolation Depth

As mentioned earlier (Chapter II.3.1.) most of the energy is dissipated in inelastic electronic collisions. Matsumura et al. \( ^{(17)} \) reported that electronic stopping was the dominant stopping mechanism until the proton energy is below 1 keV, which is also the energy dissipated in nuclear collisions. Therefore, one would expect the peak of the distribution of implanted protons to occur approximately at the same depth as the minimum of the profile of the free carrier concentration of proton bombarded GaAs.

We found that within the energy range of our experiments, the range and energy had an almost linear relationship. Our results depicted in figure IV.3 are in good agreement with the experimental and theoretical data of Matsumura et al. \(^{(17)} \) and also Mcintyre \( ^{(79)} \). In contrast, Sakurai et al. \(^{(20)} \) found the relationship linear up to 700 keV, and reported that the profile minima increased in depth by about 0.85 micron for every 100 keV increase in proton energy. Close
examination of Sakurai's results suggests that his data are also in agreement with ours within the experimental error which was reported to be about 20%.

Harada and Fujimoto studied the range-energy relationship by means of the C-V technique. Their findings indicated that proton ranges, within the energy range of 60 - 380 keV, were less than our range values. For instance, the ranges of 150 and 300 keV protons were measured to be 0.9 and 1.8 microns respectively.

For the same energies, we found the ranges to be 1.1 and 2.3 microns respectively (Chapter IV.1.1.). The reason for this large disagreement between Harada's data and other publications including this investigation is not apparent.

V.1.2. Carrier Removal and Profiles

All implants into GaAs including protons, electrons and neutrons are known to cause some modification of electrical properties. This modification depends upon the projectile species, energy and dose. It was thought that a comparison of proton bombardment with neutron and electron irradiation in GaAs could provide information relevant to the understanding of the effect of the defects on the carrier removal mechanism.

Wohlleben and Beck having calculated the number of defects, found a value of carrier removal as \( \Lambda_p = 0.28 \) electron/defect (for 3 MeV protons in GaAs).
In the case of 1 MeV electron irradiation, Grimshaw and Banbury\(^{(78)}\) obtained a value of \(\lambda_e = 2 \text{ electron/defect}\). Finally, Aukerman and Graft\(^{(76)}\) reported that on irradiation with high energy neutrons, each primary displaced atom generates a displacement cascade which on average consists of about \(10^3\) "single defects"\(^{(76)}\). Evaluating the displacement cascade as the sum of independent single defects, \(\lambda_n\) appears to be 0.2 electrons/defect. It is, however, reasonable to suspect that lattice defects produced by electron and neutron bombardment would have a different effect on the particular measured quantity. In a way, these two types of bombardment (electron and neutron) represent limiting cases for the distribution of radiation induced defects, because in electron irradiation it is almost exclusively isolated Frenkel defects that are formed,\(^{(76,77,81)}\) whereas neutrons produce mainly large displacement cascades\(^{(82)}\).

The comparison made in the previous paragraph indicates that \(\lambda_p\) lies between \(\lambda_n\) and \(\lambda_e\). The spatial distribution of defects produced by proton bombardment is also intermediate between those caused by electron and neutron bombardments. Since \(\lambda_e\) is the largest and \(\lambda_n\) is the smallest, it may be concluded that the isolated single defects produced by electron bombardment make a decisive contribution to the carrier removal. The reason that \(\lambda_n\) is small may be due in part to the formation of clusters which consist of a highly "bombarded zone" in which the carrier concentration is already low\(^{(13)}\).
For a particular dose, the width of the carrier concentration profile produced by 300 keV protons appeared to be approximately equal to that for 500 keV protons (figure IV.4). This observation is in good agreement with Brice's theoretical calculations which showed that the damage peak maintained approximately the same width for increasingly energetic implants of B⁺ into silicon. Applying Brice's analysis to our profiles (figure IV.4), several conclusions can be drawn. In particular, the damage distribution generated by 500 keV protons over the last 2.5 micron of their travel can be assumed to have the same shape as the damage distribution caused by 300 keV protons between 0 and 2.5 micron.

Protons are known to have about 0.8 - 0.9 micron isolation depth for every 100 keV of energy, in other words, protons lose their energy linearly with depth. Therefore, the damage distribution of 500 keV protons between 1.7 (corresponding to the range of 200 keV protons) and 4.25 (the range of 500 keV protons) microns can be considered to be approximately the same as that generated by 300 keV protons.

This conclusion assumes that nearly all the protons incident on GaAs maintain their direction of travel until just before they come to rest.

For a given dose, carrier removal at the front part of the profiles, where the measured free carrier concentration is constant, decreased as the proton energy increased (figure IV.4), indicating the decrease in elastic scattering cross-section. This observation
is supported by the theoretical studies of Brice who carried out the calculations for boron implants (40 - 400 keV) in silicon.

Profiling experiments of Harada and Fujimoto showed that the damage density at the surface region of profiles decreased as the implant energy increased. In addition, Pruniaux et. al. found that the ratio of the rate of carrier removal at a profile minimum to that near the surface, increased at higher incident energies. The rate of increase was found to be about a factor of 10 when the energy was increased from 150 to 300 keV. Thus, both Pruniaux et. al. and Harada et. al. confirm our observations.

Carrier removal rates $K_p$ and $K_{int}$, defined as the number of charge carriers removed by each incident ion, have been found to be independent of proton energy. Also the peak carrier removal $K_p$ up to a certain dose, was constant within the experimental error. As mentioned earlier (Chapter IV.2.3), the doses above $2 \times 10^{11}$ $H^+/cm^2$ resulted in comparatively lower carrier removal rates. This is believed to be due to the non-linear nature of carrier removal with proton dose. In other words, after most of the free carriers are removed in the bombarded region, further bombardments result in less carrier removal because the free carrier concentration in the bombarded zone is already low. In the case of 150 keV bombardments, Pruniaux et. al. observed the carrier removal rate at the peak to
decrease rapidly after the samples (GaAs) were more than 60% compensated.

Wohlleben and Beck\(^{(13)}\) produced diagrams indicating the dependence of carrier removal on the position of the Fermi level \(E_F\) (figure II.4). The carrier removal rate \(K_{(int)}\) is evidently smaller as \(E_F\) moves towards the centre of the band gap. They also found that as the initial carrier concentration increased (figure II.3), higher proton doses were needed to convert the material to semi-insulating. Their findings also suggest that carrier removal in n and p type GaAs is very similar.

V.1.3. Thermal stability of proton bombarded GaAs.

High resistivity layers produced by proton bombardment are expected to be affected by annealing because it is believed that the carrier compensation is related to radiation damage.

In order to apply proton bombardment to electronic device fabrication, the thermal stability of the proton isolated layers needs to be thoroughly investigated.

When carrier removal mechanisms were discussed in section V.1.2, it was mentioned that the carrier removal by protons was intermediate between the values for electrons and neutrons. Similarly the annealing characteristics of proton bombarded GaAs appear to be intermediate in terms of the temperature necessary for a full recovery of carrier concentration. The annealing characteristics of material bombarded with reactor
neutrons and 1 MeV electrons indicate that about 10% of the damage created by the neutrons anneals out at the same temperature as that required to recover completely the damage produced by 1 MeV electrons. The remaining neutron damage required much higher annealing temperatures to remove it. The compensated layers, in the case of 1 MeV electron bombardment, were annealed out completely at about 200°C whereas the neutron damage required temperatures in excess of 600°C\(^{77}\).

Published data and also the results of our annealing experiments suggest that lightly proton bombarded GaAs anneals out at lower temperatures than heavily bombarded layers. We found a fast annealing stage between 225 and 300°C at which about 40% recovery of carriers occurred. This is also an indication of the degree of recovery during the tin-dotting process. A further 85°C increase in temperature resulted in 75% recovery. Similarly Harada et al.\(^{15}\) also observed about 70-80% recovery on specimens, with \(n = 5 \times 10^{16} \text{cm}^{-3}\), which were bombarded with \(10^{12} \text{H}_1^+ / \text{cm}^2\) at 60 keV and annealed at 300°C for 10 minutes. The recovery was complete after annealing at 500°C for 10 minutes.

For lightly bombarded \((< 6 \times 10^{12} \text{H}_1^+ / \text{cm}^2)\) specimens, Sakurai et al.\(^{20}\) observed significant carrier recovery after annealing at 435°C for 10 minutes whereas the same heat treatment for 35 hours resulted in
very little recovery on heavily bombarded (> \(6 \times 10^{12} \text{H}_1^+/\text{cm}^2\)) specimens having an initial electron concentration of \(1 - 3 \times 10^{16} \text{ cm}^{-3}\).

In order to remove the damage from heavily bombarded GaAs, Foyt et. al\(^{21}\), had to anneal at 700°C overnight. The specimens (\(n = 2 \times 10^{16} \text{ cm}^{-3}\)) were bombarded at 100 keV with a dose of \(10^{13} \text{H}_1^+/\text{cm}^2\). Thus, our work and that of Harada\(^{15}\) seem to apply to the low dose annealing regime of Sakurai\(^{20}\) and we suggest that a possible definition for "low dose" is the dose range where the carrier removal rate is constant with increasing dose.

It seems that single energy proton bombardment as a device isolation method does not exhibit good i.e., high temperature stability. For example, high dose (\(10^{13}\) to \(10^{14} \text{H}_1^+/\text{cm}^2\)) bombarded layers are subject to some degradation in terms of their semi-insulating properties after annealing in excess of 300°C. In general, the resistivity of the proton bombarded layers increases with increasing proton dose\(^{24, 73}\) and then goes through a maximum. Conduction in the layers bombarded with doses above those which result in the maximum resistivity (i.e. overdosed) is believed to be via defect states\(^{73}\) by some form of hopping conduction. The resistivity of overdosed bombarded layers increases with increasing annealing temperature and goes through a maximum\(^{22, 73}\). Thus there is an optimum annealing temperature for any overdose bombardment in order to
achieve the maximum resistivity. This temperature has been found to be much higher (about 500°C) than the temperatures at which low dose implants (i.e., below the optimum dose, with no annealing) begin to degrade. Therefore, the method of overdose bombardment followed by annealing can produce high resistivity layers that are stable at least up to that particular annealing temperature. We observed that the shapes of the profiles did not change with annealing up to 385°C. This implies that the recovery rate near the projected range is higher than it is near the surface. According to Donnelly et al. (73), several different compensating levels which anneal at different temperatures are created by proton bombardment. The density of each level varies with depth. For any single energy bombardment and for any annealing temperature, up to 700°C, there is an optimum compensating density which does not anneal out.

As an alternative to single energy implants, Donnelly et al. (73) employed multi-energy bombardments to approximate the optimum defect density over the whole bombarded region. In this case of multi-energy, overdose bombardments followed by an anneal, good quality semi-insulating layers having thermal stability up to at least 500°C can be produced. (See chapter II 2.4.(c)).
V.1.4. $H_2^+$ and $H_3^+$ Implants.

We found that the effect of implanting equivalent doses of $H_1^+$, $H_2^+$ and $H_3^+$ ions into GaAs is identical in terms of ion range and carrier removal (See IV.2.5). The effect has also been found to be approximately independent of the ion (proton) energy in the range of 300 to 500 keV.

As mentioned earlier, the dissociation of $H_2^+$ or $H_3^+$ ions travelling in gas media has been intensively studied by a number of research workers (see, for example reference $^{87,88}$). In contrast, comparatively little data related to the implantation of $H_2^+$ or $H_3^+$ ions, is available to make an informative comparison with our observations. However, it is known that the binding energy of $H_2^+$ or $H_3^+$ ions is very low$^{46,84}$ and of the order of 4 eV$^{46,84}$. Thus, as the incident ion $H_2^+$ or $H_3^+$ passes through the first few atomic layers of the target material, the electron responsible for the binding may be lost by ionization. The collision-produced protons repel one another via a coulomb potential. This transformation results in significant modification of the energy and angular distribution of the incident beam and thus in the first instance, one might expect the effects of implanting $H_1^+$, $H_2^+$ or $H_3^+$ ions to be different.

Although the ranges and carrier removal of equivalent implants of $H_1^+$, $H_2^+$ or $H_3^+$ were found to be identical,
it seems that there are some differences in terms of damage production which are not detectable using our experimental method.

Mitchell et. al.\(^{(85)}\) performed molecular ion implants having twice the energy and half the dose of atomic ions. They found that in the case of the heavy ions As, Sb, Te and Bi, the molecular beam produced roughly 50% more damage than the atomic beam indicating that the damage production depends not only on the amount but also on the localized concentration of deposited energy.

In general, the amount and nature of lattice disorder created around the ion track depends primarily on the amount of energy deposited into nuclear processes. This deposited energy creates damage clusters within the volume surrounding the ion track. The resulting damage, in the case of molecular ions, depends strongly on the extent to which damage volumes overlap.

The first direct comparison of the damage produced by monoatomic and diatomic ions was reported by Moore et. al.\(^{(86)}\) who implanted 40 keV As\(_2^+\) and 20 keV As\(^+\) into GaAs. They found that the damage created by diatomic implants was about 50% greater than that of monoatomic.
This result was estimated from the Rutherford backscattering yields of As$_2^+$ and As$^+$ implanted specimens.

In apparent contrast, the molecular effect has been found to be negligible in the case of low-mass ion implantations.\(^{(83)}\) This was believed to be due to the fact that damage cascades created by light ions are comparatively small compared with that of heavy ions. Thus one would not expect significant overlapping to occur between the subcascades along two low-mass trajectories such as the dissociation of H$_2^+$ into two protons. To prove the point, Mitchell et al.\(^{(83)}\) carried out low-mass H$_1^+$ and D$_1^+$ implants into Ge and Si. Using the Rutherford backscattering technique, they found that the amount of damage produced by equivalent implants of H$_1^+$ (or H$_2^+$) and D$_1^+$ (or D$_2^+$) were identical, indicating the molecular effect to be negligible. Therefore the findings of Mitchell et al.\(^{(83)}\) are in good agreement with our observations.

Apart from our results\(^{(74)}\), Mitchell et al.\(^{(83)}\) are the only workers who have compared the effects of H$_2^+$ ions with H$_1^+$ ions. Unfortunately, to the best of our knowledge, there is no data available on the use of H$_3^+$ ions in damage studies.

However, there are some publications that should make us cautious about the use of H$_2^+$ or H$_3^+$ implantations instead of H$_1^+$. For instance, Caywood et al.\(^{(45)}\) reported the backscattering data of H$_1^+$.
(0.8 MeV), H$_2^+$ (1.6 MeV) and H$_3^+$ (2.4 MeV) ions incident on silicon. They found that the proton spectra from H$_1^+$ and H$_2^+$ ions were essentially the same, but the spectrum from H$_3^+$ ions was somewhat different. The difference (as explained in Chapter II.3.) was believed to be due to the channelling of protons produced by the dissociation of H$_3^+$ ions. Considering this effect, one would expect the damage profile from H$_3^+$ ion implants to be different from those of H$_1^+$ and H$_2^+$. However, our results suggest that this effect is negligibly small for H$_3^+$ implants into GaAs.

When implanting with H$_2^+$ or H$_3^+$ ions the vacuum pressure in the beam line should be low enough to prevent any possible undesirable dissociation. It has been found that, in poor vacuum conditions 10-15% of the incident H$_3^+$ beam can be attenuated by collisions with the gas atoms or molecules in the beam line of the accelerator. Berkner et. al. (87) reported that, in hydrogen + nitrogen gases, an energetic H$_3^+$ ion (400 - 1800 keV) colliding with a gas molecule can be destroyed as a result of:

(a) Electron capture

\[ \text{H}_3^+ \rightarrow \text{H}_3 \]

\[ \text{H} + \text{H}_2 \]

\[ 3\text{H} \]
(b) Dissociative excitation
\[ \text{H}_3^+ \rightarrow \text{H} + \text{H}_2^+ \]
\[ \rightarrow \text{H} + 2\text{H} \]
\[ \rightarrow \text{H}^+ + \text{H}_2 \]

(c) Ionization
\[ \text{H}_3^+ \rightarrow \text{H} + 2\text{H}^+ \]
\[ \rightarrow \text{H}^+ + \text{H}_2^+ \]

(d) Double Ionization
\[ \text{H}_3^+ \rightarrow 3\text{H}^+ \]

(The process of \( \text{H}^- \) formation is excluded).

If any of the above cases apply to our implantation, then an error would be expected in dose measurements. Because of this possibility the vacuum pressure was maintained at better than \( 5 \times 10^{-6} \) Torr. In addition, some dissociation might also occur under high electric fields greater than \( 10^8 \) Volt/cm, applied for scanning purposes, but for the scanning voltages (i.e. up to 5kv) used in our case, this type of dissociation is unlikely to happen.
V.2. Oxygen Bombardment

Introduction

The electrical isolation due to the radiation damage may be removed at temperatures in excess of about 500°C, but when oxygen ions are used, some carrier removal remains up to temperatures of 800°C (39).

Since there is a lack of basic data on carrier removal as a function of oxygen dose and energy, we have carried out a study of the dose and temperature dependence of carrier removal for an ion energy of 400 keV.

V.2.1. Dose dependence of resistivity.

We found that doses less than \(10^{13} \text{ } \text{O}^+ / \text{cm}^2\) can produce highly resistive layers before annealing but higher doses produced less resistive layers (figure IV.1).

The dose-resistivity characteristic is similar to that obtained by Donnelly et. al. (73) for proton bombardment where the resistivity increases with dose and goes through a maximum (figure V.1.).

In the dose region where resistivity decreases with increasing dose, the variation of sheet resistivity with dose for unannealed samples is similar and consistent with the work of Kato et. al. (71) who investigated the change in resistivity as a function of dose. They carried out the resistivity measurements on
FIGURE (V.1): THE RESISTANCE - AREA PRODUCT (RA) AND THE CAPACITANCE PER UNIT AREA (C/A) VERSUS DOSE OF $n^+-$GaAs ($n=4 \times 10^{18}$ cm$^{-3}$) SAMPLES BOMBARDED WITH 400 keV PROTONS ONLY. THE RESISTANCE WAS MEASURED ON A CURVE TRACER AND THE CAPACITANCE WAS MEASURED ON A BRIDGE AT 5 kHz. (AFTER DONNELLY AND LEONBERGER$^{[73]}$).
semi-insulating GaAs specimens implanted with seven different ions. Kato's data is presented together with ours in figure (V.2). As seen from this figure, within experimental error, our curve is almost identical to that obtained from samples implanted with 150 keV N⁺ ions. This agreement is reasonable since oxygen and nitrogen are very similar in mass.

In the dose region where resistivity decreases with increasing dose, hopping is probably the most likely mechanism of electrical conduction. According to Kato et. al. the resistivity saturates above a critical dose level. They also found that the resistivity-dose characteristics followed the same pattern in every sample regardless of the implanted ion.

This suggests the fact that electrical conduction in unannealed samples is due to lattice disorder produced by the implantation and not due to the ions themselves. To prove the point, Kato et. al. also studied the relation between resistivity and the degree of lattice disorder (i.e. number of displaced atoms). Their findings suggest that all the experimental values lie on the same curve despite the differences in mass and energy of the implanted ions. This data is shown in figure V.3.
FIGURE (V.2): SHEET RESISTIVITY OF Implanted GaAs layers versus dose for various ions at room temperature. (After Kato, Shimada, Shiraki and Momatsubara(71)).
FIGURE (V.3): NUMBER OF DISPLACED ATOMS, N_{DD} VERSUS RESISTIVITY, \( \rho \), FOR IMPLANTED GaAs. (AFTER KATO, SHIMADA, SHIRAKI AND MOMATSUBARA).
In addition, Kato et al. (71) investigated the temperature dependence of resistivity. For all implanted samples, the relationship was observed to be \( \log \rho_s \propto T^{-1} \) in the high temperature range. In the temperature range below 180K, the relationship could be better explained as \( \log \rho_s \propto T^{-1/4} \). This behaviour is very similar to the temperature dependence of resistivity in amorphous semiconductors.

For completely disordered GaAs, Kato et al. (71) calculated the activation energy of hopping conduction to be about 0.087 eV. The hopping distance corresponding to this activation energy was calculated to be 55Å. As seen in figure V.3, the dose required to create completely disordered layers, i.e. where the number of displaced atoms is approximately equal to the atomic density of GaAs is about \( 10^{15} \) ions/cm² which is also the highest dose used in our experiments.

In the light of Kato's (71) observations and other related work, (22, 73, 82) it is possible to interpret our results for oxygen bombarded samples in the following way; that is, the initial increase in resistivity with increasing dose, up to the maximum resistivity is due to the carrier removal mechanism, whilst beyond the maximum point, the decrease in resistivity with increasing dose may be due to tunnel-assisted hopping via defect states produced by the oxygen implantation.
V.2.2. Resistivity versus dose after 700°C annealing.

Following heat treatment at 700°C, the net increase in resistivity as a result of implantation plus annealing was 30-40% of that of unimplanted samples for doses of $10^{12}-10^{13}$ ions/cm². For higher doses the resistivity after annealing increased with increasing dose and reached an estimated value of $10^8 \Omega \cdot \square$ for a dose of $10^{15}$ $O^+/cm^2$. The assumptions made to estimate the resistivity value for $10^{15}$ $O^+/cm^2$ implant have been described in chapter IV.3.1(b).

For a fixed annealing temperature (700°C), the effect of chemical doping became more apparent as the dose increased. The effect maximized, resulting in the highest resistivity of about $10^8 \Omega \cdot \square$ for a dose of $10^{15}$ $O^+/cm^2$.

It is known that, in the case of implants with ions having similar masses to oxygen, radiation damage can be annealed out at temperatures in excess of 600°C. For instance, Kato et. al. (71) observed a complete recovery of resistivity for samples implanted with $5 \times 10^{14}$ nitrogen ions/cm² at 200 keV. This experiment suggests that there should be no significant radiation damage remaining at temperatures of 700°C and above. Hence, one can postulate that the compensation, after 700°C annealing, in oxygen bombarded GaAs is due predominantly to a doping effect and not to residual damage.
V.2.3. Temperature dependence of resistivity

We found that the resistivity of samples implanted with $10^{15}$ O$^+$/cm$^2$ increased with increasing annealing temperature reaching a saturation value of the order of $10^8 \, \Omega \cdot \square$ at 700 to 800°C. According to Favennec $10^8 \, \Omega \cdot \square$, 700°C is the minimum temperature required in order to obtain a saturated compensation effect from oxygen ions whilst also removing by annealing most of the carrier compensation due to radiation damage. In fact, our findings also indicated that layers having resistivities greater than about $10^7 \, \Omega \cdot \square$ could be achieved in such samples (implanted with $10^{15}$ O$^+$/cm$^2$) by annealing at a temperature as low as 500°C. However, this value may be partly due to the effects of radiation damage, since, some residual damage produced by $5 \times 10^{14}$ nitrogen ions has been reported after annealing at 500°C (71). Above this temperature, as explained in the previous section, the increase in resistivity with temperature is most likely to be due to the doping effect.

The temperature-resistivity characteristic of oxygen bombarded GaAs (oxygen dose $= 10^{15}$ ions/cm$^2$) is, as expected, in contrast to the characteristics of other dopant or non-dopant ions. In the case of non-dopant ions (e.g. N$^+$, Ar$^+$ and H$^+$) an initial increase in resistivity with increasing temperature reaches a maximum and then the resistivity decreases towards the original resistivity value of the unimplanted material (29,71).
For dopant ions (Zn⁺, S⁺, Se⁺, Te⁺ and Ge⁺) the resistivity first increases then goes through a maximum at about 400-500°C and then decreases reaching eventually a saturation value (71, 90, 91). This value corresponds to the doping effect of the implanted ion. One should notice that the ion doses considered here are above the optimum dose which results in maximum resistivity without annealing.

In accord with Favennec et. al. (37, 39, 41), we observed that an 800°C anneal did not result in any significant change in the properties of oxygen bombarded layers.

V.2.4. Profiles and carrier removal after 700°C annealing.

We found that the integral carrier removal rate \( K_{\text{int}} \) was dependent on oxygen dose in the dose region of \( 10^{12} \) to \( 10^{15} \) O⁺/cm². The \( K_{\text{int}} \) value decreased from about 6 electrons/oxygen ion to about \( 6 \times 10^{-2} \) electrons/oxygen ion for doses of \( 10^{12} \) and \( 10^{14} \) O⁺/cm², respectively.

According to Favennec et. al. (37, 39) the integral carrier removal rate, \( K_{\text{int}} \), is independent of dose after annealing at 700 to 800°C. The magnitude was found to be 2 electrons/oxygen ion for specimens implanted with doses up to \( 5 \times 10^{12} \) O⁺/cm² at high energies (> 400 keV). Unfortunately, Favennec et. al. (37, 39, 41) have not measured the carrier removal on higher dose (i.e. > \( 5 \times 10^{12} \)) implanted specimens.
In apparent contrast, we have not observed any significant carrier compensation in the dose region below $10^{12}$ O$^+$/cm$^2$. The reason for this disagreement is not known.

At this point, it is worthwhile to interpret Itoh's\(^{10}\) data in some detail. Using the zero-bias depletion depth values obtained by them using C-V technique (figure V.4), we have calculated the average free electron concentrations in the depletion regions of samples implanted with $5 \times 10^{12}$, $2 \times 10^{13}$ and $10^{15}$ O$^+$/cm$^2$ followed by annealing at 700 or 800°C. The average electron concentration values appeared to be about $10^{17}$, $6 \times 10^{16}$ and $2 \times 10^{16}$ cm$^{-3}$ for the three doses respectively. The electron concentration of the unimplanted material was $5 \times 10^{17}$ cm$^{-3}$. The calculated average concentration values suggest that the implanted layers have not been converted into semi-insulating material. Additionally, the carrier removal rate appears to be dependent on oxygen dose. Therefore, Itoh's\(^{10}\) results seem to be in agreement with ours.

Possible explanations for the discrepancy between Favennec's data\(^{37,39,41}\), and ours are that; (i) the effect is dependent on ion energy, (ii) the value of $K(\text{int})$ is dose dependent as also found by Itoh et.al.\(^{140}\), (iii) results may vary with the source and thermal stability of the GaAs material and (iv) outdiffusion of oxygen due to encapsulation failure may cause a
FIGURE (V.4): CARRIER CONCENTRATION PROFILES OF 50 keV OXYGEN IMPLANTED SPECIMENS. (AFTER M. TAKEUCHI 92,40).
decrease in the actual oxygen dose retained in the specimen during annealing \(^{(92)}\).

In fact, a considerable amount of oxygen outdiffusion during annealing at \(800^\circ C\) for 60 minutes has been observed by Takeuchi \(^{(92)}\) on specimens implanted with \(10^{15} \, O^+/cm^2\) at 70 keV. Despite the fact that no encapsulant was used in this experiment, the result can still be used as a supporting observation to our findings.

V.3. Argon Bombardment

Introduction

It is believed that the low electrical activity yields of dopant ion implantations in GaAs are due to residual damage resulting from inadequate annealing. In the case of dopant ion implantations, the degree of residual damage after annealing is obscured by the number of implanted ions located substitutionally and hence able to act as dopants. This difficulty in the study of residual damage can be overcome by implanting non-dopant ions so that the carriers compensated will only be those initially present from the substrate doping. Therefore, we have investigated the properties of argon - a non-dopant ion in GaAs - bombarded GaAs after annealing at high temperatures, 700 to \(800^\circ C\), to make a contribution to the understanding of the problem of forming heavily doped layers in GaAs.
Since there is a lack of basic data on argon bombarded GaAs, we will compare some of our results with the reported data on S+ implanted GaAs, because sulphur has a very similar mass to argon and also it is a well-known dopant which has been used to fabricate electronic devices.

V.3.1. **Effect of dose on residual damage.**

Our measurements of sheet carrier concentration and sheet resistivity as a function of dose showed that the amount of residual damage was still considerable. The sheet resistivity increased from 155 $\Omega$/$\square$ to about 200 $\Omega$/$\square$ for the doses from $5 \times 10^{11}$ to $3 \times 10^{13}$Ar+/$\mathrm{cm}^2$ and it was about a factor of 2 higher for a $10^{14}$Ar+/$\mathrm{cm}^2$ dose. The increase in sheet resistivity or decrease in carrier concentration can be considered as a measure of the residual damage after annealing. It seems that the degree of residual damage up to doses of $3 \times 10^{13}$Ar+/$\mathrm{cm}^2$ was not very large.

Similar results concerning residual damage have also been found in the case of other ions having similar mass numbers to argon. At this point it is worthwhile to review some of the related work reported on sulphur bombarded GaAs.

In the case of hot (200°C) sulphur implantations, Woodcock et al. (96) found that after annealing, high doping efficiencies were only obtained at low doses ($<10^{14}$S+/$\mathrm{cm}^2$). This result suggested the fact that residual damage was still significant at high doses.
More recently, Davies et al.\(^{(105)}\) found that for hot (500°C) sulphur implantations, a large amount of residual damage remained after annealing at 700°C for a dose of \(10^{14} \text{s}^+/	ext{cm}^2\). The same authors\(^{(104)}\) earlier reported that an increase in implant temperature from 200 to 500°C had not resulted in any improvement in terms of residual lattice damage.

Thus, the results of Woodcock et al.\(^{(96)}\) and Davies et al.\(^{(105,106)}\) can be compared with our data and indicate that the dose dependence of residual damage is consistent with our results.

V.3.2. Recovery of Damage.

a) Effect of implantation temperature.

For some ions, several groups have indicated that implants performed above room temperature could reduce the rate of defect production. Before we discuss our results some of the related recent work are summarized below.

Davies et al.\(^{(104)}\) found an improvement in conductivity resulting from elevated temperature (20-500°C) implantations in the case of the dopant ions Se\(^+\) and Te\(^+\). Measurements of the rate of introducing compensating defects at elevated temperatures showed only a marginal reduction from the room temperature rate. The avoidance of lattice disorder build-up also had minimal effect on carrier recovery and the amount of residual compensation after annealing.
Following an implant of boron at 1 MeV with a dose of $3 \times 10^{10}$ cm$^{-2}$ into GaAs specimens held at 250°C, Davies et. al. (104) measured the carrier removal rate to be 160 carriers/ion. The same authors (106) earlier reported that identical implants at room temperature followed by annealing at 250°C resulted in a carrier removal rate of 185 carriers/ion. This difference in the carrier removal is due to the implants at 250°C producing a net concentration of defects which is less than that formed after room temperature implant plus annealing at 250°C and is related to the fact that there is an annealing stage at about 200–250°C for implanted GaAs.

It was also discovered that there is very little to be gained by performing Si$^+$ implants at an elevated temperature (51).

In apparent contrast, Whitton et. al. (50) observed a large increase in electrical activity in sulphur implanted layers when the implant temperature was raised from room temperature to greater than 150°C. As a result of this an improvement in conductivity, by a factor of 2.5, was detected.

In the case of our argon bombardments, the amount of residual damage which manifested itself on the resistivity and carrier concentration measured after annealing, was similar for room temperature and elevated temperature implants. For instance, the resistivity measured after 800°C annealing was $2 \times 10^2$ and $2.7 \times 10^2$ $\Omega$/$\Omega$ for elevated and room temperature
implanted samples, respectively. Considering that the room temperature dose, $10^{14} \text{Ar}^+/\text{cm}^2$, was much higher than that of the hot (200°C) implant dose, $5 \times 10^{12}$, one can conclude that in the case of argon, hot implants reduced the rate of damage production to some extent.

b) Resistivity

We found that the resistivity of hot (200°C) argon implanted layers increased with increasing temperature, reaching a maximum around 400°C, and then decreasing sharply approached a saturation value at about 700 to 800°C. For room temperature implants, the annealing behaviour of resistivity was only investigated in the temperature range of 500 to 800°C and showed a parallel tendency to the hot implant case (figure IV.20)

The annealing behaviour of resistivity of dopant or non-dopant ion implanted GaAs was mentioned in the previous part of this chapter (V.2.3.). In the light of that discussion, our results are in good agreement with published work (29, 71, 90, 91, 93).

c) Carrier concentration

The carrier concentration increased monotonically with increasing temperature reaching a saturation value for both room and elevated temperature implants (figure IV.21). Hall measurements could not be obtained until after annealing at 500°C. Similar behaviour was also reported by several other workers. For example, Sansbury et. al. (93) have investigated the temperature...
dependence of sheet carrier concentration of silicon ions implanted into GaAs.

V.3.3. Carrier Removal

a) 200°C Implants

We found that for samples annealed at 700°C, the carrier removal rate, \( K(\text{int}) \) decreased with increasing dose, since the carrier concentration measured after annealing has a constant value up to doses of \( 3 \times 10^{13} \text{Ar}^+/\text{cm}^2 \). This can be better explained by the fact that only a certain amount of damage created by doses up to \( 3 \times 10^{13} \text{Ar}^+/\text{cm}^2 \) annealed out at 700°C. According to Donnelly et. al. (73), for any annealing temperature there is a certain compensating level which does not anneal out for GaAs implanted with a high dose of protons. A further increase in dose resulted in a further decrease in carrier removal rate \( K(\text{int}) \), since the change in carrier removal \( \Delta n \) is not as large as the change in dose.

For a dose of \( 5 \times 10^{12} \text{Ar}^+/\text{cm}^2 \), the carrier removal rate decreased with increasing temperature. The rate of change of \( K(\text{int}) \) was largest in the range of 400 to 600°C, corresponding to the second annealing stage of heavily bombarded GaAs (97,98,99,100).
b) Room temperature implants

For samples implanted with a dose of $10^{14}$Ar$^+$/cm$^2$, as the annealing temperature increased, the carrier removal rate decreased in a similar way to the hot implant results. Again results are indicative of the second annealing stage occurring at 400 - 600°C$^{(97-100)}$. The lower values of $K_{(int)}$ as compared with 200°C implants, may be attributed to the much higher, room temperature, implant dose.

V.3.4. Profiles

All the profile measurements were carried out on specimens implanted at 200°C and annealed at 700°C. We found that the profile minima occurred at depths of about 60 to 70% of the theoretical range and that a large amount of residual damage was present near the surface. This was most apparent in the case of 200 keV bombardment.

At this point, it is worthwhile to summarize some of the related literature which may aid our discussion.

For low dose ($< 10^{14}$ ion/cm$^2$) room temperature ion implanted GaAs, two annealing stages at about 200 and 400°C have been found by a number of workers$^{(97-100)}$ Brailovskii and Brundy$^{(101)}$ and Brailovskii et.al.$^{(102)}$ proposed that the 225°C annealing stage was due to individual point defect mobility and the formation of defect clusters which then broke up at about 400°C.
For tellurium implanted GaAs, Sealy\(^{(94)}\) observed changes in the size of dislocation loops with annealing. This observation is also indicative of defect migration during annealing.

In the case of hot (200\(^{\circ}\)) sulphur implants, Woodcock et. al.\(^{(96)}\) after annealing at 700\(^{\circ}\)C, found that the photoluminescence intensity degraded below implanted layers. This was accounted for by the migration of defects. Comparison of the depth of degradation on annealed and unannealed samples showed that defects migrated only during the hot (200\(^{\circ}\)C) implantation.

It appeared that at high doses and high implant temperatures implanted impurities diffused into the material to produce deeper profiles than predicted theoretically. For instance, Sansbury and Gibbons\(^{(93)}\), for sulphur implantations, obtained deeper profiles and compensation at the surface with high dose implants in GaAs. They calculated an enhancement of the diffusion coefficient of three orders of magnitude and concluded that it was the result of implantation damage which migrated ahead of the impurities.

In the light of the published data mentioned above, we suggest that the large amount of residual damage near the surface may be explained in terms of migration of electrical compensation centres. However, residual damage in the surface region may also be partly due to the failure of aluminium as an encapsulant.
As mentioned earlier, (Chapter IV.1.(d)), in the investigation of the thermal stability of Al-GaAs Schottky contacts, we found that the contacts degraded at temperatures above 500°C. This was thought to be due to the indiffusion of aluminium into GaAs. According to D'cruz[103] who studied the effects of aluminium as an encapsulant, the loss of Ga/As by outdiffusion into the aluminium film, indiffusion of aluminium and the formation of an interfacial layer, were the possible reasons of failure. Evidently, these effects introduce additional damage to the material. However, we believe that the major cause of the residual damage near the surface is due to defect migration rather than encapsulation failure. This tends to be confirmed for oxygen bombarded samples where the same residual damage at the surface occurred for both aluminium and silicon nitride coated specimens, figure (IV.16 and IV.17).

Assuming that the carrier concentration profiles represent a measure of damage then the measured depth of the carrier concentration minima, figure (IV.22,IV.23) is in accord with theoretical calculations of Brice[80] who found that the damage distribution typically occurs at about 70% of the projected range. This also agrees with experimental results of Matsumura and Furukawa[107] who found that the damage peak in phosphorus implanted GaP, was at a depth of about 66% of the projected range.
CHAPTER VI

CONCLUSIONS.

Some effects of $H_1^+$, $H_2^+$, $H_3^+$, $O^+$ and $Ar^+$ bombardment into GaAs have been investigated as a function of the ion dose and energy, implant temperature and annealing temperature. This chapter states the main conclusions which can be drawn from this work.

VI.1. General Conclusions

(i) Proton Bombardment

The Copeland technique has been proved to be a useful method in determining the profiles of $H_1^+$, $H_2^+$ and $H_3^+$ bombarded GaAs.

The isolation depth of protons has been determined to be about 0.85 microns for every 100 keV of proton energy.

The carrier removal rates $K_p$ and $K_{(int)}$ were constant up to certain doses above which they decreased with increasing dose. The threshold doses were found to be about $2 \times 10^{11}$ and $3 \times 10^{10}$ $H_1^+$/cm$^2$ for annealed (during tin-dotting) and unannealed as-implanted GaAs ($n = 1-3 \times 10^{15}$ cm$^{-3}$) respectively.

In the case of as-implanted material, carrier removal rates $K_p$ and $K_{(int)}$ were about $6 \times 10^4$ and 9 electrons/proton, respectively. These values are very
much higher than the ones obtained from specimens that were subjected to a heat treatment during tin-dotting (at 300° ± 20°). The carrier removal rates $K_p$ and $K_{(int)}$ for annealed specimens were about $1 \times 10^4$ and 2 electrons/proton respectively.

The proton bombarded layers have been found to be affected by low temperature annealing. A fast annealing stage was found between 225 and 300°C which resulted in about 60% recovery on $3 \times 10^{10} \text{H}_1^+/\text{cm}^2$ bombarded specimens. For the same dose the recovery ratio was about 75% at 385°C.

(ii) $\text{H}_2^+$ and $\text{H}_3^+$ bombardments

$\text{H}_2^+$ and $\text{H}_3^+$ ions dissociated into two and three protons on hitting the GaAs surface, with the ion energy being shared equally by the product H nuclei. As a result of this phenomenon, it was found that carrier removal caused by the equivalent implants of $\text{H}_1^+$, $\text{H}_2^+$, and $\text{H}_3^+$ were equal within the energy range (proton energy) 300 - 500 keV.

Carrier recovery at low annealing temperatures, 300°C, in the equivalently implanted layers was observed to be identical within experimental error.

Our results are important because they prove that equal carrier removal in GaAs can be obtained by implanting $\text{H}_1^+$, $\text{H}_2^+$ or $\text{H}_3^+$ ions. In addition, the use of $\text{H}_3^+$ ions allows the lower limit of accelerator voltage to be decreased by one-third, which is useful when using high voltage Van de Graaff machines.
(iii) **Oxygen Bombardment**

Oxygen bombardment can result in high resistivity layers which are thermally stable up to at least 700 or 800°C.

After implanting with as few as $1.5 \times 10^{11} \text{ O}^+/\text{cm}^2$ the sheet resistivity increased from about $150 \ \Omega/\square$ to $5 \times 10^8 \ \Omega/\square$ and continued to increase slightly as the dose was raised to $5 \times 10^{12} \text{ O}^+/\text{cm}^2$. For doses greater than the latter, the resistivity decreased tending towards a value of about $10^4 \ \Omega/\square$ for a dose of $1 \times 10^{15} \text{ O}^+/\text{cm}^2$.

Following heat treatment at 700° or 800°C, for doses $10^{12}$ to $10^{15} \text{ O}^+/\text{cm}^2$, the net increase in resistivity was 30 – 40% of that of the unimplanted samples.

For higher doses, the resistivity after annealing increased with increasing dose, reaching a value of about $10^8 \ \Omega/\square$ for a dose of $10^{15} \text{ O}^+/\text{cm}^2$. Profiling measurements showed that, for this dose ($10^{15}$) the thickness of the semi-insulating layer was about 0.5 microns.

On annealing, the resistivity of samples implanted with $1 \times 10^{15} \text{ O}^+/\text{cm}^2$ increased with increasing annealing temperature reaching a saturation value of the order of $10^8 \ \Omega/\square$ at 700 to 800°C. In fact, layers having resistivities greater than about $10^7 \ \Omega/\square$ were realized in such samples by annealing at a temperature
as low as 500°C, which is well above the operating temperatures of most devices.

(iv) Argon Bombardment

It has been observed that the implants performed at 200°C resulted in less radiation damage than for room temperature implantations.

Following an anneal at 700°C, the residual damage on specimens implanted at 200°C was at a constant level for doses up to about $3 \times 10^{13}$ Ar$^+$/cm$^2$. Consequently, the carrier removal rate $K_{\text{int}}$ decreased with dose. The increase in resistivity for doses up to $3 \times 10^{13}$ Ar$^+$/cm$^2$ was about 30% whereas, the increase for $10^{14}$ Ar$^+$/cm$^2$ was about 100%. Hence, the residual damage was still considerable.

The temperature dependence of the resistivity of GaAs bombarded with argon at 200°C followed the pattern found in the case of GaAs implanted with non-dopant ions. The resistivity increased with temperature, reaching a maximum around 400°C then it decreased with increasing temperature.

From the profiling experiments performed on specimens implanted at 200°C and annealed at 700°C, the profile minima occurred at depths of about 60 to 70% of the theoretical range. Also, a large amount of residual damage was present near the surface. This was more apparent in the case of low energy implants. In the light of published data, it was thought that the residual
damage in the surface region was most likely to be due to the migration of defects from the implanted region.
FUTURE WORK

In the light of our results and published data, we suggest that a more detailed study is required of the following topics:

a). Multiple energy proton bombardment, such as dose dependence of maximum annealing temperature.

b). Study of the annealing characteristics of $H_2^+$ and $H_3^+$ bombarded GaAs.

c). Characterisation of defect migration during the annealing of GaAs implanted with argon and oxygen ions.

In addition, it would aid our understanding of implanted GaAs if the following were studied:

d). Trapping levels which cause high resistivity when protons or $H_2^+$ and $H_3^+$ ions are used.

e). The cause of the chemical doping by oxygen ions.

Furthermore, measurements of lateral spread of oxygen, argon and other heavy ions may provide useful information for device applications.
APPENDIX I.

List of publications resulting from this work:-

1. B.J. Sealy, R.K. Surridge and S. Gecim

2. S. Gecim, B.J. Sealy, K.G. Stephens
   "Carrier removal after H⁺, H₂⁺ or H₃⁺ implants into GaAs" Elec. lett. Vol. 12, No. 25, p.668 (1976)

3. H. Matsumura, S. Gecim, K.G. Stephens
   "Lateral spread of the proton isolation layer in GaAs" Ion Implantation in semiconductors and other materials ed. F. Chernow, Plenum Press, New York (1977) pp.159-166

4. S. Gecim, B.J. Sealy, K.G. Stephens

5. S. Gecim, B.J. Sealy, K.G. Stephens and Y. Ono
   "Carrier removal in GaAs" To be published.
where; \( R_i \) = resistance of the implanted region
\( R_{1i} \) = resistance in the direction of the current
\( R_2 \) = resistance of the interface region located between the implanted zone and substrate.

From our electrical measurements, the value of the sheet resistance was determined to be of the order of \( 10^{-5} \Omega/\square \). This value was thought to be the sheet resistance of the interface region due to a shorting effect. This was concluded by the fact that the electrical properties in the implanted region did not change until about 5000\( \AA \) of implanted material had been removed by etching. This observation led to the conclusion that
the implanted region was of high resistance (See, figure IV.16).

Now, we attempt to estimate the value of resistance of the implanted region:

The measured sheet resistance, \( R_s = 10^3 \, \Omega / \square \)

From the figure (app. II), \( R_1 \) and \( R_2 \) can be expressed as:

\[
R_2 = R_s \frac{l}{w} \, \Omega \\
R_1 = \rho_1 d_1 / A \, \Omega
\]

where; \( l/w \) is the measured aspect ratio and 
A is the contact area.

If we assume \( R_1 \approx R_2/10 \)
then 
\[
\rho_1 d_1 / A = R_s \frac{l}{10w} \, \Omega \text{(cm)}
\]
\[= R_s A l / d_1 w \, \Omega \text{(cm)}
\]

The resistance of the implanted region, \( R_1 \), can be written as: (See figure app. II)

\[
R_1 = \frac{\rho l}{d_1 w} = R_s A l^2 / 10 d_1 w^2 \, \Omega
\]

where \( R_s = 10^3 \, \Omega / \square \)
\( l = 3 \times 10^{-1} \, \text{cm} \)
\( A = 10^{-3} \, \text{cm}^{-2} \)
\( d_1 = 5 \times 10^{-5} \, \text{cm} \)
\( w = 10^{-1} \, \text{cm} \)
Hence, $\rho_i = 6 \times 10^3 \ \Omega \cdot \text{cm}$.

Since, $\rho_i = \rho_1$ and $R_{si} = R_i w/l$

where $R_{si}$ is the sheet resistance, then $R_{si}$ can be written as:

$$R_{si} = \frac{R_A l}{10 A_{1/w}} \ \Omega/\square$$

Thus $R_{si} = 10^3 \times 3 \times 10^{-1} \times 10^{-3} / 10 \times 25 \times 10^{-10} \times 10^{-1} \ \Omega/\square$

Hence the sheet resistance, $R_{si}$, of the implanted material is about $10^6 \ \Omega/\square$. 
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