THE ENERGY AND MASS DEPENDENCES OF THE CARRIER REMOVAL CROSS
SECTION IN HIGH ENERGY LIGHT ION IRRADIATED GaAs.

by

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Thesis submitted to the Department of Electronic and Electrical
Engineering, University of Surrey, for the degree of Doctor of
Philosophy. (December 1984)
ABSTRACT

In this study the energy and mass dependences of the carrier removal cross section for high energy (0.25-2.0 MeV) light ion (H⁺, D⁺ and He⁺) irradiation of n-type GaAs are investigated.

The materials used were of two types: (i) semi-insulating bulk GaAs and (ii) Vapour Phase Epitaxially (VPE) grown n-type GaAs on Semi-insulating substrate. The bulk material was implanted with Se⁺, Zn⁺ and Cd⁺ ions at 390-400 keV and annealed (700° and 900°C) to create a thin (0.5 μm) n- and p-type conductive layers, with carrier concentrations of 1 to 7x10^{17} cm⁻³. The carrier concentrations for the Epitaxial materials were between 2.1x10^{15} to 3.2x10^{17} cm⁻³.

The irradiations were carried out using the Van de Graaff accelerators at the University of Surrey and at AERE, Harwell. The ion doses were between 1x10^{10} to 5x10^{13} cm⁻². The materials were irradiated at room temperature and at 8° off the normal to the surface.

The measurement techniques used were "insitu" sheet conductivity and also Hall effect measurements. From the rates of change of the sheet conductivity and carrier concentration with the ion dose, values for the carrier removal rate (CRR) and carrier removal cross section (\(σ_{CR}\)) were calculated. These cross sections were compared to the elastic displacement cross section derived using Kinchin and Pease [116] theoretical model (\(σ_{KP}\)).

It was found that the energy dependence of the cross section agrees with the theoretical prediction, but the mass dependence,
at energies below 500 keV, was found to diverge from the theoretical mass dependence. Molecular ions (H$_2^+$ and H$_3^+$) were found to dissociate upon impact with the surface of the target, with the resulting particles behaving similarly to Protons.

The carrier removal rate was found to depend on the initial carrier concentration of the irradiated material, which is attributed to the movement of the Fermi level through the shallowest defect level reported ($E_1 = E_c - 0.12$ eV). From this dependence, values for defect introduction rates (DIR) for this level and for other deeper levels were estimated. The comparison of the DIR for different ions, showed that Deuterons and Protons followed the isotopic mass dependence, whereas Helium differed.

The surface layers of some samples were doped with Deuterons and it was demonstrated that the presence of the Deuterons has little effect upon the carrier removal cross section during 1.5 MeV Proton irradiation.
ACKNOWLEDGEMENTS

I sincerely like to thank Dr. P.L.F. Hemment for his most invaluable advice and understanding throughout this work. I am also indebted to Professor K.G. Stephens for his continual support through the difficult periods of this project.

It is a pleasure to acknowledge the technical assistance provided by Mr. J.E. Mynard and the most helpful staff of the D.R. Chick accelerator laboratory at the University of Surrey. I also wish to thank Dr. G. Dearnaley and Dr. J.F. Turner for making the facilities at AERE, Harwell generously available. I should also thank Dr. I.R. Sanders of Plessey Research, (Caswell) Ltd. for the supply of the materials.

Finally, I like to thank Dr. M. Tosunoglu without whose help and encouragements this thesis may not have been written.
This work is dedicated to my parents

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CHAPTER ONE

1. THE INTRODUCTION

1.1 General Background

With the development of Nuclear reactors during the 1940's, it became apparent that radiation can cause physical changes to materials; this provided the impetus for studying the field of atomic collisions in solids. From the onset of these studies it was realized that energetic ions can be used also to constructively modify the properties of the surface layers of a solid by the process of ion implantation. In the last two decades, ion implantation has become an established technique for impurity doping of semiconductors in the Microelectronics Industry. It offers accurate control of the dose and high precision in defining both the depth of the dopant and its lateral positioning. This degree of control has made ion implantation more advantageous than the rival high temperature equilibrium doping processes, such as thermal diffusion and thermal alloying [9].

In research, high energy light ion irradiation has been extensively used by material scientists for surface analysis techniques such as Rutherford Backscattering Analysis (R.B.S) [45] and Particle Induced X-ray Emission (P.I.X.E) [107].

An unavoidable feature of ion implantation is the creation of damage, which is caused to the target matrix by the energetic ions. Radiation damage can modify the physical properties of the solid that depend on the regular periodicity of the crystal lattice, such as the electrical and thermal conductivity and also the optical and the
metallurgical properties [88, 8, 58, 195]. This damage is undesirable when doping a semiconductor and must be removed by annealing [92]. Much success has been gained by thermal annealing [92]. But during recent years furnace annealing has been superseded by directed energy techniques, such as laser and electron beam annealing, as well as short time-pulsed thermal and optical annealing [92].

Radiation damage can also be used constructively as in the case of light ion irradiation (See next section), through processes such as light ion isolation techniques [61], radiation enhanced diffusion [141], impurity gettering, enhanced etching, beam assisted etching and ion beam lithography [153].

1.2 Application of light ion irradiation damage

The type of crystalline damage produced by light ions generally consists of well separated point defects, which are formed when an atom has been displaced from the lattice site. At high doses of ions, the density of these point defects becomes so large that defects can conglomerate to form large defect complexes, such as displacement cascades.

It is found that defects give rise to associated localised energy levels in the band gap, and according to their defect structure, charge state and the position of the Fermi level in the band gap, these defects can manifest acceptor or donor like characteristics [137]. In certain materials, for example in GaAs, such defects can act as trapping centers that are able to compensate the charge carriers in the crystal. In high defect density regions, the degree of compensation can be so large that the material may become semi-insulating. This can
be achieved by the use of light ions, in particular Protons, and has been given the name of Proton isolation [61], and is used during device fabrication to isolate various components [125]. Other ion species, such as Helium, Oxygen and Argon ions have also been used for this purpose [125], However, due to their relatively heavier mass and therefore limited range, their use is not common. In the case of Oxygen, in GaAs, the ions can act as chemical dopants and are seldom used to create damage centres for compensation. Recently, the use of Deuterons has been reported and it has been shown that they can yield much improved isolation [182,183].

In order to predict the changes in the electrical conductivity caused by light ion irradiation, there is a need to characterise the more basic processes of damage production (see chapter 3). One of the results of such a study would be an improved ability to control the electrical properties of device wafers, particularly when it is desirable to form a buried semi-insulating layer. Similarly, in using RBS analysis to measure the damage present in a crystal, the analysing beam can itself create damage, which may yield spurious results [122].

1.3 The aims and methods of the project

The aim of this project is to investigate the roles of elastic and inelastic energy loss processes in the creation of damage during the irradiation of GaAs with high energy, light ions. The range of ions and the energies studied were chosen to match the conditions used for Proton isolation and during RBS analysis.

The method employed was to irradiate GaAs single crystals with high energy (<2 MeV) light ions (H⁺, D⁺ and He⁺) and to monitor the
change in the sheet conductivity with increasing ion dose. From this change it is possible to calculate a rate of removal of charge carriers (CRR) and, by making certain assumptions also, to determine the defect introduction rate (DIR). In turn, the DIR can be used to calculate a cross section for atomic displacement. The particular assumptions which must be made are:

1. That each defect level only captures one electron.
2. No defect annealing occurs.
3. Defect Introduction Rate is independent of depth.

The experimental values of the derived cross section and the dependence upon ion energy and mass have been compared to theoretical values, for the atomic displacement cross section, calculated using the the Kinchin and Pease elastic displacement theoretical model [116]. By this means it has been possible to determine the process dominant in creating defects in this irradiation regime.

It will be shown that the CRR for Proton and Helium irradiations correlates well with the mass and energy dependence as predicted by Kinchin and Pease model, with Deuterons showing general agreement with the theory, although at low ion energies enhanced CRR have been measured.
CHAPTER TWO

2 RADIATION DAMAGE STUDIES

The consequence of atomic displacement caused by nuclear irradiation was first realized by Wigner in 1943 [221], when he associated the atomic displacements with the phenomena of "stored energy", which increased the total energy of the host lattice. Subsequent to this observation research programmes, devoted to the study of damage and damage mechanisms in reactor materials, were developed.

In the early experiments, Electrons and Neutrons proved to be of importance in the studies of defects and their properties. Although the first reported use of Electrons for the production of defects was in 1911, but they were not employed in the study of radiation damage until 1950's, when the effects of irradiation on solid state detectors were investigated [172]. At the same time, Neutrons were used to investigate the effects of radiation damage on reactor materials. In general the early radiation damage studies served two purpose; to establish the life expectancy of materials exposed to reactor radiation and as a diagnostic technique to study the defect production mechanism.

During the past 30 years the effects of radiation damage on the elemental semiconductors, Si and Ge, have, also, been studied and are well documented [53], but for compound semiconductors the studies have been on a more modest scale. Recently, however, irradiation effect in GaAs has been investigated more fully, and now with the use of Proton isolation techniques [61], the semiconductor device engineer has become more interested in the effects of light ion irradiation on GaAs
One of the most sensitive techniques used for the measurement of radiation damage is the electrical conductivity measurements [102]. Since this is the technique used in this study, the main emphasis of this literature survey will be on the effect of irradiation on the electrical properties, such as the electrical conductivity and consequently carrier removal rate, CRR, and defect introduction rate, DIR.

In this chapter, the first section surveys the earlier work relating to Electron and Neutron irradiation effects in Si and Ge. The second section reviews the most recent published work on light ion radiation damage in GaAs and other III-V compound semiconductors.

2.1 Early radiation damage studies

Irradiation of elemental semiconductors with highly energetic Electrons and Neutrons has been an extremely valuable tool for the study of defects in solids [109,118]. These particles, if sufficiently energetic, can cause atomic displacements, creating a defect pair, consisting of a vacancy and an interstitial, that is known as Frenkel pairs [209]. These primary defects may then move independently and may combine with impurity atoms or other vacancies or interstitials to be annihilated or to form Vacancy-Impurity pairs or aggregates such as multi-vacancies and strings of interstitials [165,173].
2.1.1 Defect types

The earliest experimental recognition of defects involved Electron and Neutron irradiations of diamond type crystal, such as Si and Ge [109]. The first defect identified and studied in depth was the vacancy. Watkins [209], primarily using the Electron paramagnetic resonance technique (EPR) [212], studied the vacancy and its properties. Much work has been done since, and several multi-vacancies (up to penta-vacancies [165]) have been identified. There have also been observations of other defects such as interstitials, vacancy-impurity complexes as well as extended defects such as rod-like defects [173], whose atomic configuration may consist of strings of vacancies. In the following subsections the main defect types are discussed:

(i) Isolated vacancy:

Many different forms of isolated vacancies have been reported in the elemental semiconductors. The most frequently encountered ones in the literature are two unstable but dominant forms, which are associated with two charge states of the isolated lattice vacancy, $V^-$ and $V^+$. Evidence exists for the additional states $V^{--}$ and $V^0$ [209].

In the case of the simple vacancy, Watkins [209] determined an introduction rate of $\sim 0.1 \text{ cm}^{-1}$ in pulled n-type silicon during a room temperature irradiation with 1.5 MeV electrons. The production rate of vacancies is found [34,216] to be dependent on irradiation temperature and the position of the Fermi level. Similarly Mackay et al [138] found that during a low temperature irradiation, the production rate of vacancies in n-type material is $\sim 100$ times larger than in p-type
material. They concluded that vacancy production processes have energy barriers, so that the probabilities of vacancies recombining and being liberated are dependent on both the Fermi level and the temperature. At low temperatures, the vacancy production rates are thought to be strongly dependent upon ionization which occurs during the Electron irradiations [184]. For temperatures above 300°C it has been suggested [87] that the kinetic energy of the lattice atom may in itself assist the displacement of the vacancy.

(ii) Divacancy (V + V):

This defect is produced either directly, as a result of multiple displacements, or indirectly by the agglomeration of two vacancies. Their creation depends on the energy of the ion, where higher energies tend to produce multiple displacement defects. Corbett and Watkins [50] investigated the dependence of divacancy production on the ion energy and found that the rate of production increased by a factor of seven in the energy range of 0.7-1.4 MeV. Bemski et al [11] studied the energy dependence for energies above 1.5 MeV and reported much slower rates for the production of divacancies.

Corbett and Watkins further investigated the production of divacancies by including the dependence on crystal orientation. Using EPR technique they found that more divacancies are produced along the beam direction than along the off-axis direction and also noted that the production rate along <100> axis to be, in general, higher than <111> or <110> axis.

Watkins et al [212] reported a rate of production of divacancies of about 0.008 cm⁻¹, which is found to be an order of magnitude less
than that for the single vacancy.

(iii) Vacancy-Impurity complexes:

These defects were first identified by showing the effect of impurities presence, in Si, on the defect annealing behaviour [33,214,10]. Two defect types were identified; these being the vacancy-oxygen complex, (V+0), known as the A-centre and the vacancy-phosphorus complex, (V+P) known as the E-centre.

The A-centre [213] has been shown to be created as a result of an oxygen atom attaching to two of the four atoms neighbouring the vacancy, with the other two atoms forming a molecular bond. In n-type pulled Si crystals, with a high oxygen concentration [211], the A-centre's EPR spectrum is dominant and is identified with the negative charge state of substitutional oxygen. As oxygen is normally interstitial, the defect can be viewed as a vacancy trapped by an interstitial oxygen [211].

The E-centre [213] has been shown to be a phosphorus atom sitting on a substitutional lattice site neighbouring a vacancy, with two of the surrounding atoms forming a molecular bond.

Bemski et al [11] have shown that the overall production rate of the A-centre is an order of magnitude larger than the divacancy production rate. Watkins et al [214] found the rate of production of these complexes to be dependent on the charge state of the vacancies.

(iv) Interstitials:

When a vacancy is formed as a result of an atomic displacement, then an interstitial is also formed. Relatively little is known about
this defect except that it appears to be very mobile, more so in p-type Si than n-type. During a 4 K irradiation of Al doped p-type Silicon, Watkins et al [53] found an EPR spectrum arising from the interstitial Al\(^{++}\) which had the same production rate as the isolated vacancy. From this and other evidence he concluded that in p-type material the silicon interstitial is highly mobile even at low temperatures and moves through the lattice until trapped by a substitutional Aluminium atom, which is then ejected into an interstitial site. Such low temperature mobility led to the conclusion that the movement of the interstitial must be athermal and may be caused by the alternate capture of an electron and a hole, which changes the charge state of the interstitial and hence assists its movement. This is known as the Bourgoin mechanism [212] and has been detected in Aluminium [208], Boron and Gallium [207] doped Silicon.

The interstitial in the tetrahedral or bond-centered site does not exhibit defect levels within the band gap [179]. This may be the explanation for the lack of direct experimental detection of the interstitial related levels. Another reason for the detection difficulty may be the migration of interstitial at low temperatures by an athermal process stimulated by irradiation or illumination [213]. Isochoronal annealing experiments do not increase the chance of detection either since the interstitial activation energy coincides with the activation energy of divacancy and certain impurity interstitials as well as the A-centre's activation energy [78].
2.1.2 Defect introduction studies

The Defect Introduction Rate, DIR, has been found to depend on the energy, mass, dose, flux of the incident particles and on the irradiation temperature. It also depends on the crystal orientation, the crystal growth method and the impurity level as well as the position of the Fermi level in the band gap, (see the following sub-sections for references). The experimental determination of these dependencies are summarized in this section.

Displacement energy:

The most important parameter which is used in the description of the displacement process is the displacement energy, $E_d$, which is the minimum energy necessary to displace an atom. Therefore the earlier studies were concentrated on the determination of the values of $E_d$ in various crystalline solids. Seitz (1949) [172] and Kohn (1954) [120] made the predictions about the value of $E_d$ and Klontz and Lark-Horowitz [118] experimentally calculated the displacement energy for Si and Ge. Since their work many other workers have determined values for $E_d$ in the elemental and compound semiconductors, an inventory of which appears in the review by Crawford and Slifkin [53], see table 6 in chapter 3.

Orientation dependence:

From the theoretical consideration of the displacement energy it was assumed that the damage production should be anisotropic. However Brown and Augustyniak [34], in the first study of its kind, found that the onset of damage to be similar in the three principle
crystallographic directions. Haddad and Banbury [93], in contrast, found the damage rate to be dependent on the crystal orientation. Their results were confirmed by Hemment and Stevens [104], who suggested a "preferred windows" model for the anisotropy of damage production. Other workers [51,83], using EPR technique, found anisotropy in the production of particular defects and confirmed the above work. Kryukova et al [123] and George et al [82] disputed these finds and attempted to explain the anisotropy dependence shown by Haddad et al, by the level of ionization present in the crystal.

For GaAs, Eisen [64] showed that more As atom related defects are created than Ga atom related defects for an irradiation in the <111> direction. More recently Pons [167], confirmed this result, and using a GaAs model explained that in the Ga sublattice the Ga atoms obstruct the path of recoil atom and thus slow them down more rapidly.

Temperature dependence:

Brown and Augustyniak [34] were the first to study the temperature and the energy dependence of the damage production rate. Whan [217] and Whan and Vook [218], using infra-red spectroscopy in Si and Ge, found an exponential temperature dependence on the damage production rate, see figure 1. Novak [158] and Vook and Stein [188] extended these studies, using electrical measurements, to include the Fermi level dependence as well.

These authors distinguished two types of defects, the Irradiation Temperature Dependent (ITD) and the Irradiation Temperature Independent (ITI) defects. They showed that ITI defects fit the divacancy production rate, where as ITD defects fit the energy dependence
Figure 1. Temperature dependence of the production rates of defects in Si and Ge from infrared studies of Whan [218].
observed by Haddad and Banbury [93], and interpreted these results in terms of a charge state-dependent metastable pair model.

Impurity dependence:

The variation of the defect introduction rate upon the impurities was first investigated by Watkins [210]. Using EPR technique, he found that in Si, group III impurities (B, Al, Ga, In etc.) play an important role in the production of the defects. Stein and Vook [187] using electrical measurements and Whan and Vook [218] using optical techniques confirmed the above work. The enhancement of damage production in n-type Si partially compensated with Boron (group III) serves as a strong additional confirmation of the essential role that is played by the group III impurities in the trapping of the interstitials. The damage rate in p-type material (with the same doping of Boron) is lower than in n-type material indicating that the Fermi level position and the resulting charge state of the defects are also important in the process of damage production.

The effect of oxygen and phosphorus presence on the defect level has already been discussed in section 2.1.1. and further confirms the above, that the trapping of vacancies increases the level of damage since no vacancy-interstitial recombination can occur.

Vavilov [202], from the change in the reciprocal Hall mobility measurements, found that in p-type Si (that is doped with Al and B atoms) the mobility change depends on both acceptor impurity type and its concentration. It was shown that the effective scattering centre introduction rate, $\Delta(\frac{1}{\mu})$, is considerably higher in Al than in B doped material. These may imply that some multi-charge centres are
introduced in the Al doped material. Vavilov proposed that this effect is due to the impurity atom size and its ability to form vacancy-acceptor complexes [200]. Similarly, this impurity size effect was observed for the E-centres in n-type Si [201]. The donor impurity is seen both in Si [35] and Ge [33] to cause single acceptor type defects, which reduces the overall charge carrier concentration, after annealing. But does not affect the mobility since the resulting neutral centres are ineffective for charge carrier scattering.

For group V impurities, Klontz [119] showed that defect trapping also occurs. Lehar and Whitehouse [129] showed that in doubly doped Ge both with group III and V impurities, the carrier removal rate is much lower than in singly doped material (group V), implying that group III impurities actively assist the mutual annihilation of the damage products. In general, Massarani et al. [140] bombarded Boron doped synthetic diamond with electrons and by monitoring the conductivity changes decided that an exponential change occurs in the conductivity with compensation centre concentration.

Wada et al. [205], using Electron Spin Resonance, found the production rate for various defects to be dependent on the donor density in Si, as shown in figure 2 and table 1, and for the production rate dependence on the electron energy they showed the results as in figure 3.
Figure 2. The production rates of each complex defect as a function of impurity concentration in Si as reported by Vook et al. [205].

Figure 3. Production rates of each complex defects as a function of electron energy in Si as reported by Vook et al. [205].
Material growth methods:

Stein [187] showed that for crucible grown material, which has high level of oxygen, A-centre and other oxygen related defects predominate. Watkins [210], on the other hand found that the production rate of vacancies, at 20 K irradiation of Si, was similar for floating zone grown material and the vacuum pulled material and only varied for different doping levels.

Flux dependence:

Gerasimenko [83] for Si and Moore et al [148] for GaAs showed that the overall damage introduction rate is dependent upon the ion flux. Gerasimko showed that the damage rate increases with increasing beam flux over the flux range of 0.2 $\mu$A/cm$^2$ to 50 $\mu$A/cm$^2$. This was attributed to the local heating or ionization of the crystal, that can cause the migration of the defects and, therefore, reduce the probability of their annihilation.

More generally, Kol'chenko and Lomako [121] using 28 MeV electrons, found the DIR and CRR to be independent of the carrier concentration, the chemical nature of the donor species but to be weakly dependent on the conductivity type. Kalma et al [112] showed that CRR has only very weak dependence upon the irradiation temperature. Moore et al [148] and Lang et al [126] investigated the effect of ion beam flux and local heating and found that the CRR increases with the beam flux and the subsequent beam heating.

Finally Vook [204] and many other workers [126] have demonstrated that defects have a greater stability in compound semiconductors than
### COMPLEX DEFECTS

<table>
<thead>
<tr>
<th>LEVELS (eV)</th>
<th>TYPE</th>
<th>DESIGNATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c - 0.17$</td>
<td>(V+O)</td>
<td>&quot;A&quot;</td>
</tr>
<tr>
<td>$E_c - 0.30$</td>
<td>(V+V+P)</td>
<td></td>
</tr>
<tr>
<td>$E_c - 0.47$</td>
<td>(V+P)</td>
<td>&quot;E&quot;</td>
</tr>
<tr>
<td>$E_c - 0.39$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_c - 0.54$</td>
<td>(V+V)</td>
<td></td>
</tr>
<tr>
<td>$E_v + 0.55$</td>
<td>($V^2 + 0$) or (V)$^3$</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. The complex defects as shown on figure 2, and their identification and associated energy levels in Si [205].

### DEFECTS ENERGY LEVELS DIR (cm$^{-1}$)

<table>
<thead>
<tr>
<th>DEFECTS</th>
<th>ENERGY LEVELS</th>
<th>DIR (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>$E_c - 0.08$</td>
<td>1.8</td>
</tr>
<tr>
<td>E2</td>
<td>$E_c - 0.18$</td>
<td>2.8</td>
</tr>
<tr>
<td>E3</td>
<td>$E_c - 0.41$</td>
<td>0.7</td>
</tr>
<tr>
<td>E4</td>
<td>$E_c - 0.71$</td>
<td>0.08</td>
</tr>
<tr>
<td>E5</td>
<td>$E_c - 0.90$</td>
<td>0.1</td>
</tr>
<tr>
<td>H1</td>
<td>$E_v + 0.29$</td>
<td>0.7</td>
</tr>
<tr>
<td>H2</td>
<td>$E_v + 0.41$</td>
<td>intrinsic</td>
</tr>
<tr>
<td>H3</td>
<td>$E_v + 0.71$</td>
<td>intrinsic</td>
</tr>
</tbody>
</table>

Table 2. The defects levels and their DIRs for GaAs irradiated with 1.0 MeV Electrons, as reported by Lang and Kimberling [128].
elemental semiconductors. This could be due to the easier migration of a vacancy in elemental than in compound semiconductors.

2.1.3 Defect-level identification studies

In this section the work carried out on defect identification, mainly on GaAs, is reviewed. Each defect can be identified by the defect level it creates in the band gap of the semiconductor.

In the early 1960's Aukerman and Graft [2] were the first group to study the electrical effects of electron irradiation of crystalline GaAs. From Hall effect measurements, they showed the existence of a level in between $E_c-0.12$ and $E_c-0.15$ eV [3]. Kalma and Berger [111], subsequently, showed that this level was responsible for most of the carrier removal at room temperature, and they estimated a CRR of $1.6 \text{ cm}^{-1}$ to $2.2 \text{ cm}^{-1}$ for 1 MeV electrons. Pegler [166] showed that the position of the Fermi level was most important and affected the rate of removal of the carriers. By varying the carrier concentration of the material, hence the position of the Fermi level, he showed that for $E_F$ below the level, the CRR was about $0.5-1.0 \text{ cm}^{-1}$ and for $E_F$ above the level, the CRR to be about $6.0 \text{ cm}^{-1}$. This defect corresponds with a level identified, by Lang [127], in DLTS spectra (designated E1) that give a CRR of $0.6 \text{ cm}^{-1}$.

In table 2, the most important levels identified in electron irradiated GaAs and the defects associated with them are presented [128]. It should be noted that the energy of the levels indicated are not certain and vary between each experiment, depending on the measurement techniques employed.
2.2 Radiation damage studies in GaAs

In this section the effects of Proton, Deuteron and Helium irradiation on GaAs are discussed. The first section is dedicated to irradiation effects in GaAs, when the elastic energy loss process is the main contributor to damage production. Proton isolation and the various defects and their associated energy levels in the band gap, the defect distributions and variation in the defect introduction rates with irradiation energy, dose, temperature and the presence of the impurities in the irradiated material are discussed.

In the second section the effects of light ion irradiation in GaAs under conditions when the inelastic energy loss processes are the main contributor to the damage production are discussed. The models advanced and the various explanations for the ionization induced defects are reported and values for DIR and CRR are given. In the third section the recently proposed Deuteron isolation technique are discussed.

2.2.1 Elastic radiation damage studies

The change in the electrical conductivity of GaAs irradiated with Protons was first investigated by Wohllenben and Beck [225]. Using 1 MeV Protons, they showed that the carrier concentration and the mobility of the charge carriers were both reduced and that the CRR is independent of the original carrier concentration. They concluded that a quasi-continous distribution of deep trapping levels is produced in the band gap. They found that the CRR due to the damage produced by Proton irradiation to be more than the Electrons [91] and less than
Neutrons [221] induced damage, but having a magnitude closer to the level of damage that is caused by Electrons. Thus concluding that the defects must be similar and that they must be isolated point defects. Following irradiations of both n- and p-type material, they decided that both donor and acceptor types of defects could be formed.

Pruniaux et al [168], used a Capacitance-Voltage technique to determine the free carrier depth profile in GaAs samples irradiated with 150 keV Protons, for up to a dose of $1.2 \times 10^{11} \ \text{cm}^{-2}$, see figure 4. They found that the CRR at a depth of 0.3 $\mu$m (the limiting depth in their experiment) was $\sim 1.2 \times 10^4 \ \text{cm}^{-1}$ and at a depth of 1.1 $\mu$m (corresponding to the Proton projected range, marked with an arrow on the figure) to be $\sim 6 \times 10^4 \ \text{cm}^{-1}$. The CRR for this experiment is defined as the removal rate at the "carrier concentration with depth" minimum (note the maximum of the profile in figure 4). Also they reported that the CRR at the profile minimum was observed to decrease rapidly after the sample was more than 60% compensated, and that the ratio of the CRR at the profile minimum (1.1 $\mu$m) to that near the surface (0.3 $\mu$m) increases with the ion energy and is $\sim 10$ for the irradiation energy of 300 keV. They derived an integral CRR, in variance to the above CRR, over the whole of the profile to be about $\sim 4 \times 10^4 \ \text{cm}^{-1}$, and they suggested that CRR occurred because of two trapping levels at 0.4 and 0.8 eV above the valence band.

Murphy et al [152] showed that electron traps are introduced in n-type GaAs ($\sigma = 10^8 \ \text{Ohm-cm}$), for doses of up to $10^{15}$ Proton/cm$^2$. These workers also showed that during subsequent irradiation, up to a dose of $10^{16}$ Proton/cm$^2$, the resistivity did not increase. For even Higher doses these workers report a more rapid decrease in the resistivity and
Figure 4. The variation of the carrier concentration in n-type GaAs due to 150 keV Proton irradiation, with incremental dose of $1 \times 10^{10}$ Protons/cm$^2$ [168].

Figure 5. Resistivity as a function of dose for 300 keV Protons irradiated GaP. The resistivity at dose of $3 \times 10^{11}$ cm$^{-2}$ has an upper value of $2 \times 10^2$ Ohm-cm. [180]
attribute this decrease to the on-set of hopping conduction. Spitzer [180] reported a similar behaviour in GaP, as shown in figure 5. Harada et al [95] used Proton and Helium irradiations in the energy range of 60-400 keV to show that the CRR at the profile minimum to vary with the ion dose and energy, as shown in figures 6 and 7. Gecim et al [79] carried out similar experiments and studied the effects of annealing and reported the values of the CRR as shown in table 3.

Sakurai et al [170] performed similar irradiations and observed that photoluminescence from the band edge decreased rapidly with the ion dose. As they observed no photoluminance peak, they suggested that the Proton irradiation creates deep non-radiative levels.

Okunev et al [161] found similar decreases as Sakuri et al and showed that a decrease in n-type (Te-doped) GaAs was greater than in p-type (Zn-doped) material for the same dose of Protons and attributed this effect to the formation of Ga$_2$V$_{Ga}$Te$_3$ complexes.

Favennac et al [70] irradiated Ga$_{1-x}$Al$_x$As with 200-1200 keV Proton and found that the resistivity increased with the ion dose up to dose of $6 \times 10^{12}$ cm$^{-2}$, above which saturation occurred. They suggested energy levels of $E_v + 0.35$ eV and $E_v + 1.0$ eV.

Mitchell et al [147] investigated the damage caused by Proton and Deuteron irradiations, and included the use of diatomic beams of twice the energy. They concluded that the damage production rates for the mono- and di-atomic species of H$^+$ and D$^+$, with the same particle energy are identical. Sweetman et al [193] using lower energies, arrived at the same conclusion. Gecim et al [79] used a high frequency Capacitence-Voltage profiling technique to determine the CRR for equivalent doses of H$^+$, H$_2^+$ and H$_3^+$. They found no dependence on the
Figure 6. Carrier concentration as a function of dose for 60 and 150 keV Proton irradiated GaAs. [95]

Figure 7. Carrier concentration depth profiles in GaAs samples irradiated at a dose of $2 \times 10^{11}$ cm$^{-2}$ of Protons, over the energy range of 200-300 keV [95].
<table>
<thead>
<tr>
<th>IRRADIATION ENERGY (keV)</th>
<th>ANNEALED CRR (electrons/Protons)</th>
<th>UN-ANNEALED CRR (electrons/Protons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>$1.4 \times 10^4$</td>
<td>$6 \times 10^4$</td>
</tr>
<tr>
<td>400</td>
<td>$1.4 \times 10^4$</td>
<td>$6 \times 10^4$</td>
</tr>
<tr>
<td>500</td>
<td>$1.2 \times 10^4$</td>
<td>$6 \times 10^4$</td>
</tr>
</tbody>
</table>

Table 3. CRR for Proton irradiated GaAs as reported by Gecim [79].
energy, over the range 300-500 keV, and confirmed that on average the H$_2^+$ and H$_3^+$ ions, on impact with the surface, dissociate into equi-energy Protons. Similarly Golovchenko et al [89] studying the effect of Protons on carbon foils and Caywood et al [42] studying Silicon, both confirmed these results.

Donnelly et al [61] have investigated the effect of single and multiple energy Proton irradiations of highly doped GaAs. They found that multi-energy irradiations fully compensate GaAs crystals which had an initial carrier concentration as high as $5 \times 10^{18}$ cm$^{-3}$. An optimum dose was shown to exist for the attainment of the maximum resistivity in crystals with a given doping level. If this dose is exceeded it is then necessary to anneal (at 500°C) in order to recover the peak resistivity.

Speight et al [178] have shown that a dose of $4 \times 10^4$ Proton/cm$^2$/energy step is necessary to obtain the maximum resistivity, in material with initial carrier concentration of $10^{18}$ cm$^{-3}$. These workers showed that the compensated material was stable for temperatures of up to 400°C and that after an anneal at 500°C the resistivity was still greater than $10^8$ Ohm-cm, the maximum attained by irradiation. At higher temperatures, the resistivity fell to $10^3$ Ohm-cm.

Proton isolation is used in the fabrication of optical devices. Dyment et al [62] found that the optical absorption increases linearly for a dose of up to $10^{17}$ Proton/cm$^2$ in p-type bulk material and found that the optically active defects could be annealed at 450-500°C. They concluded that optical recovery was more rapid than the decrease in the electrical resistivity during the annealing, thus indicating lower
activation energies for the defects responsible for the optical absorption centres. This effect has been used by Favennec et al [71] to fabricate optical wave guides.

The defect level most commonly reported in Proton irradiated material is $E_3$ [225] which is identified as the isolated Ga vacancy [145]. From DLTS [127] studies of Proton irradiated GaAs the levels shown in figure 8 have been found. Levels $E_4$ and $E_5$ have no definite assignment and it has been suggested [121] that these are related to impurities or clusters of defects (see table 5). Martin et al [139] recently gave a review of Proton induced defects in GaAs and found that for low doses, energy levels at $E_{cv} - 0.55$ and $E_{cv} + 0.70$ eV exist and they also observed the levels $E_2$ and $E_3$.

### 2.2.2 Inelastic radiation Damage studies

Many groups [144,163,63,36] have demonstrated that high velocity light ions create lattice disorder in the early part of their track, where inelastic energy loss processes dominate (refer to section 3.2). Amongst the first experimentors were Mayer et al [144], who, by using ion backscattering, reported the presence of excess damage, even at temperatures at which recombination of Frenkel pairs can occur. Pabst and Palmer [163] using the ion channelling technique to study defect production, found 8 times as many displacements as could be attributed to elastic collisions. They found this discrepancy to be lower for Helium than Proton irradiation.

Eer Nisse [63] has observed an energy-dependent ionization induced contribution to the compaction of fused silica. He found that for light mass and higher energy ions this effect was larger, and
Figure 8: DLTS spectra for n-type GaAs irradiated with 1 MeV electrons, at 300 K. [127]
concluded that inelastic processes (ionization) causes this effect.

Bulgakov et al [36] found unusually broad damage distributions in Proton irradiated Si and attributed this to inelastic processes as well. Kimmerling et al [145] reported certain anamolies regarding the depth distribution of defects produced along the tracks of the incident Protons. In order to test the above idea, Dearnaley [59] irradiated GaP and from the depth distribution of the observed optical absorption sites, concluded that electronic energy loss processes are very important in this partially ionic crystal.

Haskell et al [146] have found that during the 1.8 MeV He irradiation of As doped Si, the As atoms can move from substitutional sites to non-substitutional positions. The removal rate of the As atoms was found to be independent of the As concentration, indicating that the displacement of As atoms occurs through the interaction of the analysing beam with the lattice atom.

Light ion channeling has been used by Pabst et al [163] to derive a cross section for the displacement of Si atoms by 300 keV Proton and 275 keV Helium ions. These cross sections exceeded the Kinchin and Pease [116] cross section, see section 3.2.3. They concluded that inelastic processes are active in the production of Frenkel pairs. Using a similar experimental technique, Kool et al [122] found the damage produced during light ion irradiation to be 30 times greater in As-doped Si than in the undoped material, see figure 9. Furthermore, Palmer [164] suggested that a combined elastic collision and outer shell electron ionization is a possible explanation for these results.

In contrast Hemment et al [103] irradiated Si and found the cross section for the removal of free carriers to be comparable to the value
determined using the Kinchin and Pease (K-P) elastic scattering model. Also when they considered the ratio of the cross sections for He and H, they found agreement with the prediction due to K-P model. They concluded that the elastic collision is the rate controlling mechanism for damage creation near the surface when Si crystals are irradiated with high energy (>1.5 MeV), light ions (H, He). This was confirmed by Wiggers et al [220] for lower energy Proton irradiations in Si.

For Ge [5, 25], GaAs [197] and GaP [59] it has been reported that the defect production caused by 300 keV Protons is again significantly in excess of that predicted by the Kinchin and Pease elastic scattering model.

The proposed ionization induced displacement models

An energetic ion travelling through a semiconductor can cause the excitation of electrons in both the outer shell (valence band) and the inner shell of the atoms. Many models have been proposed to explain the contribution to the displacement process of the ionization and excitation of the atoms. Varley [199] suggested one of the first models, in which he considered the effect of ionization on the interatomic potential and suggested that the atomic bonding can be considerably weakened, or may even be broken in the locality of the ionization. He argued that an elastic scattering event, then, needs less energy transfer to displace the atom.

Fleischer et al [77], proposed the 'ionization spike' model. They suggested that local ionization, along the ion track, can produce a continuous line of positively charged atoms, which repel one another by coulombic forces, which can be great enough to cause an atomic
Figure 9. The initial migration rate of As atoms versus the primary energy of the projectiles. The upper points are found after random impact of Helium and lower ones after random impact of Proton ions. This figure is taken from reference 164. The solid curves show the values of the cross sections as calculated from the Kinchin and Pease elastic displacement model [116].
displacement.

Zaikovskaya et al [226], studied the effect of inner shell excitation and suggested that resistance changes that they were monitoring with ion dose was very similar to the ionization of the Silicon K-shell and therefore proposed that the displacement may be due to the inner shell electron excitations, see figure 10. However Norris [156] carried out a similar experiment and found no significant change in the resistance. He concluded that the earlier experimental results were due to a change in the contact region as a result of the irradiation.

Pabst [162] used Proton and Helium irradiations and found that a combined L- and M-shell ionization may give rise to multiply charged atoms [31], which will experience an intense coulomb repulsion and a possible atomic displacement. This multiple-ionization damage has been challenged by Kimmerling and Poate [115] on the grounds that the multiply charged atoms will have short life times and, thus, atomic displacement will not occur.

Dearnaley [55] suggested a model, involving vacancy production due to the elastic collision, near the centre of the cylindrical region of ionization that surrounds the ion track, with several or all of its neighbours being ionized. Since this state of ionization involves the rupture of the bonds binding atoms and because of a strong elastic strain field surrounding the vacancy, there will be a finite possibility of displacement. This model is different from the one suggested by Fleischer, who derives the necessary force from the coulomb repulsion only, whereas Dearnaley's model includes the strain field surrounding the vacancy.
Figure 10. The variation with electron energy $E_1$ of the observed relative resistance increase in p-type epitaxial Si, as a result of electron irradiation at 120 K (circles), compared with the Si K-shell ionization cross section (full curve) [164].
Moshavets [151] has proposed an impurity-ionization mechanism first suggested by Karpov [113], for defect production. He suggests a further mechanism, in addition to the simple ionization, that can create damage. The process is referred to as Defect reaction [114,181] and includes the impurity ionization mechanism. He proposes that the ionization of the host atom, with the donor impurities substitutionally placed, gives rise to a pair of positive ions. Hence, through Auger processes, the host atom can become multiply charged and the intense coulomb repulsion field can displace either the host atom or the impurity atom. He concludes that this mechanism is different to Varley's model, as in this model the presence of impurities are necessary.

Vavilov et al [203] discuss the concept of potential displacement, introduced by Kiv [117], and indicate that localised electronic excitation can deform the local atomic potential configuration, that can lead to athermal displacement of the atoms. They include a discussion on impact-ionization processes [108] and give experimental evidence for this process [150].

Vavilov et al [174] suggest a defect creation process in compound semi-conductors similar to the model due to Mashovet et al [151]. They concluded that for every inner-shell ionization a Frenkel pair will be produced.
2.3 Deuteron radiation damage studies

Recently, better electrical isolation has been achieved by Steeples et al [183] using Deuterons rather than Proton irradiations. They reported that the bulk resistivity of Deuteron irradiated GaAs can have a value which is up to 20 times higher than in Proton irradiated material. They also found that the same resistivity could be achieved for Deuterons doses which were two orders of magnitude lower than for Portons. These workers used multi energy irradiations, as suggested by Donnelly [61] and reported a dose dependence as shown in figure 11. They also showed that the isolated regions of the compensated material had much better thermal stability under iso-choronal annealing.

They associated this enhanced effect to chemical bonding of Deuterons to Ga Atoms, which are non-substitutional and in the vicinity of an Arsenic vacancy. They also noted that relatively no strain is introduced as a result of the irradiation, since the lattice strain can in itself be effective in producing carrier removal centres.

In searching for the underlying reason for this difference, they further suggested that the initial knock-on damage is similar for Protons, Deuterons and Tritons, and presumed that the trend should be monotonic with mass. The occupied sites by any of the isotopes were said to be no different and an interaction between the implanted hydrogenous atoms and the Arsenic vacancies was established. They recognized that there will be differences in energy levels and the carrier removal cross section with each isotope [54,60].

The model advanced to describe the effect of Deuteron irradiation was based on non-radiative recombination of the electrons and holes
Figure 11. As implanted resistivity of n-type GaAs as a function of dose following Proton, Deuteron and Triton irradiation. [183]
during the irradiation process. These workers discussed two different recombination mechanisms to account for the isotopic effect, which they considered to arise from the establishment of different final populations of the structural (intrinsic) defects, with the consequent of the enhanced compensation for Deuterons. One of the two mechanisms is recombination-assisted diffusion [190], whereby the energy released may have great effects on the local diffusion or dissociation of the crystal defects. The second mechanism involves the competition between recombination at (i) lattice defects and (ii) at centres decorated with Hydrogens, where it is suggested that the Hydrogenous centers are more effective in recombination than other lattice defect centers.

They also considered the origin of the very different behaviour of the implanted Protons and Deuterons, indicating that the major part of the thermal energy liberated in recombination, that is the band gap energy, must be dissipated in the form of an integral number of Phonons. They proposed that the residual energy, will be the rate determining factor for the recombination by multi-Phonon emission. That is when the residual energy is large the recombination rate will be slower and the recombination-enhanced processes at the other centres will be correspondingly more important.

They also recognised other possible models including (i) effects on nucleation of the complex defects modifying the energy transfer between different species, or (ii) on the recombination-enhanced motion of defects involving Hydrogen.

An alternative model suggested by Dearnaley [56] involves the production of neutrons during the Deuteron irradiation, these being created by nuclear reaction.
Steeples, Saunders and Smith [183] review the above work and indicate a carrier removal rate of 20 electrons/Deuteron at $10^{13}$ cm$^{-2}$/energy step and explain the decrease in the resistivity with hopping conduction, at doses in excess of $10^{14}$ cm$^{-2}$/energy step.

They find, by extrapolation, that the compensated material should reach a maximum resistivity after $10^4$ hours at 130°C. Also it is found that at 250°C the compensation centres stabilise, thus promoting carrier removal. Investigating the effects of Si, Ge, Sn, S, Te and Se dopants on the compensation process, they find Te and Se doped material gives poor results and explained this to be a consequence of their low diffusion coefficients, which reduces the formation rate of defect complexes. They consider the isolation of two batches of IMPATT diodes, one isolated using Protons and the other with Deuterons at 15 times the Proton dose, and find no difference in the performance and the reliability of the diodes.

Harrison and Martin [97] independently carried out similar experiments and showed that Deuterons offer many advantages over Hydrogen irradiation. They carried out "cold" (30 K) implants and found more complete compensation than in similar material irradiated at room temperature. They showed that the depth of carrier removal is dose and dose rate dependent. They suggest that "cold implants" can replace the long established room temperature isolation technique, since "cold implants" give similar isolation layers as the multi-energy irradiation at double the energy.

Newman et al [154] carried out infra-red absorption measurements on Proton and Deuteron irradiated GaAs, GaP and InP. They proposed a model involving irradiation induced ionization that can lead to
enhanced diffusion of the defects, causing the consequent rearrangement of certain damage centres. The extent to which this process is operative depends on the particular isotope of Hydrogen that is implanted, this is because of the difference in the localized vibrational mode frequencies of the Hydrogen atoms bonded to the host atoms. They report defect level E3 and realize that other levels must also be present.

Blood [20] carried out DLTS and C-V measurements on low dose (10^{10}-10^{11} \text{ cm}^{-2}), 300 \text{ keV Deuteron and Proton irradiated n-type GaAs}, see figure 12. He found that both isotopes produce the same electron traps as Electrons and calculated an integrated carrier removal rate, \text{CRR(D)r2.4 CRR(H)}, that is closer to the ratio of the isotopic masses and significantly different from the Steeples results [183]. He also recognised E3 and E4 levels and at low doses found no fundamental differences between the primary defect production processes for the two isotopes. But he found the concentration of levels E3 and E4 to be twenty times the concentration of levels E1 and E2, and decided that levels E3 and E4 are probably responsible for the carrier removal.

In the near surface region (0.8-1.0 \text{ \mu m}), the concentrations of the levels were found to be similar, and he concluded that levels E1 and E2 must contribute to the integrated CRR. This is in good agreement with Kalma et al [111] results, who used electron irradiation and identified the E2 level to be the dominant defect in the near surface layer.

Blood also showed that peak carrier removal occurs at a depth of 2.5 \text{ \mu m} for 300 \text{ keV D^+ and H^+ ions}, where they both lose energy mostly by inelastic processes. This is in accordance with a depth of 2.6 \text{ \mu m}
Figure 12. DLTS spectra for GaAs irradiated with 300 keV Deuterons and Protons and 1 MeV electrons [20].

<table>
<thead>
<tr>
<th>ION SPECIES</th>
<th>ION DOSE (cm$^{-2}$)</th>
<th>INTEGRAL CRR electrons/Ion</th>
<th>CARRIER CONCENTRATION (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protons</td>
<td>$9.6 \times 10^{10}$</td>
<td>$5.4 \pm 0.2$</td>
<td>$2 \times 10^{15}$</td>
</tr>
<tr>
<td>Deuterons</td>
<td>$3.4 \times 10^{10}$</td>
<td>$1.3 \pm 1$</td>
<td>VPE</td>
</tr>
<tr>
<td>&quot;</td>
<td>$1.4 \times 10^{10}$</td>
<td>$20 \pm 5$</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>$9.6 \times 10^{10}$</td>
<td>$12 \pm 2$</td>
<td>$3 \times 10^{15}$ LPE</td>
</tr>
</tbody>
</table>

Table 4. CRR for 300 keV Proton and Deuteron irradiation in GaAs at 77 K, using C-V profiles as reported by Blood [20].
determined by Matsumara and Stephens [143]. Table 4 shows the integrated carrier removal for different isotopes [20]. Indicating that for low doses the ratio of CRR follows the isotopic mass ratio. But for higher doses CRR for Proton falls leading to the unexpected differences in Deuteron and Proton removal rates. It should be noted that the results shown for low dose Deuteron removal rates, from Blood [20] compares well to the removal rates reported by Steeples [183] for relatively high dose irradiations.
3 MECHANISM OF RADIATION DAMAGE

In coming to rest, within a target, high energy ions interact and collide, individually or collectively, with the nucleons and the electrons of the target atom. These interactions fall into two categories. Firstly, the interaction of the ions with the crystal nucleons which involves elastic (hard) collisions, with high energies transferred between the two particles. This is the dominant process contributing to the production of damage. Secondly, the interaction of ions with electrons in the solid, which is a continuous process of inelastic (soft) collisions that is characterised by low energy transfers. In general this latter mechanism merely slows down the ions.

The energy lost by the ions is balanced by an energy gained by the nucleons and the electrons of the target atoms. In the elastic regime the energy transferred to an atom (knock-on energy) may be sufficient to break atomic bonds, when generally the atom will be displaced permanently from a lattice site, creating a free atom and a vacancy (a Frenkel pair). The ejected atom, the primary knock-on, may have sufficient kinetic energy to cause further atomic displacements, secondary displacements. The ion and the displaced atoms continue to create more displacement until their energy falls below a characteristic energy for the solid, known as displacement energy $E_d$ (see section 3.2.1), where $E_d$ is the minimum energy required to displace an atom from the lattice site. The accumulation of these displacement events may lead to a cascade of displacements.
The incident particle, once slowed down to an energy below $E_d'$, can substitute an atomic vacant site, substitutinal, or can be positioned between the atomic arrays, constituting an interstitial. Accumulation of these defects is the radiation damage that will affect the crystal properties.

The first section in this chapter sets out the various mechanism responsible for the energy loss in a solid. The second section is concerned with the mechanism responsible for the damage production. In the final section the ranges of light ions in semiconductors are discussed.

3.1 Energy loss

The energy transferred during a scattering process is due to two major mechanism:

1) The elastic or nuclear processes

2) The inelastic or electronic processes

These processes are considered in the following sub-sections. It should be noted that the inelastic or the electronic process includes the charge exchange energy loss as well (see section 3.1.3).

The earliest theory developed to describe the process of energy transfer from a high velocity particle to a stationary atom was by Bohr in 1913 [21,22], who developed a semiclassical quantitative model which described the essential features of the process.

Bethe [13,14], in 1930, confirmed Bohr's work using a quantum
mechanical treatment. Lindhard and co workers (1954) [131,134,132,135] and Firsov (1959) [73,74,76] have also contributed to the understanding of the energy loss processes for low energy (eV to keV) ion irradiation.

Figures 13(a) and (b), are schematic of the ion energy loss, showing the Proton stopping cross sections in silicon. The general shapes of the curves are applicable to all other ion and target combinations.

For Protons in Silicon, Lindhard et al suggested that the elastic stopping accounts for only 2% of the total energy loss at 10 keV and up to 16% for the ion energy of 1 keV, with the rest of energy loss being due to inelastic processes. Therefore at high energies, > 100's keV, light ion energy is lost by the inelastic processes. The important parameter here, is the orbital velocity of the outer shell electron of the lattice atom. For ion velocities greater than this velocity the inelastic energy loss processes dominate, but as the energy drops below the orbital velocity the elastic losses become more significant and eventually dominate.

Figure 14 shows the dependence of the elastic and inelastic energy loss processes upon the ion energy, for Protons, Deuterons and Helium ions. These theoretical dependences were calculated from the monte carlo calculations of the TRansport of Ions in Matter (TRIM and PRAL), made available by the computer programmes compiled by Biersack et al [16]. This programme follows each individual ions trajectories and the recoiling atoms with time making random collisions with the target atoms. The ion-atom interaction potential function (see section 3.1.1) is based upon a semi-empirical fit to the stopping behaviour of
Figure 13(a). The energy dependence of the stopping powers, with a = LSS and Firsov predictions, b = $V_0 Z_2/3$ dependence, c = $2V_0 Z_1$ dependence, d = Bethe, Bloch and Lindhard (Dielectric) derivations, e = Relativistic effects.

Figure 13(b). Schematic representation of the stopping powers with ion energy.
Figure 14. Elastic and Inelastic energy loss for Proton, Deuteron and Helium ions in GaAs, as calculated by PRAL2 [16].
ions.

3.1.1 Elastic energy loss

The elastic energy loss occurs as a result of small impact parameter, $P$, binary collisions, between the energetic ion and a target nucleus. This process may be analysed by considering the classical laws of conservation of energy and momentum. The collision may be represented by the Rutherford semi-classical approach, in the laboratory system of coordinates, as shown in figure 15, where the mass, $M$, atomic number, $Z$, and the energy of each particle is shown. The subscript 1 denotes the ion and 2 the target atom. The energy, $T$, transferred between the ion and the atom can vary from a value of zero for a distant collision (large $P$), to the maximum value, of $T_m$, for the head-on collision when:

$$T_m = \frac{4 M_1 M_2}{(M_1 + M_2)^2} E_0$$

Where $E_0$ is the energy of the incident particle. For a displacement to occur, there is a minimum energy transferred necessary, which is just capable of breaking the bonds and causing an atomic displacement, this energy is known as the displacement energy, $E_d$. The minimum energy that an ion has to have in order to create displacement is known as the threshold energy, $E_{th}$. This energy is derived by substituting $E_d$ for $E_0$ in equation 1, and has values of 10 eV to 1 keV, for light ions in low mass targets, where $E_d = 10-20$ eV [194].

For computational purposes it is convenient to change from the laboratory frame of reference to the centre of mass coordinates, figure
Figure 15. Laboratory system of coordinates for a collision between an ion of $M_1, Z_1, E_0$ with a stationary atom $M_2, Z_2$ leading to a recoil atom with energy $T$. [57]

Figure 16. Center of mass system for the same collision as in figure 15.
16. In the latter, the angle of the scattering can be defined in terms of an integral of the ion energy, the impact parameter and the interatomic potential.

In order to exactly describe the ion-atom scattering events it is necessary to know the precise form of the interatomic potential associated with the particles, however, the exact form of this potential is not known [81], and various forms for $V(r)$ at varying particle separations, $r$, have been suggested, see the following text.

**The interatomic potential, $V(r)$**

In the discussion of atomic collisions, there are two useful reference points in the scale of atomic separation: (i) the Bohr radius of the Hydrogen atom, $a_0 \approx 0.53$ Å, which gives the approximate position for the atomic electron shells, and (ii) the spacing between the neighbouring atoms, $D$, in the crystal, which is typically $\approx 2.5$ Å.

a) When $r>D$, the valence shell of the particles can overlap, leading to an attractive interaction of the type that forms the chemical bonds (Van der Waal forces). This interaction is very weak and is, therefore, not considered.

b) When $a_0 < r < D$, the closed inner shell electrons begin to overlap and since only one electron can occupy a closed shell, Pauli's exclusion principles, therefore their energy levels must be changed and since all the lower levels are full, then they can only be ejected. The extra energy necessary is supplied by the work done in forcing the atoms together and therefore constitutes a positive potential energy of interaction. This is known as the closed shell repulsion and is of the exponential form, and may be represented by the Born and Mayer
Figure 17. Various approximations for the interatomic potential with the interatomic separations. [16]
c) When $r < a_o$, the nuclei become the closest pair of charged particles, but due to the electrostatic screening of the nuclear charges by the inner most electrons, their coulomb interaction is reduced. This interaction may be described by the Screened Coulomb potential. Where a Thomas-Fermi model of an atom [133] has been employed to deduce the effective charge density of an atom and to estimate the screening of the Coulomb potential [22]. The form of this potential is a combination of the Born-Mayer potential and the simple Coulomb potential.

For the intermediate regions, Lindhard et al [135] and Firsov [74], both using the Thomas-Fermi model of an atom, have derived a potential, which is a Coulombic potential with the screening functions added on. The numerical value of this function has been tabulated by Gombas [90] and Firsov [75].

Brinkman [29] has used an empirical relation, that can approximate the form of $V(r)$ in the intermediate region. At small separations their expression tends to a simple Coulomb potential and at large separations the expression approaches the Born-Mayer potential.

Nielsen [155] has suggested an inverse square potential fitted to the exponentially screened Coulomb potential. Abrahamson [1], using the Fermi-Dirac statistics to treat the electron cloud, has derived a potential, containing terms corresponding to the screened Coulomb and electronic interactions.

Biersack and Ziegler [16] have recently reported a very exhaustive computer calculation of the interatomic potential by considering Coulomb interaction, the electron excitation energy, the
exchange energy between electrons and a correction factor for the screening function. This calculation and other forms of the interatomic potential are shown on figure 17.

The energy loss can only be calculated for simple forms of the potential such as Coulomb or the inverse potentials. In all other cases numerical methods have to be employed, such as the universal potential suggested by Biersack and Ziegler [16].

Approximations can also be used to determine the energy loss. These include: (i) the impulse or the momentum approximation method [215], which is only applicable to glancing angle collisions, and (ii) the hard sphere radius model [38], which is the most widely used approximation, where the interatomic potential is assumed to approximate to a step function potential of width $R_0$, where $R_0$ is the atom's hard sphere radius.

3.1.2 Inelastic energy loss

A comprehensive theoretical treatment of the inelastic energy loss processes covering all the energies of interest, can not be formulated because of the different approximations concerning both the scattering and the contribution of different electrons in a solid. The first discussion of inelastic stopping of fast charged particles considered the energy regime where the velocity is $\gg V_o$, where $V_o = e^2/\hbar$ is the orbital velocity of the Hydrogen atom. Bohr [21] in 1913, using a classical mechanical approach, predicted that the influence of the fast ion on an atom may be regarded as a sudden small external perturbation and that a rapid transfer of energy from the ion to the electron will result.
Using the Rutherford semi-classical approach, described in the section 3.1.1, and by approximating the collision to a two body event, a formula can be derived for the maximum energy transfer for a head-on collision between the incident ion and an orbital electron of the target atom, similar to equation 1, where this time $M_2$ is equal to the mass of an electron. In general, the energy transferred to the electron will be much smaller than that given to an atom, typical values are shown in table 5.

This treatment can only provide an order of magnitude for the inelastic energy loss. A better treatment is made for the case in which an ion is considered to experience a soft collision, where it is assumed that the direction of the motion and the speed of the ion are essentially unchanged. This is a valid assumption since, for collisions with large impact parameters, the momentum of the electron is in a direction normal to the trajectory of the ion. This treatment, again, gives an order of magnitude for the inelastic energy loss.

However, if the distances of approach are of the same order of magnitude as the deBroglie wave lengths, a quantum mechanical treatment must be used. Bethe [13] gave a quantum-mechanical derivation based on the plane wave Born approximation method. For low energy collisions he derived a similar formulae to Bohr's, but included a factor for the mean ionization and excitation energy, $I$.

Bloch [18], later, extended this derivation by further adding correction terms for the relativistic effects and density effects for very high velocities. For the low velocities, he added the shell correction term, to allow for non-participation of inner shell electrons, which become significant at low velocities.
<table>
<thead>
<tr>
<th>Energy loss mechanism</th>
<th>maximum energy transferred by 1.5 MeV Proton in GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic</td>
<td>80 keV to an atom</td>
</tr>
<tr>
<td>Inelastic</td>
<td>3 keV to an electron</td>
</tr>
</tbody>
</table>

Table 5. Calculated values of maximum energy transfer to an atom and to an electron for 1.5 MeV Proton irradiated GaAs, as derived from equation 1.
The mean ionization and excitation energy, $I$, derived by Bethe [19] is an approximate weighted average of all the excitation and ionization processes possible for a given atom, based on the Thomas-Fermi model of the atom [133]. The theoretical calculation of this energy is difficult and, therefore, is usually determined empirically from very accurate measurements of the energy loss or ion range. The value of $I$ is as shown:

$$I = KZ \quad \text{(2)}$$

Where $Z$ is the atomic number of the target atom.

$K$ is the proportionality factor $\approx 10 \text{ eV}$.

Many other workers [69, 46] have also determined the value of $I$, both experimentally and theoretically, and have found good agreements between the two.

For the shell correction, a single variable, such as $I$, is insufficient to express the stopping. This is because the correction for each of the atomic shells have to be considered. Therefore shell correction is the sum of the mean corrections to the K-shell, L-shell etc, energy loss [206].

Bethe's equation [44] is independent of the target medium and ion energy and only dependent on the ion by the scaling factor of $Z_i^2$. Therefore making the extrapolation from one ion to the next possible [32].

Firsov [73] and Lindhard et al [135] give a theoretical description for the energy loss, in the low velocity region, where the
Bethe formulae does not apply. At such low velocities, of the orders of few eVs, because the inner-shell electrons contribute less to the energy loss, very large corrections are needed to the Bethe formulae. The probability of neutralization, also becomes large so that the collision is similar to a hard sphere elastic collision in a reference frame moving with the ion. The Lindhard expression is based on the elastic scattering of the free electrons in the static field of a screened point charge, and adequately describes the variation of the stopping power with energy.

In the model suggested by Firsov, it is assumed that at small ion-atom separations a quasi-molecule is formed. The electrons from both atoms may then cross the instantaneous boundary between the particles to assume the momentum of the atom to which they are temporarily attached. Thus the electron from the ion loses momentum in transferring to the initially stationary target atom and those from the struck atom gain momentum in transferring to the incident ion. These momentum exchanges occur at the expense of the energy loss from the incident ion. Firsov used the Thomas-Fermi statistical model of the atom to calculate the electronic energy loss of ions moving through a gas. He showed that the energy transfer decreases with increasing impact parameter, also he showed that this increase is linear with the ion velocity and has a $E^0.5$ dependence, where $E_0$ is the initial ion energy.

More recently, Cheshire and others [43,68] have used other atomic wave functions [66] to give Firsov's classical model more validity.

The models so far discussed, consider binary collisions between an ion and the target atom. An alternative procedure suggested by Fermi
et al [72], is to regard the absorber as a Fermi gas of electrons, the density and the energy distribution of which are given by the Thomas-Fermi. Lindhard et al [133], further developed the idea, by assuming that the incident ion can be treated as a positive charge, $Z_1 e$, with this charged particle losing energy to individual electron, at close distances. For the large distances, this charged particle, loses energy to collective electron plasma resonance processes in the free electron gas. They showed that, provided the ion velocity is less than the velocity of an electron with an energy equal to the Fermi energy; then the energy loss is proportional to $E_0^{0.5}$, the atomic mass and numbers of the ion and the target atom. More recent work by Bottiger et al [24] have revealed a periodic dependence of the energy loss upon the atomic number of the ion.

Both Firsov and Lindhard theories are suitable for a first order determination of the inelastic energy loss, with typical values, in the energy range 1 keV to 100 keV, in the order of several eV/Å. As shown on the figure 14, with an increase in ion energy the inelastic processes begins to dominate.

For ion energies of order 1 MeV, the ion-electron energy transfer, in a Coulomb potential field, validates an impulse approximation. In this treatment the energy loss is determined by integrating the differential cross section equation. The limits of which are between the minimum energy required to effect excitation, that is excitation energy $E_e'$, and the maximum energy, equal to $4(M_0/M_1)E_0$. The result of this integration applies only to one electron and for an accurate result the integration has to be for all the electrons in the target atom. Defining $I_e$ as an average excitation
energy, the inelastic energy loss becomes [122]:

\[
\frac{dE}{dx} = \frac{N e^2 Z^2 e^{\frac{l}{M Z^2 E}}}{16 \pi e^2 M_0 E_0} \ln \frac{\hbar M_0 E_0}{M_e l_e}
\]

Because of the slowly varying logarithmic term, the above equation shows that the inelastic energy loss rate decreases approximately as \( E_0^{-1} \) at high energies, but at lower energies assumes a maximum value which occurs at ion velocities equal to the electron velocities, with the electron energy equal to Fermi energy. This higher energy regime is applicable to light ions of energy 1-10 MeV. For Proton and Helium ions in GaAs, the inelastic energy loss is in the order of 10-100 eV/Å (see figure 14).

3.1.3 Charge exchange energy loss

An ion moving through a solid with a velocity close to the orbital velocity of its outer electrons has a high probability of capturing an electron from the target atoms [57]. This process can contribute to the total inelastic energy loss since the moving ion loses energy in the removal of the electrons which it captures. The cross section for the capture and loss of electrons are strong functions of the velocity of the moving ion and Bohr [22] has derived approximate expressions for both the light and heavy ions. For light ions Bohr found the ratio for the capture to loss of an electron to be only slightly dependent on the atomic number of the stopping medium, and proportional to the ion velocity to the power of five. This ratio
for Protons incident on GaAs suggests that for low energies (\text{keV}), Protons have 50% probability of being ionized. But as the ion energy increases this charged fraction rapidly increases until at energies of the order of MeV, the uncharged component becomes negligible. The contribution to the inelastic energy loss is therefore only significant at energies above 100 keV.

In the case of heavier ions, several electrons may have orbital velocities comparable to the ion velocity, in this case the capture and loss cross sections have been estimated using $V^*$, a characteristic velocity corresponding to the orbital velocity of the outer shell electrons of the moving ions.

The electrons captured or lost by an ion can be in any unoccupied bound state, resulting in the ion being either in a ground- or excited state, whereby ions can then lose one or more electrons due to coulomb excitation. The electrons within an ion may be excited to higher states and then decay either with or without emission of one or more electrons [194]. In most cases, they will decay via X-ray or electron emission [194].

3.2 Radiation damage

3.2.1 Displacement energy, $E_d$

The magnitude of the displacement energy, $E_d$ (defined in section 2.1.2) is dependent on the chemical bond energy and the crystallographic direction in which the displacement occurs. Seitz [172] suggested that an atom on a lattice site is located within an isotropic square well potential, and he reasoned that under equilibrium
conditions, a displacement would only occur, if the particle's energy was twice the sublimation energy. He further argued, that under dynamic conditions a displacement would only occur if the particle has more than twice this energy, that is four times the sublimation energy. For most solids the sublimation energy is about 5-6 eV and thus on average $E_d$ will have a value of 20-25 eV.

Bauerlein [7] and Sigmund [174] define $E_d$ as the energy required to break sufficient atomic bonds to free the atom. This energy for tetrahedrally bonded structures such as Si, Ge and GaAs is about four times the bonded energy (2-4 eV), giving a value of 8-16 eV for $E_d$. A value in the range 6-20 eV is usually measured for semiconductors.

The value of $E_d$ is anisotropic, so that for the determination of a particular $E_d$, contours of displacement threshold with the angles of ion scattering have to be considered [67]. This anisotropy has been predicted both analytically [175] and by computer simulation [85]. For metals it has been reported [67,85] that $E_d$ may vary between 15 and 80 eV, depending on the direction of displacement.

For compound semiconductors where the nearest neighbour atoms are generally of a different species the value of $E_d$ will depend on the species of atom being displaced. Baroody [6] has confirmed the above and reports that if the transferred energy to the target atom is much larger than $E_d$, then the displacement becomes insensitive to the atomic species.

Using the Seitz isotropic square well approximation, the probability of displacement is assumed to be zero for energies below $E_d$ and abruptly rises to unity at $E_d$. More complicated probability functions [49] predict the rise from zero to unity to be over a very
small energy range.

The value of \( E_d \), reported for GaAs [53], at room temperature is about 9.0 eV for Ga atom displacement and 9.4 eV for As atoms. Other workers have reported the value of \( E_d \) for both Ga and As atom displacement to be in the order of 10-25 eV [53]. Most recently a value of 10 eV has been reported by Pons et al [228]. However in the work reported here, for the calculation of K-P cross section, an average value of 17.5 eV [7] has been assumed. Assuming this particular value for \( E_d \) does not greatly effect the overall conclusions. This is because the relative values rather than the absolute values of the cross section (which are proportional to \( E_d \)) are considered.

3.2.2 Defects and cascades

For heavy ions the energy loss during a two body elastic scattering event is usually large (see section 3.1.1). This, coupled with a short mean free path between the collisions, of the order of the interatomic spacing, leads to a damage cascade, and the formation of regions of high concentration of defects, as shown on figure 18. In this region each knock-on atom will leave behind a vacancy and will itself constitute a fast moving interstitial which, eventually will come to rest towards the outer periphery of the cascade. Therefore resulting in a vacancy-rich central zone and an interstitial-rich outer zone [29].

For light ions, fewer secondary displacements are created, due to the lower recoil energy available (see section 3.1.2). With the mean free path between collisions being very large, each cluster of defects
<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>DISPLACEMENT ENERGY (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIAMOND</td>
<td>80</td>
</tr>
<tr>
<td>GRAPHITE</td>
<td>25-33</td>
</tr>
<tr>
<td>SILICON</td>
<td>11-45</td>
</tr>
<tr>
<td>GERMANIUM</td>
<td>13-25</td>
</tr>
<tr>
<td>GaAs</td>
<td>9.0 (Ga)</td>
</tr>
<tr>
<td></td>
<td>9.4 (As)</td>
</tr>
<tr>
<td></td>
<td>9-25</td>
</tr>
<tr>
<td></td>
<td>17.5</td>
</tr>
</tbody>
</table>

Table 6. The displacement energy for various semiconductors as reported by Crawford and Slifkin [53] and [230].
is set well apart and no overlap occurs, with each cluster containing very few displacements. The angle of scattering at each collision is very large, causing a "zigzag" in the ion path, as shown in figure 19.

The displacement processes occur in a time interval of $10^{-13}$ seconds. The damage has an excess energy, which can only be dissipated as thermal vibrations, with a typical lifetime of $10^{-12}$ secs [196]. Therefore the cooling of this region is thought to be by atomic processes rather than electronic conduction processes [57].

For the purpose of comparison the transmitted energy from a projectile to an atom is plotted against the projectiles energy, for electrons, Proton and Neutrons in figure 20.

3.2.3 The density of atomic displacements

The number of primary displaced atoms, $N$, per unit volume and unit time generated by the incident ion of energy, $E$, is given by the rate reaction equation,

$$N = N_0 \sigma_n(E) \phi$$

Where $N_0$ = The atomic density.

$\sigma_n(E)$ = The cross section for elastic collision.

$\phi$ = The total integrated ion flux or dose.

The average number of displaced atoms in a cascade, $g(T)$, is a function of the energy spectrum of the primary displaced atom, $T$, which is dependent on the original ion energy, $E$. Therefore the total number of displaced atoms including primary and secondary displacement becomes:

$$N_d = N_0 g(E) = N_0 \sigma_n(E) \phi g(T)$$
Figure 18. A schematic of the effects of a heavy ion irradiation of a solid target.

Figure 19. A schematic of the effects of light ion irradiation of a solid target.
Figure 20. The maximum transmitted energy \( T_m \) and average transmitted energy \( T \) versus the incident ion energy, for Proton, electron and neutrons in Si. [4]
The appropriate cross section, $\sigma_n(E)$, for high energy light ions is the Rutherford cross section. In order to find Nd, only an estimate for $g(T)$ is necessary, since $N_0$ and $\rho$ are known in equation 4.

Two distinct models, with different physical assumptions have been suggested in order to estimate the value for $g(T)$ [169]. In the first model suggested by Snyder and Neufeld [176] and Harrison and Seitz [98], it is assumed that the displacement energy, $E_d$, is lost at every displacement event. Therefore, the primary displaced atom, after the collision with the secondary displaced atom, has an energy of $(T-E_d)$ and will continue to create more displacements until its energy falls below $E_d$.

In the second model, proposed by Kinchin and Pease [116], it is assumed that $E_d$ is not lost to the lattice and therefore the primary displaced atom will recoil from the collision with full energy transfer. They further assume that if the atom recoiling from the collision has energy less than $2E_d$, no new displacement can be created by that particular atom. Both models assume two body collisions between hard spheres with no inelastic kinetic energy loss occurring.

Kinchin and Pease calculated $g(T)$ to be as:

$$g(T) = \begin{cases} 
0 & T < E_d \\
1 & E_d < T < 2E_d \\
T/2E_d & 2E_d < T < E_i \\
E_i/2E_d & T > E_i 
\end{cases}$$

---(6)
Where $E_i =$ The minimum energy required to ionize
the target atom, (ionization energy).

But Snyder and Neufeld, assuming Rutherford type scattering and
counting replacement events as a displacement, obtained:

$$g(T) = \begin{cases} 1 & 0 < T < 2E_d \\ 0.5 \left( \frac{T}{E_d} \right) & T > 2E_d \end{cases} \quad -----(7)$$

Finally Harris and Seitz, assuming a sharp threshold for displacements,
but otherwise employing Snyder and Neufeld model obtained:

$$g(T) = \begin{cases} 1 & 0 < T < E_d \\ 0.5 \left( \frac{T+E_d}{E_d} \right) & T > E_d \end{cases} \quad -----(8)$$

In general, by ignoring $E_i$ at $T \gg E_d$ in Kinchin and Pease model, $g(T)$ becomes:

$$g(T) = \frac{E}{2E_d} \quad -----(9)$$

Which means, physically, that atoms in the cascade continue to multiply
until their energy falls below $2E_d$, and the number of atoms with energy
$2E_d$ is expected to be $E/2E_d$.

Others [171, 174] have tried better fit approximations to the
interatomic potential than the hard sphere model, but have made little
difference to the overall number of displaced atoms and the K-P model.
has remained a good order of magnitude estimate for $g(T)$.

For light ions, the K-P model overestimates the defects, because of the domination of inelastic processes. This is well demonstrated by the studies in GaAs [40], indicating that the number of displaced atoms falls below the K-P estimations.

Therefore the K-P model has been generalized to include the inelastic energy loss and the consequential reduction in the total number of displacements is given by [174]:

$$f(E)$$

$$g(T) = K \frac{f(E)}{E_d} \quad (10)$$

Where $K$ is a constant of the order of 0.4

$f(E) =$ The fraction of ion energy expended

in elastic, non-excitational collisions

More realistic treatment of the K-P model [133, 222, 26] considers an evaluation of the relative contribution of elastic and inelastic energy loss processes, through either theoretical and/or experimental estimates of the rates of the energy loss. With the general results that for ion energies below the ionization energy, $E_i$, the value of $g(T)$ is reduced below the K-P value by about 10 to 20%. But for ion energies above $E_i$, the value of $g(T)$ increases at a rate that is linear with the ion energy.

Other factors contributing to the overestimation of the K-P model are ion channelling effects, partial annealing and ion beam
focusing. The channelling can be accounted for by making modification to the K-P equation,

An estimate of the maximum number of displacements \( g(T) \) for energetic (MeV), light (Proton) ions can be derived from equation 7. It is assumed that the energy loss for the energy range \( T \gg E_i \) is due exclusively to ionization effects, and for \( T \ll E_i \) is a result of elastic scattering processes. Therefore, \( E_i \) determines the maximum value for the displacement density. As a general rule \( E_i = M_2 \) (in units of keV), which for GaAs is equal to 72 keV. Thus, for GaAs, the value of \( g(T) \) is \( 2 \times 10^3 \) displacement per ion [39].

Finally the cross section, \( \sigma_{KP} \), calculated for the production of frenkel pairs, which can be derived from the Kinchin and Pease elastic displacement model is given [122] as:

\[
\sigma_{KP} = \frac{2 \pi a_0^2 M_1 Z_1^2 Z_2^2 E_R^2}{M_2 E_o E_d} \ln \frac{4 M_1 M_2 E_o}{(M_1 + M_2)^2 E_d} \quad \text{-------(11)}
\]

Where \( M_1, M_2 \) and \( Z_1, Z_2 \) are the atomic mass and atomic number of the incident ion (labeled 1) and the target atom (labeled 2). \( a_0 \) is the Bohr radius, \( E_R \) the Rydberg energy 13.6 eV and \( E_d \) the displacement energy.
3.3 Ion range

The knowledge of the depth of penetration of ions in a solid is of prime importance both in ion implantation and the study of radiation damage. The total range of an ion is the total distance travelled by the ion from the surface of the material to the point where the ion comes to rest. The collision events for each ion are random and all ions do not follow the same path and are spread at the end of the ion path in a Gaussian distribution, with the distance from the surface of the material to the distribution maximum known as the average projected range, $R_p$.

Much work has been done to determine values for $R_p$, both theoretically and experimentally. In the following two subsections the major theoretical and the experimental studies are discussed.

Theoretical considerations

The first extensive table for the range of ions in various material was by Northcliffe and Schilling [263] in the early 70's. Since then many others [110,84,27,223,105,169], using the same theoretical approach, have published more detailed tables. They all break the range calculation into two parts;

(1) The energy loss considerations

(2) The scattering due to binary collisions
These workers, mathematically, have followed the ion through the above processes until the ion has come to rest. The theoretical consideration for all these calculations are based on the work of Lindhard, Scharff and Schiott [135], known as the LSS theory.

The LSS theory develops analytical expressions for both the electronic and nuclear stopping of ions and then sets up a Boltzmann transport equation to solve the statistical problem of the final ion distribution. For the numerical solution, the transport equation is expanded and moments of the distribution are obtained with the first moment defined as the mean range Rp, the second as the straggling ΔRp, the third as the skewness etc.

More recently, Littmark and Ziegler [136], have used transport equations to solve the ion range distribution, in which they have maintained the LSS formulae approach, but used a new expansion to the transport equations. This gave them the relative freedom of adjusting the dominance of nuclear or electronic interactions.

For high energy light ions Cowern [52] has suggested a new analytical method for the calculation of ion range distributions. By considering high energies, his treatment uses the simple physics of ion-atom collisions and simple collision statistics, and by neglecting screening and the influence of nuclear forces on the scattering cross section [37], he simplifies the treatment even further. He also assumes the ions to be fully stripped of electrons over most of their trajectory and therefore to a good approximation uses the simple Bethe theory [13], without the inclusion of the shell corrections. As a simplified first approach, he approximates the electronic straggling by treating the target electrons as free electrons, following Bohr [22].
Using the above assumptions and formulae he found the distributions to have Gaussian peaks, due to electronic straggling, together with a long, low intensity tail stretching towards the target surface. These tails arise from the nuclear collisions, as shown in figure 21.

**Experimental considerations**

Proton range data for energies of up to 2.5 MeV have been determined for GaAs, InP, GaSb and GaAlAs by Henshall et al [105]. Speight et al [178] showed that there is a good agreement between the experimental results and theoretical prediction.

Earlier Okunev et al [161] used the range-energy relationship of Protons in GaAs to determine the depth of penetration of 2–5 MeV Protons. Their experimental values matched the theoretical Bethe-Bloch equation and they characterised the range as:

$$R = C E^\gamma$$  \hspace{1cm} (12)

Where $R$ and $E$ are the Proton range and energy and $C$ and $\gamma$ are constants and have values in the order of 5 and 1.5, respectively.

More recently Cocito et al [47] and Snyman et al [177] have determined the range in GaAs by measuring the insulating layer thickness, created by 300 keV Protons. Cocito et al suggest that the general rule of 1 $\mu$m for every 100 keV Proton energy, that was obtained by Spitzer [180], is a good first approximation.

Favennec et al [70] have evaluated an experimental relationship for the Proton range and the insulating layer thickness, for GaAs and
Figure 21. The range distribution of high energy light ions. The slash markers on each curve indicates the approximate level below which nuclear collisions noticeably contribute to the distribution [52].
GaAlAs in the energy range 300-1200 keV and at dose levels of $10^{12}$ to $2 \times 10^{13}$ cm$^{-2}$.

Since their earlier experiment, Speight [178] have used chemical staining on n-type GaAs for 200-1000 keV energy range and dose range of $10^{13}$-$5 \times 10^{15}$ cm$^{-2}$.

Mathiot et al [142] have used similar techniques for 60-300 keV energy range and higher doses of $5 \times 10^{15}$-10$^{16}$ cm$^{-2}$. Using free carrier profiles Harada et al [95] and Harrison et al [97] for low dose of $10^{10}$-$10^{13}$ Protons/cm$^2$ in the energy range 60-400 keV, determined the range as shown on figure 22.

Cocito, using other techniques, show that the thickness of the insulating layer is larger than the projected range. They attribute this to the lattice defect migration, target properties and the implantation conditions. Their results are as shown on figure 23.

Snyman similarly measured the range using Transmission Electron Microscopic technique and found that the damage profile about the mean range correlates well with the LSS values. However, they find the profile to vary linearly with Proton dose, but to be independent of ion energy and annealing temperatures.
Figure 22. Range and energy relationships for Proton in GaAs. [95]

Figure 23. Depth and energy relationships for Protons in GaAs. [97]
CHAPTER FOUR

4 EXPERIMENTAL TECHNIQUE

4.1 Sample preparations

4.1.1 Materials

The GaAs samples used in this study were prepared from two types of materials (also see table 7):

Type 1) From wafers (of 1-3 cm² area) cut from undoped bulk semi-insulating ingots, in the <100> plane, with one face mechanically and chemically polished. After cleaning, these wafers were implanted and annealed to produce both n- and p-type conductivity layers of thickness 0.5 μm, and are referred to as the ion implanted samples.

Type 2) From wafers (of 1-4 cm² area) grown by Vapour Phase Epitaxial (VPE) growth method, in the <100> plane, on semi-insulating substrates of resistivity > 20 K Ohm-cm, referred to as epitaxial samples. There were two sets of samples prepared from type 2 wafers, Epi I and Epi II sets.

The first set (Epi I) had a carrier concentration, \( n_0 \), in the range 2.7x10^{15}-3.2x10^{17} \text{ cm}^{-3}, and thicknesses of 0.7-8.0 \text{ μm}. Subsequently they were chemically etched down to a thickness of 0.7-2.0 \text{ μm} (see section 4.1.3).

The second set (Epi II) were device grade wafers with carrier concentration of between 2.1x10^{15}-9.2x10^{16} \text{ cm}^{-3}, and thicknesses of 0.31-0.66 \text{ μm}. These wafers were kindly supplied by Plessey Research (Caswell) Ltd.
<table>
<thead>
<tr>
<th>WAFER</th>
<th>DESIGNATION</th>
<th>MATERIAL</th>
<th>MEASURED CARRIER CONCENTRATION (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>Ion implanted samples</td>
<td>Bulk S.I. n- and p-type &lt;100&gt;</td>
<td>1x10¹⁷ * to 7x10¹⁷ *</td>
</tr>
<tr>
<td>Type 2</td>
<td>Epi I samples</td>
<td>VPE/S.I. n-type &lt;100&gt;</td>
<td>2.7x10¹⁵ to 3.2x10¹⁷</td>
</tr>
<tr>
<td></td>
<td>Epi II samples</td>
<td>VPE/S.I. n-type &lt;100&gt;</td>
<td>2.1x10¹⁵ to 9.2x10¹⁶</td>
</tr>
</tbody>
</table>

Table 7. GaAs material used in this study, -S.I. = Semi-Insulating material -VPE/SI= Vapour Phase Epitaxy on S.I. material

(* peak carrier concentration for ion implanted material)
4.1.2 Preparation of ion implanted samples (type 1 wafers)

The ion implanted samples were formed by implanting type 1 wafers, with Se\(^+\), Zn\(^+\) or Cd\(^+\) ions, using the 500 keV implanter at the University of Surrey. Details of this machine is given in section 4.2.1.

The implantation conditions are as shown on Tables 8. The Se\(^+\) and Zn\(^+\) implantations were carried out at 200\(^\circ\)C to enhance self annealing [124]. The ion dose, energy and the subsequent annealing conditions were chosen so that a conducting layer of thickness not exceeding 0.5 \(\mu\)m, with a carrier concentration between 1 and \(7 \times 10^{17}\) cm\(^{-3}\) would be formed [124]. The dose rates were kept low, 0.2-2.0 \(\mu\)A/cm\(^2\), to avoid beam heating. The implantations were carried out at 8° off the \(\langle 100\rangle\) direction to avoid channelling. The vacuum pressure within the implanter was kept to better than 1x10\(^{-6}\) torr.

Two annealing schedules were used, as shown on Table 8. For both schedules, it was necessary to deposit an encapsulant on the implanted surface of the sample, to avoid the out diffusion of Arsenic [192]. The schedules used were as follows:

1) Anneal temp: 700\(^\circ\)C
   
   Anneal time: 15 minutes in flowing gas (90\% N\(_2\) and 10\% H\(_2\))
   
   Encapsulant: Evaporated Aluminium of thickness 0.3-1.5 \(\mu\)m

2) Anneal temp: 900\(^\circ\)C
   
   Anneal time: 30 seconds in flowing Nitrogen gas
   
   Encapsulant: Chemical Vapour Deposited (CVD) Silicon Nitride
   
   \((\text{Si}_3\text{N}_4)\) of thickness 700-1000 \(\AA\)

For the second annealing schedule the encapsulant growth and
<table>
<thead>
<tr>
<th>CONDUCTIVITY TYPE</th>
<th>ION IMPLANTATION CONDITION</th>
<th>ANNEALING SCHEDULES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ION ENERGY (keV)</td>
<td>ION DOSE (cm$^{-2}$)</td>
</tr>
<tr>
<td>n-type</td>
<td>Se$^+$</td>
<td>390 5x10$^{13}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2x10$^{14}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400 3x10$^{13}$</td>
</tr>
<tr>
<td>p-type</td>
<td>Zn$^+$</td>
<td>400 1x10$^{13}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3x10$^{13}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1x10$^{15}$</td>
</tr>
<tr>
<td></td>
<td>Cd$^+$</td>
<td>350 2x10$^{13}$</td>
</tr>
</tbody>
</table>

Table 8. Ion implantation condition and the annealing schedules for type 1 wafers (Ion implanted samples)
annealing were carried out in two steps. The first step, of duration 30 seconds, achieved the encapsulant growth at a temperature of 580-600°C in an atmosphere of ammonia, silane and nitrogen. During the second step the temperature was raised to 900°C for a further 30 seconds, in an atmosphere of flowing nitrogen, to anneal the sample.

After annealing, the encapsulant was removed in hot concentrated hydrofluoric acid followed by several rinses in distilled water and methanol.

These wafers were then diced into 4mm x 4mm samples either by cleaving or by means of diamond impregnated wire saw. These samples were subsequently sand blasted into cloverleaf shapes, Van der Pauw's geometry [198], necessary for the sheet conductivity and Hall effect measurements.

4.1.3 Preparation of epitaxial samples (type 2 wafers)

The first set of epitaxial material (Epi I), see table 9, were chemically etched to give the required layer thickness of less than 0.5 μm. The etchant used was $\text{H}_2\text{SO}_4$:$\text{H}_2\text{O}_2$:$\text{H}_2\text{O}$ in the ratio 3:1:1. The etch rate at room temperature was measured to be 315 Å/sec, but the surfaces etched were pitted. It was found that a good surface finish was obtained by maintaining the etchant at the temperature of 40 °C, where etch rate were found to be about 1000 Å/sec. Lida et al [130] report etch rates larger by a factor of ten, at the same temperature. The difference obtained in the absolute value of etch rate is assumed to be partly due to the lack of control over the etchant temperature and the subsequent non-planar etching over the sample surface.

The second set of epitaxial wafers (Epi II), see table 10, were
<table>
<thead>
<tr>
<th>MANUFACTURER</th>
<th>CARRIER CONCENTRATION (cm(^{-3}))</th>
<th>CARRIER MOBILITY (cm(^2)V(^{-1})s(^{-1}))</th>
<th>MEASURED THICKNESS after etching (um)</th>
<th>CARRIER CONCENTRATION (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.1x10(^{15})</td>
<td>6400</td>
<td>0.2-1.0</td>
<td>(2.7±0.5)x10(^{15})</td>
</tr>
<tr>
<td></td>
<td>1.4x10(^{16})</td>
<td>5000</td>
<td>0.9-1.6</td>
<td>(8.4±2.6)x10(^{16})</td>
</tr>
<tr>
<td></td>
<td>7.0x10(^{16})</td>
<td>4800</td>
<td>1.0</td>
<td>(1.1±0.1)x10(^{17})</td>
</tr>
<tr>
<td></td>
<td>1.3x10(^{17})</td>
<td>4500</td>
<td>0.7</td>
<td>1.4x10(^{17})</td>
</tr>
<tr>
<td></td>
<td>4.0x10(^{17})</td>
<td>3400</td>
<td>1.0</td>
<td>1.4x10(^{16})</td>
</tr>
<tr>
<td></td>
<td>1.3x10(^{18})</td>
<td>2500</td>
<td>1.4-1.9</td>
<td>(3.2±0.8)x10(^{17})</td>
</tr>
</tbody>
</table>

Table 9. Vapour Phase Epitaxial VPE material used. (EPI I)

<table>
<thead>
<tr>
<th>CARRIER CONCENTRATION (cm(^{-3}))</th>
<th>CARRIER MOBILITY (cm(^2)V(^{-1})s(^{-1}))</th>
<th>THICKNESS (um)</th>
<th>CARRIER CONCENTRATION (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5x10(^{16})</td>
<td>4900</td>
<td>0.36</td>
<td>(2.1±7.9)x10(^{15})</td>
</tr>
<tr>
<td>6.8x10(^{16})</td>
<td>4800</td>
<td>0.58</td>
<td>(5.3±1.1)x10(^{16})</td>
</tr>
<tr>
<td>8.5x10(^{16})</td>
<td>4500</td>
<td>0.40</td>
<td>(6.2±0.6)x10(^{16})</td>
</tr>
<tr>
<td>1.2x10(^{17})</td>
<td>4100</td>
<td>0.31</td>
<td>(6.5±1.1)x10(^{16})</td>
</tr>
<tr>
<td>1.2x10(^{17})</td>
<td>4100</td>
<td>0.38</td>
<td>(9.2±4.2)x10(^{16})</td>
</tr>
</tbody>
</table>

Table 10. Vapour Phase Epitaxial material used. (Epi II)
of the required layer thickness and no etching was necessary.

These epitaxial wafers were diced into squares and shaped prior to the alloying of electrical contacts, for the sheet conductivity and Hall effect measurements.

4.1.4 Electrical contacts

n-type material For all n-type samples tin contacts were alloyed at about 300°C, in an inert gas atmosphere. These contacts were prepared by placing small pieces (1/10 mm) of high purity tin on the surface of the sample, which was placed on a hot stage. The system was first flushed with hydrogen, which had been passed through hydrochloric acid (HCl). This atmosphere acted as a flux to aid formation of the contacts. The stage was then heated, in an atmosphere of flowing hydrogen, and after about 10 seconds alloying occurred [80].

p-type samples For the p-type samples gold contacts of diameter of 1/2 mm and thickness of 500-1000 Å were evaporated. Subsequent heat treatment was not required as these contacts were ohmic, with a low contact resistance.
4.2 Irradiation details

Four particle accelerators were used in these experiments, details are summarized in table 11.

The 500 keV heavy ion accelerator and the 2 MeV Van de Graaff accelerator, were used at the D. R. Chick accelerator laboratory at the University of Surrey, (section 4.2.1.).

The Cockcroft-Walton and the 3 MeV Van de Graaff accelerators were generously made available by the Atomic Energy Research Establishment (AERE), Harwell (section 4.4.).

4.2.1 Irradiation facilities at the University of Surrey

500 keV heavy ion accelerator

This accelerator was used for the implantation of dopant ions, to form a conductive layer (see section 4.1.2). The details of this accelerator are described in references 124 and 192.

2 MeV Van de Graaff accelerator

This accelerator was used for the light ion irradiations. Figure 24 is a schematic diagram of a Van de Graaff accelerator [41]. The endless rubber belt is used to transfer charge from a low voltage source to the high voltage terminal. The charge accumulates on the terminal and gives rise to a Potential difference between the terminal and the earth plane. This potential difference is then graded down the length of an accelerator tube, by a continuous resistance divider chain.
<table>
<thead>
<tr>
<th>ACCELERATOR</th>
<th>ION SPECIES</th>
<th>ION ENERGY</th>
<th>ION DOSE (cm$^{-2}$)</th>
<th>PURPOSE</th>
<th>LOCATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 keV Heavy Ion Accelerator</td>
<td>Se$^+$</td>
<td>390 keV &amp; 400 keV</td>
<td>3x10$^{13}$ to 2x10$^{14}$</td>
<td>Formation of ion implanted layer n-type</td>
<td>D.R. CHICK Laboratory University of Surrey</td>
</tr>
<tr>
<td></td>
<td>Zn$^+$</td>
<td>350 keV &amp; 400 keV</td>
<td>1x10$^{13}$ to 1x10$^{15}$</td>
<td>and p-type</td>
<td></td>
</tr>
<tr>
<td>2 MeV Van de Graaff</td>
<td>H$^+$, H$^+_2$</td>
<td>0.17 MeV to 2.0 MeV</td>
<td>5x10$^{10}$ to 5x10$^{13}$</td>
<td>Light ion irradiation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$^+_3$, He$^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cockcroft-Walton</td>
<td>D$^+$, H$^+$</td>
<td>30 keV</td>
<td>4x10$^{10}$ to 2x10$^{13}$</td>
<td>Deuteron doping</td>
<td>AERE Harwell Oxon.</td>
</tr>
<tr>
<td>3 MeV Van de Graaff</td>
<td>D$^+$, H$^+$</td>
<td>0.25 MeV to 1.5 MeV</td>
<td>2x10$^{10}$ to 5x10$^{12}$</td>
<td>Light ion irradiation</td>
<td></td>
</tr>
</tbody>
</table>

Table 11. The accelerators used in this study.

(AERE= Atomic Energy Research Establishment)
Figure 24. A schematic of the mechanical charging system for Van de Graaff electrostatic generator. [41]

Figure 25. A schematic vertical section through a typical single ended Van de Graaff accelerator.
So that the positive ions in travelling through the accelerator tube experience an ever decreasing positive potential field.

Positive ions are produced in an r.f. ion source [189] which is housed inside the high voltage terminal, see figure 25. Hydrogen, Helium and Oxygen gases are leaked into the source and a plasma is established. The positive ions are extracted from the plasma using an electrode positioned by the ion source, and are then accelerated up to the full kinetic energy along an accelerator tube. The accelerated ion beam, on leaving the accelerator tube, is defined and collimated using a number of slits and is mass analyzed using a magnet. The required ion is then further resolved and geometrically shaped by the use of deflection plates and directed at the specimen chamber, shown on figure 26.

The vacuum pressure in the specimen chamber and the beam line was better than $6-7 \times 10^6$ torr, to reduce the chance of formation of neutral beam and ion energy loss [12]. The ion source vacuum pressure was kept at lower pressure than $1.5 \times 10^6$ torr, so that no impurities could enter the system.

The samples were placed in the specimen chamber, using a sample holder plate mounted on a sample holder, the schematic of the plate is shown on figure 27. The samples were secured to a PTFE block with the aid of four bronze clips that were placed on the sample's contacts. The clips made the necessary contact for the electrical measurements, and also acted as a shadow mask to screen the contact regions from the ion beam. The sample and the clips were covered by a beam defining aperture of area $0.54 \text{ cm}^{-2}$, ensuring that only the central region of the samples would be irradiated.
Figure 26. Schematic of the University of Surrey 2 MeV Van de Graaff accelerator, showing the analyzing magnet, the beam line and the target chamber used in this experiment.
Figure 27. The irradiation configuration used at the University of Surrey.
The sample holder plate was then mounted on the sample holder, and was positioned by the use of a travelling carriage on the sample holder behind a suppressor aperture and a further larger beam defining aperture, see figure 27.

The ion beam was centered on the sample holder larger aperture plate by means of dc bias applied to the scanning plates, shown on figure 26, and rastered across the sample by the application of a triangular shaped bias, so that an ion beam of uniform density irradiated the sample.

4.2.2 Light ion irradiation

At the University of Surrey, the samples were irradiated with $H_1^+$, $H_2^+$, $H_3^+$ and $^4He^+$ ions. A summary of the light ion irradiation details are shown on table 12. The majority of the irradiations were at an ion energy of 1.5 MeV.

The basic experiment was to irradiate the sample with an "incremental dose" of ions of between $5 \times 10^{10}$ to $1 \times 10^{11}$ cm$^{-2}$ and to measure the consequential change in the sheet conductivity, $\sigma_s$. This was continued for 7-10 incremental irradiation steps, for a particular ion mass and energy combination, up to a total dose of $1 \times 10^{11}$-$5 \times 10^{12}$ Proton/cm$^2$. The relatively small doses ensured that the change in sheet conductivity remained linear with dose, as explained in section 4.3. The choice of ion mass and energy was then changed and the same procedure was repeated. The maximum dose was always below $5 \times 10^{13}$ Proton/cm$^2$ dose, for a material with carrier concentration of about $5 \times 10^{16}$ cm$^{-3}$. 
<table>
<thead>
<tr>
<th><strong>ION SPECIES USED</strong></th>
<th>$H_1^+, H_2^+, H_3^+$ and $^4\text{He}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ION ENERGIES USED</strong></td>
<td>0.17 - 2.0 (MeV)</td>
</tr>
<tr>
<td><strong>ION DOSES USED</strong></td>
<td>Minimum $5 \times 10^{10}$ (cm$^{-2}$)</td>
</tr>
<tr>
<td></td>
<td>Maximum $5 \times 10^{13}$ (cm$^{-2}$)</td>
</tr>
<tr>
<td><strong>ION DOSE RATES USED</strong></td>
<td>1 - 5 (nA.cm$^{-2}$)</td>
</tr>
</tbody>
</table>

**TABLE 12.** The irradiation details
4.2.3 Dosimetry

In this section the dosimetry for the irradiation at the University of Surrey is only discussed, for the irradiation at AERE see section 4.4.

The ion dose was determined from the integral, with respect to time, of the ion current incident upon the sample, see the schematic diagram in figure 28. Assuming the charge state of the ions are known then the incident ion dose, or fluence (ion/cm$^2$), can be directly determined.

By electrostatically scanning the ion beam over the sample, a current reading is obtained which is an average of the instantaneous ion beam current. The average beam current used was usually about 50% of the instantaneous beam current. Greater values could lead to the saturation of the input amplifier and consequently errors in the ion dose measurements. Figure 29 shows the effect of various instantaneous currents and the averaged currents on the rate of change of sheet conductivity with dose. Within experimental errors, of 10–20%, no apparent variation can be observed in the rate of change in sheet conductivity with ion dose for different beam currents.

Dosimetrical errors, due to background counts, were about 15 of the incremental dose for 10 nA full scale deflection current setting of the current integrator. In few experiments where very low ion doses were irradiated ($<10^{10}$ cm$^{-2}$), where current settings of 100 nA were used, the errors were larger and were estimated to be about 40%.

Other errors in the measurements of ion beam were a consequence of the many erroneous component currents which flow through the target
Figure 28. Ion beam monitoring and measurement circuit.
Figure 29. The variation of the sheet conductivity with dose for 1.5 MeV Proton irradiation for various ion beam instant and average currents.
chamber [100], and were estimated to be about 2-5%, see the appendix. Thus the maximum dosimetric errors were considered to be about 20%.

Current densities of 1-5 nA/cm$^2$ were used for the irradiations. The effect of varying the current density between 1-10 nA/cm$^2$ for Proton irradiation was investigated, as shown on figure 29. Within experimental errors, rate of change in sheet conductivity with ion dose remains constant. The current densities for high energy lower mass ions were chosen so that the average beam current was of the order 1 nA, and for heavier ions the beam currents were kept below 0.5 nA.

All irradiations were carried out at room temperature and at 8° to the surface normal. The vacuum pressure in the specimen chamber was 3-7x10^-6 torr, using a liquid nitrogen cold trap above an oil diffusion pump.

4.3 Electrical measurements

The electrical conductivity and the free carrier concentration of the irradiated samples were measured in three ways, as follows:

1) Sheet conductivity measurements in the Van de Graaff target chamber, after each incremental dose irradiation.

2) Hall effect measurements before and after each irradiation set

3) Differential Hall effect measurements, after all irradiations.
Figure 30. a) Block diagram of the measurement circuit, b) configuration for (i) Sheet resistivity and (ii) Hall resistivity measurements.
<table>
<thead>
<tr>
<th>Switch 1</th>
<th>Switch 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( I^+ \rightarrow ab )</td>
<td>( V \rightarrow cd )</td>
</tr>
<tr>
<td>2 ( I^+ \rightarrow bc )</td>
<td>( V \rightarrow da )</td>
</tr>
<tr>
<td>3 ( I^- \rightarrow ba )</td>
<td>( V \rightarrow dc )</td>
</tr>
<tr>
<td>4 ( I^- \rightarrow cb )</td>
<td>( V \rightarrow ad )</td>
</tr>
<tr>
<td>5 ( I )</td>
<td>( V )</td>
</tr>
</tbody>
</table>

Figure 30.c) table showing the switching positions used for the sheet resistivity measurements.
4.3.1 Sheet conductivity

The sheet conductivity was determined using samples with a four terminal Van der Pauw geometry.

The measurement circuit is shown in figure 30 and includes a Keithley constant current source and a high internal resistance digital voltmeter (Solarton A200 DVM). The wafer switch S1 has two positions, the first shorts the sample contacts and is selected when measuring the ion beam current. The second position, is selected when measuring the sheet conductance, using the configurations shown in figure 30 (c).

For each measurement set, four voltage readings \( V_{cd}, V_{da}, V_{dc} \) and \( V_{ad} \) and a value for the constant current \( I_c \) is obtained. Substituting these measurements in equation 11, due to Van der Pauw [198], a value for the sheet conductivity can be determined:

\[
\frac{1}{\sigma_s} = \rho_s = \left( \frac{\pi}{\ln 2} \right) \frac{R_1 + R_2}{2} f\left( \frac{R_1}{R_2} \right)
\]

Where

\[
R_1 = \frac{1}{2} \frac{V_{cd} + V_{dc}}{I_c} \quad \text{and} \quad R_2 = \frac{1}{2} \frac{V_{ad} + V_{da}}{I_c}
\]

\( f(R_1/R_2) = \text{Van der Pauw's transcendental expression.} \)

For these measurements, the constant current was set at 50-70 \( \mu A \). This range of current was determined, in the preliminary experiments to be suitable.
The effects of light illumination, temperature increase and vacuum pressure on the sheet conductivity were, also, investigated and were found to produce a maximum change of less than 1%, and therefore were ignored.

4.3.2 Hall effect

The Hall effect is a galvanomagnetic effect, which is extremely sensitive to free electron density in a crystal. It involves measurements of the electric field set up when a magnetic field is applied at right angles to a current flow of electrons in a solid. The magnitude and the sign of the field can be used to determine the number and type of the majority carriers in the sample (see section 4.5).

Using the Van der Pauw geometry, enables values of the resistivity of the sample to be determined (see section 4.5). Therefore if the Hall effect and the resistivity measurements are carried out on the same sample, values for \( n_s \) and \( \mu_s \) can be derived. The magnetic field applied for the Hall effect measurements had a value of ±5 KG and was created by two water cooled coils.

The switching relay unit [124] was manually operated and sequentially gave measurement values for various configurations of voltage, current and magnetic field as shown in table 13. The data obtained after computation gave the values for the sheet Hall coefficient, \( R_{hs} \), the sheet resistivity, the carrier concentration and the sheet mobility.

The sheet resistivity has been calculated using equation 11 in section 4.3.1., and the sheet Hall resistivity is given by:

\[
R_{hs} = \frac{R_H}{d} = \frac{1}{B} \frac{\Delta V_B}{Ic}
\]

\[\text{(14)}\]
Table 13. Sequence of Hall effect measurements.

<table>
<thead>
<tr>
<th>SWITCHING SEQUENCE</th>
<th>CURRENT 50 A</th>
<th>MEASURED VOLTAGE</th>
<th>MAGNETIC FIELD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Iab⁺</td>
<td>Vcd</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ibc⁺</td>
<td>Vad</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ibd⁺</td>
<td>Vac</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Ibd⁺</td>
<td>Vac</td>
<td>B⁺</td>
</tr>
<tr>
<td>5</td>
<td>Ibd⁺</td>
<td>Vac</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Ibd⁺</td>
<td>Vac</td>
<td>B⁻</td>
</tr>
<tr>
<td>7</td>
<td>Iab⁻</td>
<td>Vdc</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Ibc⁻</td>
<td>Vda</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Ibd⁻</td>
<td>Vca</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Ibd⁻</td>
<td>Vca</td>
<td>B⁺</td>
</tr>
<tr>
<td>11</td>
<td>Ibd⁻</td>
<td>Vca</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>Ibd⁻</td>
<td>Vca</td>
<td>B⁻</td>
</tr>
</tbody>
</table>
Where $B$ is the magnetic field in unit of Tesla

d is the active layer thickness

$I_o$ is the constant current

$\Delta V_B = [V]_B-[V]_{B=0}$ (see table 11)

Having obtained $\sigma_s$ and $R_{Hs}$, the sheet carrier concentration can be calculated as follows:

$$n_s = \frac{r}{e R_{Hs}} \quad ----- (15)$$

Where $r \sim 1$, Hall scattering factor, that depends on the scattering mechanism and the impurity concentration.

e is the electric charge

the mobility may be determined as:

$$\mu_s = \frac{R_{Hs}}{\rho_s} \quad ----- (16)$$

4.3.3 Differential Hall measurements

Selected samples were depth profiled using differential Hall effect measurements. After each Hall effect measurement, a thin layer (~200-400Å) was chemically etched after which the Hall measurements were repeated. Using the equations in reference [102], differential values of the carrier concentration and the mobility were calculated. These values were plotted against the total depth removed to give a depth profile. By comparing these profiles with profiles from un-irradiated samples, it was possible to determine the change in the
carrier concentration as a result of the ion irradiation.

The etchant used was a solution of $\text{H}_2\text{SO}_4: \text{H}_2\text{O}_2: \text{H}_2\text{O}$ in the volume ratio of 1:1:125. The samples were immersed in the etchant for 1-2 minutes, which resulted in the removal of a layer of thickness of about 300Å. After a thorough rinsing in water, to remove all traces of the etchant, the samples were placed in a beaker of distilled water, that maintained the sample at a constant temperature and reduced the thermomagnetic effects, for the subsequent Hall effect measurement.

These measurements were continued until the voltage reading became unstable. The samples were then cleaned and a step height measurements was made using a Rank-Taylor-Hobson talystep, to determine the total etch depth.
4.4 Deuteron experiments

Deuteron irradiations were carried out at AERE, Harwell using the 3 MeV Van de Graaff and the Cockcroft-Walton accelerators, see tables 11 and 14. Two different sets of irradiations were carried out, as follows:

1)To determine the carrier removal rate of high energy (0.25 to 1.5 MeV) Deuterons and Protons, as summarized in table 15.
2)To dope samples with Deuterons, by low energy (30 keV) implantation, the details of which are shown on table 16.

For these irradiations, it was not possible to measure the changes in the sheet conductivity in the target chamber and the samples were therefore, measured at Surrey before and after each irradiation, as described in section 4.3.2. The irradiation geometry and the experimental details were similar to those used at Surrey.

After these irradiations and measurements some of the samples were further irradiated, at the University of Surrey, with 1.5 MeV protons. This experiment enabled the carrier removal rate (see section 4.5.1) in the Deuteron implanted GaAs to be determine.

Selected samples were heat treated at 325°C for 10 minutes (with no encapsulant) [4], to anneal out the Deuteron implantation damage.
<table>
<thead>
<tr>
<th>IRRADIATION DETAIL</th>
<th>Van de Graaff ACCELERATOR</th>
<th>Cockcroft-Walton ACCELERATOR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ION ENERGY</strong></td>
<td>0.25, 0.5, 0.75</td>
<td>30 KeV</td>
</tr>
<tr>
<td></td>
<td>1.5 (MeV)</td>
<td></td>
</tr>
<tr>
<td><strong>BEAM CURRENT</strong></td>
<td>10-15 nA</td>
<td>3 nA</td>
</tr>
<tr>
<td><strong>CURRENT RANGE</strong></td>
<td>20 nA</td>
<td>10 nA</td>
</tr>
<tr>
<td><strong>AREA</strong></td>
<td>8.03 cm²</td>
<td>9.08 cm²</td>
</tr>
<tr>
<td><strong>SUPPRESOR</strong></td>
<td>750 V</td>
<td>300 V</td>
</tr>
<tr>
<td><strong>&quot; VOLTAGE</strong></td>
<td>RING</td>
<td>CYLINDRICAL</td>
</tr>
<tr>
<td><strong>&quot; GEOMETRY</strong></td>
<td>4-5 cm</td>
<td>5-7 cm</td>
</tr>
<tr>
<td><strong>&quot; DIAMETR</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>VACCUM PRES.</strong></td>
<td>$10^{-3}$-$10^{-4}$ Torr</td>
<td>$10^{-5}$-$10^{-6}$ Torr</td>
</tr>
<tr>
<td><strong>ORIENTATION</strong></td>
<td>9° OFF NORMAL</td>
<td>7° OFF NORMAL</td>
</tr>
</tbody>
</table>

**TABLE 14.** Experimental parameters used at AERE, Harwell for Deuteron irradiations.
### TABLE 15 High energy irradiations at AERE, Harwell

<table>
<thead>
<tr>
<th>ION</th>
<th>ENERGY (MeV)</th>
<th>DOSE (cm(^{-2}))</th>
<th>ANNEALED</th>
<th>1.5 Mev PROTON TEST</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>1.5</td>
<td>5x10(^{11})-5x10(^{12})</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2x10(^{10})</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>D(^+)</td>
<td>1.5</td>
<td>2x10(^{10})-5x10(^{12})</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>5x10(^{11})</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>7x10(^{10})-3x10(^{11})</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2x10(^{10})</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>

### TABLE 16 Low energy implantations at AERE, Harwell

<table>
<thead>
<tr>
<th>ION and ENERGY (keV)</th>
<th>DOSE (cm(^{-2}))</th>
<th>ANNEALED</th>
<th>1.5 Mev PROTON TEST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton 30</td>
<td>4.2x10(^{11})</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td></td>
<td>1.0x10(^{12})</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td>2.0x10(^{12})</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td></td>
<td>1.0x10(^{13})</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td>2.0x10(^{13})</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>Deuteron 30</td>
<td>4.2x10(^{10})</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td></td>
<td>4.2x10(^{11})</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td></td>
<td>1.0x10(^{12})</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td>2.0x10(^{12})</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td></td>
<td>1.0x10(^{13})</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td>2.0x10(^{13})</td>
<td>YES</td>
<td>NO</td>
</tr>
</tbody>
</table>
4.5 Data analysis

4.5.1 Carrier removal cross section

This experiment was designed to monitor the number of carriers removed as a result of the radiation damage. Where the number of carriers removed is directly proportional to the number of defects created by the irradiation. To quantify, carrier removal rate, CRR, has been defined as:

\[
CRR = \frac{\Delta n}{\phi} = \frac{(n_o - n_f)}{\phi} \quad \text{(17)}
\]

Where \( n_o \) = The initial carrier concentration

\( n_f \) = The carrier concentration after a dose \( \phi \).

By substituting CRR in the standard rate reaction equation, see equation 3, a value for the carrier removal cross section can be derived:

\[
\sigma_{CR} = \frac{1}{N_o} \frac{\Delta n}{\phi} \quad \text{(18)}
\]

Where \( N_o \) = Atomic density (for GaAs=4.87x10^{22} \text{ cm}^{-3})
4.5.2 Analysis of the experimental data

In the following section the derivation of the CRR and the carrier removal cross section, \( \sigma_{\text{CR}} \), from the sheet conductivity and the Hall effects measurements will be described.

**Analysis of sheet conductivity data**

The free charge carrier concentration can be generally related to the specimen conductivity, \( \sigma \), as follows:

\[
\sigma = \frac{1}{\rho} = ne\mu_e + p\mu_h \quad ---(19)
\]

Where \( n, \mu_e \) and \( p, \mu_h \) are the carrier concentrations and the mobilities of electrons and holes, respectively. Since the material used were mainly n-type then:

\[
\sigma = ne\mu_e \quad ---(20)
\]

For the p-type material similar arguments can also be followed.

Thus for the "insitu" sheet conductivity measurements, see section 4.3.1, the change in the value of sheet conductivity with ion dose, \( \frac{\Delta \sigma}{\Delta \phi} \), can be related to the number of carriers removed per incident ion, CRR, and subsequently to the carrier removal cross section. Both the CRR and the cross section are determined by making assumptions and approximations as follows:

1) The mobility of the charge carriers remains constant under our irradiation conditions and is independent of ion dose, as reported by Hemment et al [299]. It will be shown in section 5.1.3, that this
assumption is an approximation and the calculated cross section should be used with caution.

2) The charge carriers are uniformly distributed over the thickness of the active layer. This assumption is valid for the dopant atomic profile, especially for the epitaxial material, where the dopant profile is uniform with depth. Furthermore, by assuming that the majority of the dopant atoms become active and that there is negligible compensation due to impurities, it may be assumed that the charge carrier profile closely follows that of dopant profile. For the ion implanted material, where the dopant profile follows a Gaussian distribution, it is possible to approximate the profile to a step function distribution; with the consequence of an uncertainty in the value of the carrier concentration of the order of 20 to 30%.

It should be noted that the assumed uniform distribution may not be valid at the interfaces. But since the material used was n/S.I. material, that is with no junction at or about the interface, it is assumed that no significant depletion of charge carriers is likely. Similarly it can be argued that at the surface the uniformity of charge carriers is again changed by very little.

3) The defect density is independent of depth and hence the carrier removal is uniform over the thickness of the conductive layer. This is a valid assumption since the projected range of the light ions is much greater than the conductive layer thickness, < 1.0 μm. Thus the rate of energy deposition in the earlier part of the ion track does not appreciably vary with the depth and may be considered to be uniform (see figure 13).

Using the first two assumptions, it may be shown that:
\[ \sigma_{CR} = \frac{1}{N_0 d e \mu_e} \frac{\Delta \sigma_s}{\Delta \phi} \] -----(21)

Where \( d \) = The active layer thickness

\( e \) = The electronic charge

\( \mu_0 \) = The initial mobility

Here, as in the first assumption, \( \mu_0 \) is considered to remain constant. But this is an over simplification, since the mobility degrades even at the relatively low levels of defects introduced in this study. For the ion implanted material this assumption does not introduce large errors as there is a much higher level of defects already present in the crystal.

**Analysis of Hall effect data**

The carrier concentration can be obtained from the Hall coefficient \( R_H \) as, for n-type material,

\[ n = \frac{\mu_h}{\mu_e} \frac{1}{R_H} \] -----(22)

Where \( \mu_h \) is the ratio of the Hall mobility to the conductivity mobility. The magnitude and the temperature dependence of this ratio has been determined empirically [204, 149] and shown to be close to unity. By making this assumption the errors introduced in the measurement will be \( \pm 15\% \).

By accepting the second and third assumption made in section 4.5.2, a second value for the CRR and the cross section may be derived.
In this case degradation of the mobility is accounted for. The values derived are therefore:

\[
\sigma_{\text{CR}} = \frac{1}{N_0} \text{CRR} = \frac{n_s - n_{s_0}}{N_0 \phi} = \frac{1}{N_0 \phi} \Delta n_s
\]  

(23)

Where \(\Delta n_s\) = the reduction in \(n_s\) with ion dose \(\phi\).

It is also possible to determine the CRR and CR cross section from the carrier concentration depth profile (section 4.3.3). No assumptions need to be made regarding the degradation of the mobility and the parameters may be calculated directly using the equations 17 and 18. The measurement of the depth profiles was not usually possible since most samples were irradiated with many ions of different mass and energy. However, few samples were depth profiled in order to determine the values of CRR and the cross section derived from this method.

4.5.3 Normalization procedures

The changes in the absolute values of the sheet conductivity or the charge carrier concentration, for a given ion and increment of dose, were found to vary between samples diced from the same wafer. At times the variations were up to 50-100% of one another. Because of this variability, the measured values of the sheet conductivity and carrier concentration have been normalized to an initial value of unity. In order to make comparison between samples the dose for each sample has been scaled by the same factor. Therefore for visual presentation and ease of comparison the figures in the results chapter have been normalised to the initial values. This will obviously not effect the slopes of the lines in the figures.
5 EXPERIMENTAL RESULTS

The experimental results are presented in five sections. In the first section, Section 5.1, the dependence of the sheet conductivity on the irradiation dose is shown and the determination of the rate of change of sheet conductivity with dose is discussed. Sections 5.2 and 5.3 present the normalized data for the dependence of sheet conductivity and carrier concentration on the ion dose and the derived carrier removal rates. The degradation of mobility with the irradiation dose is detailed in Section 5.4 and in Section 5.5 the effect upon the carrier removal rates of Deuteron doping is presented.

In the figures presented for the normalized data (in section 5.2, 5.3 and 5.4) each line represents the best fit line to data from 5 to 10 different samples prepared from the same wafer. This is in contrast to the presentation of the data in the next chapter were each data point represents one sample only.

5.1 Dose dependence of sheet conductivity

Figure 31 shows the variation of the sheet conductivity during irradiation with 1.5 MeV Protons over the dose range of $5 \times 10^{11}$ to $1 \times 10^{13}$ cm$^{-2}$ in a sample prepared from a material with carrier concentration of $1.2 \times 10^{17}$ cm$^{-3}$. This is a typical set of data and three regions can be identified on this graph, as shown on the figure. The first region, region "a", usually occurs over the dose range of $5 \times 10^{10}$ to $1 \times 10^{11}$ Protons/cm$^2$ and is where the sheet conductivity increases to a value of about 3-5% of the unirradiated sheet conductivity.
Figure 31. Typical experimental plot of the change of the sheet conductivity with ion dose as a result of 1.5 MeV Proton irradiation of n-GaAs with an initial carrier concentration of $1.2 \times 10^{17}$ cm$^{-3}$. 
conductivity value, in materials with initial carrier concentration in the range $10^{15}$ to $10^{17}$ cm$^{-3}$. This region is attributed to the surface states and the subsequent saturation of such states [185]. For CRR calculations this region is avoided and in practice the first incremental dose is made large enough to overcome this initial change.

Within region "b", the sheet conductivity has a linear dependence upon dose and the gradient of the line, $\frac{\Delta \sigma_s}{\Delta \phi}$, is used to calculate the CRR. This linear dependence is observed for a change in the sheet conductivity of 30 to 50% of the unirradiated value, for Proton doses of $1 \times 10^{12}$ to $5 \times 10^{12}$ cm$^{-2}$. Any further irradiation (region "c") causes a non-linear variation in the sheet conductivity with ion dose, until at high doses, typically $1 \times 10^{13}$ Proton cm$^{-2}$, the conductivity reaches a steady value at about 80 to 100% of the unirradiated value.

For the linear region, region "b", the gradient, m, and the coefficient of correlation, r, for the best fit line to the data points are derived using the linear regression method. The gradient of the line fitted is equal to $\frac{\Delta \sigma_s}{\Delta \phi}$; and since very little scatter have been observed in the data point, it is justified to consider the coefficient r as the degree of linearity of the data points. Non-linearity values, $(1-r)$, of up to 0.2 were tolerated. This range of acceptable values was large enough to accommodate the spread in the data points due to systematic errors, but was small enough to exclude the data points from the non-linear region, region "c". During Proton irradiation experiments at least seven data points were used to gain a good statistical values for both m and r. The variation in the values of m obtained from 7 up to 10 data point were from 5% up to 10%.

A typical set of data showing the variation of the sheet
conductivity with the dose of 1.5 MeV Helium ions is presented in figure 35. The number of data points used to determine $\frac{\Delta \sigma}{\Delta t}$, in this figure, is reduced because of the more rapid rate of change in the sheet conductivity with dose. For Helium it was customary to take between 3 to 6 points, which gave between 10% to 20% variation in the value of the slope of the best fit line.

By using each sample several times, for various ion and energy combinations, the relative values of the rate of change in sheet conductivity with the ion dose were found, as illustrated in figures 32 and 33. These are typical sets of results. The best fit lines to the data points clearly show the relative values of the rate of change in the sheet conductivity with ion dose.

The lines on both figures are discontinous, this is due to the recovery of the sheet conductivity on each occasion that the Van de Graaff accelerator parameters were changed. Beam heating and the subsequent cooling down were thought to be largely responsible for this recovery. To check this effect a set of preliminary experiments were carried out to investigate the recovery of sheet conductivity with time and temperature. Figure 34 shows the change with time, after a relatively small dose ($5 \times 10^{11}$ cm$^{-2}$) of Proton at 1.5 MeV that resulted in to 20% change in the sheet conductivity. It can be seen that after 4-7 minutes the rate of change in the sheet conductivity slows down and reaches a value 1-2% of the post-irradiation value for the sheet conductivity. The time that usually elapsed between each resetting of the ion accelerator was between 5-10 minutes and similar recoveries as in figure 34 were experienced. This recovery also must have occurred during the "insitu" measurements, that is after each
Figure 32. Change in the sheet conductivity with ion dose as a result of Proton irradiation at different energies.

Figure 33. Change in the sheet conductivity with ion dose as a result of 1.5 Mev H$_1^+$, H$_2^+$, H$_3^+$ and He$^+$ ion irradiation.
Figure 34. Variation of the sheet conductivity with time, after 1.5 MeV Proton irradiation dose of $5 \times 10^{11}$ cm$^{-2}$. 
Figure 35. Typical variation of sheet conductivity with dose as a result of 1.5 MeV Helium ions irradiation.
incremental dose irradiation. However the measurements were always carried out systematically and the time that elapsed between each measurement were of the order of few seconds.

The rate of change of the sheet conductivity with temperature was also investigated and a similar recovery rate to that shown in figure 34 was recorded. It was concluded, therefore, that the major cause of the recovery was due to temperature variation.

5.2 Dose dependence of the normalized sheet conductivity

In this section the variations of the normalized sheet conductivity with the dose of 1.5 MeV ions are presented. Each figure presented, shows the data points from a particular material type, irradiated similarly, that is the ion implanted material or the Epi material etc. Each solid line shown on the figures, on the other hand, is the best fit line to the data points from the samples sliced from the same wafer and, therefore, have the same carrier concentrations. So typically each line may represent the data for between 2 to 5 samples.

Ion implanted samples

Figures 36 and 37 show the dependence of the normalized sheet conductivity with the dose of 1.5 MeV Protons for both the n- and p-type ion implanted samples. For the n-type ion implanted material, figure 36, distinctive groups of data points can be observed. The slope of the best fit lines to these points have been calculated and the resulting CRR are tabulated in table 17.

For the 700°C and the 900°C annealed samples the values of the
Figure 36. Normalized sheet conductivity against the normalized dose of 1.5 MeV Proton irradiation of n-type GaAs samples (Ion implanted).
Figure 37. Normalized sheet conductivity against the normalized dose of 1.5 MeV Proton irradiation of p-type GaAs samples (Ion implanted).
<table>
<thead>
<tr>
<th>CONDUCTIVITY TYPE</th>
<th>IMPLANTATION CONDITIONS</th>
<th>ANNEALING TEMPERATURE</th>
<th>SLOPE OF THE LINE</th>
<th>CARRIER REMOVAL RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DOSE ION ENERGY cm² keV</td>
<td>°C</td>
<td>x10⁻³</td>
<td>cm⁻¹ x10³</td>
</tr>
<tr>
<td>n-type</td>
<td>3x10¹³ Se⁺ 400</td>
<td>700</td>
<td>0.33</td>
<td>3.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>0.30</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>5x10¹³ 390</td>
<td>700</td>
<td>0.46</td>
<td>4.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>0.35</td>
<td>8.33</td>
</tr>
<tr>
<td></td>
<td>2x10¹⁴</td>
<td>700</td>
<td>2.44</td>
<td>19.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>0.11</td>
<td>0.44</td>
</tr>
<tr>
<td>p-type</td>
<td>2x10¹³ Cd⁺ 350</td>
<td>900</td>
<td>0.06-0.53</td>
<td>1.5-6.4</td>
</tr>
<tr>
<td></td>
<td>1x10¹³ Zn⁺ 400</td>
<td>700</td>
<td>0.02</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>1x10¹⁵</td>
<td>700</td>
<td>0.08</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 17 CRR for n- and p-type ion implanted material, derived from sheet conductivity measurements.
CRR increase with the doping concentration, except for the material implanted with $2 \times 10^{14}$ Se$^+$/cm$^2$ and annealed at 900°C.

For the p-type ion implanted material, figure 37, again, distinct groups of data points can be observed. It should be emphasised that for the P-type material the results are not conclusive since very few p-type samples were investigated and only exploratory experiments were completed. The slope of the lines and the values of the CRR are listed in the lower part of table 17.

**Epitaxial samples**

Figures 38 and 39 show the normalized sheet conductivity plotted against dose of 1.5 MeV Protons, for samples prepared from Epi I and Epi II materials. The CRR values derived hence, are tabulated in table 18, with the upper part of the table showing the results for the Epi I material. The lower part of the table is for Epi II material and is divided into two parts to distinguish between the different irradiations carried out at Surrey University and at AERE (see section 4.2).

For the Epi I material, with initial carrier concentration values of between $2.7 \times 10^{15}$ to $8.4 \times 10^{16}$ cm$^{-2}$, an increase in the value of CRR is observed with increasing carrier concentration. The materials with carrier concentrations of $1.4 \times 10^{17}$ and $3.2 \times 10^{17}$ cm$^{-3}$, however did not follow the same trend, this was attributed to the fact that these two materials were doped with Sulphur. But still for the two materials it is noticed that CRR increases with the increase in the carrier concentration. It is essential to note that each best fit line is fitted to the data points from 5 to 10 samples.
Figure 38. Normalized sheet conductivity against the normalized dose of 1.5 MeV Proton irradiation of n-type GaAs samples (Epi I).
Figure 39. Normalized sheet conductivity against the normalized dose of 1.5 MeV Proton irradiation of n-type GaAs samples (Epi II).
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>MEASURED CARRIER CONC. cm(^{-3})</th>
<th>SLOPE OF THE LINE x10(^{-3}) cm(^{-1})</th>
<th>C R R x10(^3) cm(^{-1})</th>
<th>PLACE OF IRRADIAT.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPI I</td>
<td>2.7x10(^{15})</td>
<td>1.41</td>
<td>2.43</td>
<td>Surrey</td>
</tr>
<tr>
<td></td>
<td>1.4x10(^{16})</td>
<td>2.41</td>
<td>4.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.2x10(^{17})</td>
<td>5.61</td>
<td>16.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.4x10(^{16})</td>
<td>6.02</td>
<td>8.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.4x10(^{17})</td>
<td>1.05</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>EPI II</td>
<td>5.3x10(^{16})</td>
<td>1.02</td>
<td>3.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.2x10(^{16})</td>
<td>1.49</td>
<td>5.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.5x10(^{16})</td>
<td>0.63</td>
<td>5.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.1x10(^{15})</td>
<td>0.55</td>
<td>2.91</td>
<td>AERE</td>
</tr>
<tr>
<td></td>
<td>6.2x10(^{16})</td>
<td>2.16</td>
<td>7.40</td>
<td>AERE</td>
</tr>
<tr>
<td></td>
<td>9.2x10(^{16})</td>
<td>2.66</td>
<td>16.55</td>
<td>AERE</td>
</tr>
</tbody>
</table>

Table 18. CRR for EPI I and EPI II material irradiated with 1.5 MeV Protons (from figures 38 and 39)
For the Epi II material, irradiated at Surrey University, the CRR increases with increasing carrier concentration. Although the materials used had very similar carrier concentrations (between $5.3 \times 10^{16}$ and $6.5 \times 10^{16}$ cm$^{-3}$), but still an increase in the value of CRR of about 40% was observed.

For the irradiation at AERE, similar increases in the values of CRR with the initial carrier concentration were observed. The value of CRR increased by a factor of 5 over carrier concentration range of $2.1 \times 10^{15}$ to $9.2 \times 10^{16}$ cm$^{-3}$. The data points for best fit line (labelled 4) for the material with $2.1 \times 10^{15}$ cm$^{-3}$ carrier concentration are outside the range of figure 39 and an extrapolation is only shown.

For 1.5 MeV Deuterons and Helium irradiation, figures 40 and 41 show the variation of normalized sheet conductivity with the ion dose. Tables 19 and 20 respectively indicate the values of CRR, as derived from these figures.

For the Deuteron irradiations, again, an increase in the CRR with the initial carrier concentration can be observed.

For Helium ions, no definite trend can be observed. Although it is noted that the CRR obtained for the Epi II material is generally lower, by a factor of 4 to 5, than the values obtained for the samples prepared from the Epi I material. In general the errors in the calculation of CRR were estimated to be about $\pm 37\%$, from the sheet conductivity.
Figure 40. Normalized sheet conductivity against the normalized dose of 1.5 MeV Deuteron irradiation of n-type GaAs samples (Epi II), carried out at AERE.

Figure 41. Normalized sheet conductivity against the normalized dose of 1.5 MeV Helium irradiation of n-type GaAs samples (Epi I and Epi II).
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>MEASURED CARRIER CONC.</th>
<th>SLOPE OF THE LINE</th>
<th>C R R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>x10^{-3}</td>
<td>x10^{3} cm^{-1}</td>
</tr>
<tr>
<td>EPI II</td>
<td>2.1x10^{15}</td>
<td>0.40</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>6.2x10^{16}</td>
<td>2.90</td>
<td>9.02</td>
</tr>
<tr>
<td></td>
<td>9.2x10^{16}</td>
<td>3.70</td>
<td>22.49</td>
</tr>
</tbody>
</table>

Table 19. CRR for 1.5 MeV irradiation of Epi II samples, at AERE

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>MEASURED CARRIER CONC.</th>
<th>SLOPE OF THE LINE</th>
<th>C R R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>x10^{-3}</td>
<td>x10^{3} cm^{-1}</td>
</tr>
<tr>
<td>Ion impl.</td>
<td>1x10^{17}</td>
<td>3.1</td>
<td>33.55</td>
</tr>
<tr>
<td>Epi I</td>
<td>2.7x10^{15}</td>
<td>6.7</td>
<td>68.51</td>
</tr>
<tr>
<td></td>
<td>1.4x10^{16}</td>
<td>24.0</td>
<td>46.6</td>
</tr>
<tr>
<td></td>
<td>3.2x10^{17}</td>
<td>32.0</td>
<td>76.1</td>
</tr>
<tr>
<td>Epi II</td>
<td>5.3x10^{16}</td>
<td>2.6</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>6.2x10^{16}</td>
<td>2.7</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Table 20. CRR for 1.5 MeV Helium irradiation for all samples.
5.3 Dose dependence of the normalized carrier concentration

The carrier concentration was determined from Hall effect measurements, as described in section 4.3.2. From these measurements only two data points per sample were obtained, before and after each irradiation, thus the points shown on the figures are limited. But each best fit line represents up to 5 different samples sliced from the same wafer. The number of different materials investigated were limited, this was because the majority of the samples were used for the "insitu" multiple irradiation, and thus Hall measurements were not always possible. Figure 42 shows the normalized carrier concentration plotted against the dose of 1.5 MeV Protons, and values of the CRR presented in table 21. The best fit lines to data points for the samples prepared from the two wafers, $n_o = 5.3 \times 10^{16}$ and $6.2 \times 10^{16}$, were found to have the same gradients and the are shown as one line (line 1 on figure 42). Line 2, is for the samples prepared from the Epi I wafer with an initial carrier concentration of $2.7 \times 10^{15}$ cm$^{-3}$. For samples diced from the Epi II material, with a carrier concentration of $2.1 \times 10^{15}$ cm$^{-3}$, the gradient of the best fit line was found to be very close to line 2 and is not drawn on the figure. As can be seen from table 22 the value of the CRR increases with the doping concentrations.

Similarly, the values for the CRR in samples prepared from Epi II, as a result of 1.5 MeV Deuteron and Helium irradiations, were found and are listed in tables 22 and 23, respectively. For 1.5 MeV Deuteron irradiations, the CRR is found to increase with the doping concentrations. But for the Helium irradiations, no dependence of CRR with doping is evident, since samples from only two materials were investigated.
Figure 42. Normalized charge carrier concentration against the normalized dose of 1.5 MeV Proton irradiation of different materials.
### Table 21. CRR derived from Hall effect measurements for various materials irradiated with 1.5 MeV Protons, from figure 42.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>MEASURED CONCENTRATION</th>
<th>C R R \times 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion impl.</td>
<td>1 \times 10^{17}</td>
<td>11.2</td>
</tr>
<tr>
<td>EPI I</td>
<td>2.7 \times 10^{15}</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>8.4 \times 10^{16}</td>
<td>3.40</td>
</tr>
<tr>
<td>EPI II</td>
<td>2.1 \times 10^{15}</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>5.3 \times 10^{16}</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>6.2 \times 10^{16}</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>6.5 \times 10^{16}</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>9.2 \times 10^{16}</td>
<td>4.48</td>
</tr>
<tr>
<td>MATERIAL</td>
<td>MEASURED CONCENTRATION</td>
<td>C R R</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td>cm⁻³</td>
<td>x10³</td>
</tr>
<tr>
<td>EPI II</td>
<td>2.1x10¹⁵</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>6.2x10¹⁶</td>
<td>5.41</td>
</tr>
<tr>
<td></td>
<td>9.2x10¹⁶</td>
<td>13.92</td>
</tr>
</tbody>
</table>

Table 22. CRR of 1.5 MeV Deuterons in Epi II material at AERE.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>MEASURED CONCENTRATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm⁻³</td>
</tr>
<tr>
<td>EPI II</td>
<td>5.3x10¹⁶</td>
</tr>
<tr>
<td></td>
<td>6.2x10¹⁶</td>
</tr>
</tbody>
</table>

Table 23. CRR of 1.5 MeV Helium in Epi II material at Surrey.
Figure 43 shows the values of CRR against the initial carrier concentrations, for 1.5 MeV Protons, Deuterons and Helium irradiations. The increase in the values of the CRR with doping can clearly be seen in this figure. The dotted line drawn through the Helium points are only to guide the eye. The errors encountered in the calculation of CRR, in general, from the Hall effect measurements were estimated to be about 50% (see appendix).

**Differential Hall effect profiling**

Selected samples were depth profiled and the CRR determined from the integral over the carrier concentration depth profile (see section 4.3.3). The values of the CRR obtained, for samples diced from Epi II are listed in table 24, for 1.5 and 0.5 MeV Proton irradiations. The total uncertainty in the calculation of the CRR is estimated to be 50%, in each case. This experiment served to confirm trends and the order of magnitude of the CRR.

5.4 **Mobility degradation**

The mobility was found to degrade by about 20% to 30% in material with a carrier concentration of up to $10^{17}$ cm$^{-3}$, as a result of ion irradiation.

Figure 44 presents the degradation of mobility in various materials, for a dose of 1.5 MeV Protons, where both axis have been normalized to the initial value of the mobility. The slope of the best fit lines are tabulated in table 25. The same trend is evident for all of the samples, namely a more rapid mobility degradation in the lower doped material. Each line on the figure represents the data obtained
Figure 43. The variation of the carrier removal rate with initial carrier concentration. The irradiating particles were Protons, Deuterons and Helium at 1.5 MeV, using Hall effect measurements.
Table 24. CRR values derived from differential Hall measurements of Epi II samples irradiated with 0.5 and 1.5 MeV protons.

<table>
<thead>
<tr>
<th>MEASURED CARRIER CONCENTRATION (cm(^{-3}))</th>
<th>ION ENERGY (MeV)</th>
<th>CRR (x10^3) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1x10(^{15})</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>5.3x10(^{16})</td>
<td>1.5</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>6.6</td>
</tr>
</tbody>
</table>
Figure 44. Normalized charge carrier mobility against the normalized ion dose of 1.5 MeV Protons.
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>MEASURED CARRIER CONCENTRATION $\text{cm}^{-3}$</th>
<th>RATE OF MOBILITY CHANGE WITH DOSE $\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I/I</td>
<td>$1 \times 10^{17}$</td>
<td>0.51</td>
</tr>
<tr>
<td>EPI I</td>
<td>$2.7 \times 10^{15}$</td>
<td>7.70</td>
</tr>
<tr>
<td></td>
<td>$8.4 \times 10^{16}$</td>
<td>1.70</td>
</tr>
<tr>
<td>EPI II</td>
<td>$6.2 \times 10^{16}$</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>$5.3 \times 10^{16}$</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Table 25. Mobility degradation due to irradiation of ion implanted, Epi I and Epi II samples with 1.5 MeV Protons.
from one sample only. These samples were irradiated at the University of Surrey and, therefore, the variation in the mobility was kept within the linear region of the change in sheet conductivity with ion dose. For one sample prepared, from Epi II material \((6.2 \times 10^{16} \text{ cm}^{-3})\), the degradation was continued until the change in mobility became non-linear at about 35% of the initial value, for a dose of \(1 \times 10^{13} \text{ Proton/cm}^2\). The errors in the calculation of mobility is estimated to be about 1-2\% (see appendix).

Figure 45, for the material irradiated at AERE, presents the mobility degradation due to 1.5 MeV Protons and Deuterons, where the mobility degradation rates are listed in table 26. Figure 46 shows the rate of mobility degradation against the initial carrier concentration.

Figures 47 and 48 show the energy dependence of the mobility degradation rates, for Proton and Deuteron irradiations respectively. The degradation rate is found to decrease with increasing irradiation energy. Table 27 and figure 49 show the accumulated results of the previous two figures, where for Deuterons a more rapid rate of change in mobility degradation are observed, than for Protons.

The degradations of mobility in similar samples, for 1.0 MeV Deuterons and 0.5 MeV Protons are found to be similar. This is consistent with the relative CRR shown in the previous section. It is, therefore, concluded that in these experiments Deuterons creat damage at a rate which is typical of a projectile of mass 2 amu.
1.5 MeV proton: (1) $2.1 \times 10^{15}$ cm$^{-3}$
(2) $9.2 \times 10^{16}$ cm$^{-3}$
1.5 MeV deuteron: (3) $2.1 \times 10^{15}$ cm$^{-3}$
(4) $6.2 \times 10^{16}$ cm$^{-3}$
(5) $9.2 \times 10^{16}$ cm$^{-3}$

Figure 45. Normalized charge carrier mobility against the normalized dose of 1.5 MeV Protons and Deuterons of Epi II samples.

Figure 46. Dependence of the mobility degradation upon the initial carrier concentration of samples irradiated with 1.5 MeV Protons and Deuterons.
Table 26. Mobility degradation in Epi II samples due to irradiation with 1.5 MeV Protons and Deuterons.

<table>
<thead>
<tr>
<th>ION</th>
<th>MEASURED CARRIER CONCENTRATIONS (cm⁻³)</th>
<th>RATE OF MOBILITY CHANGE WITH DOSE x10³ (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton</td>
<td>2.1x10¹⁵</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>9.2x10¹⁶</td>
<td>2.23</td>
</tr>
<tr>
<td>Deuteron</td>
<td>2.1x10¹⁵</td>
<td>2.42</td>
</tr>
<tr>
<td></td>
<td>6.2x10¹⁶</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>9.2x10¹⁶</td>
<td>3.38</td>
</tr>
</tbody>
</table>
Figure 47. Dependence of the normalized mobility upon the normalized ion dose for Proton irradiation in the energy range of 0.5 to 1.5 MeV.

Figure 48. Dependence of the normalized mobility on normalized ion dose for Deuteron irradiation in the energy range of 0.25 to 1.5 MeV.
<table>
<thead>
<tr>
<th>ION ENERGY (MeV)</th>
<th>MOBILITY DEGRAD. PROTON x10³</th>
<th>MOBILITY DEGRAD. DEUTRON x10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>1.15</td>
<td>1.38</td>
</tr>
<tr>
<td>1.0</td>
<td>1.82</td>
<td>3.07</td>
</tr>
<tr>
<td>0.75</td>
<td>2.34</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>3.09</td>
<td>11.51</td>
</tr>
<tr>
<td>0.25</td>
<td>-</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Table 27. Mobility degradation due to Protons and Deuterons irradiation of Epi II samples at various energies, from figures 47 and 48.
Figure 49. The energy dependence of the degradation of mobility with ion dose in samples irradiated with Protons and Deuterons.
5.5 Deuteron doping effect on the carrier removal rates

Samples from the Epi II set were implanted with 30 keV Deuterons and Protons at AERE, Harwell (see section 4.4). These samples were subsequently irradiated with 1.5 MeV Protons at the University of Surrey, to determine whether the presence of the Deuterons modifies the CRR during the Proton irradiation. Selected samples were heat treated to anneal out the damage caused during the implantation of the Deuterons and, therefore, study the effect of Deuteron doping only.

The implanted doses were between $4.2 \times 10^{10}$ to $2 \times 10^{13}$ cm$^{-2}$, which gave a volume concentration in the range $1 \times 10^{15}$ to $5 \times 10^{17}$ cm$^{-3}$. These concentrations were determined by assuming that the implanted profiles of Deuterons and Protons could be approximated to a step function. Details of the implanted material and the estimated volume concentrations are listed in table 28.

The materials used had carrier concentrations of $6.5 \times 10^{16}$ and $9.2 \times 10^{16}$ cm$^{-3}$, which lie within the range of the volume doping profiles of table 28. Samples implanted with Deuteron doses of greater than $2 \times 10^{12}$ cm$^{-2}$ were found to be of high resistance and could not be used for further experiments.

1.5 MeV Protons irradiation test

Figure 50 shows dependence of the carrier removal rate (obtained from sheet conductivity measurements) upon the volume concentrations of Deuteron and Proton doping, both annealed and un-annealed samples. The CRR of 1.5 MeV Protons in undoped material is indicated by the arrow.
Table 28. Implanted dose and estimated volume conc. for 30 keV Proton and Deuteron implants in A and B samples.

\[ A = 9.2 \times 10^{16} \text{ cm}^{-3} \quad \text{and} \quad B = 6.5 \times 10^{16} \text{ cm}^{-3} \]

![Graph showing the dependence of the carrier removal cross section upon the Deuteron volume concentration and implanted Deuteron dose.](image-url)
CHAPTER SIX

6 DISCUSSION

The discussion is presented in three sections. The first section considers the variation of the carrier removal cross section with ion energy, mass (section 6.1.1) and ion molecular species (section 6.1.2).

In the second section the dependence of the carrier removal rate upon the initial carrier concentration of the irradiated material is considered (section 6.2.1), and an estimate of the defect introduction rate, DIR, is made (section 6.2.2.).

In the third section the change in the carrier removal rate in samples doped by Deuteron implantation is discussed (section 6.3.1), and comparisons are made with high energy Deuteron irradiations (section 6.3.2).

6.1 Carrier removal cross section

By making the assumption that, on average, one lattice defect is required for each carrier removed [103], then it is possible to calculate a carrier removal cross section. This cross section may then be used as an indication of the amount of damage created by the irradiation. It is appropriate to compare the carrier removal cross section with the elastic displacement cross section for Frenkel pair production, which is calculated from the model suggested by Kinchin and Pease [116]. Such a comparison determines the dominant energy loss process responsible for the damage production in the conditions set by this experiment.
6.1.1 Mass and energy dependence

Energy dependence

The dependences of the carrier removal cross section upon ion energy for Protons and Deuterons are shown on figures 51 and 52 respectively, where the cross section has been derived from the sheet conductivity measurements. Each data point on this figure is derived from an experimental determination of the CRR, which required 5 to 7 increments of dose (see section 5.1.2).

Figure 51 shows the energy dependence of the carrier removal cross section in the Epi II material \(n_0=5.3 \text{ and } 8.4 \times 10^{16} \text{ cm}^{-3}\) for Proton irradiations. The dashed lines are the best fit line to the experimental points. It is emphasised that in this section each data point represents one sample and the best fit line is drawn to the data points from samples diced from the same wafer. The solid line shows the energy dependence of the cross section derived from the Kinchin and Pease elastic displacement model [116] (see section 3.2.2). The displacement energy, \(E_d\), is assumed to be 17.5 eV. The error in the experimental values is estimated to be about 37\%, as described in the appendix.

Similar data for Deuteron irradiated samples is shown in figure 52. Here samples were prepared from materials with initial carrier concentration of \(6.2 \times 10^{16} \text{ and } 9.2 \times 10^{16} \text{ cm}^{-3}\). In this experiment, samples were irradiated at AERE, Harwell; whilst the conductivity measurements, both before and after the irradiations, were made at University of Surrey. For this reason the carrier removal cross section was determined after only one irradiation. The large spread in
Figure 51. The carrier removal cross section as a function of energy for Proton irradiated epitaxial samples, with $n_0 = 8.4 \times 10^{16}$ cm$^{-3}$ (Epi I) and $5.3 \times 10^{16}$ cm$^{-3}$ (Epi II), derived from the sheet conductivity measurements. The solid line represents the theoretical energy dependence for a particle of mass 1 amu, calculated using the Kinchin and Pease theory [116].
Figure 52. The carrier removal cross section as a function of energy for Deuteron irradiated epitaxial samples, with $n_0=6.2 \times 10^{16}$ cm$^{-3}$ and $9.2 \times 10^{16}$ cm$^{-3}$ (Epi II), derived from the sheet conductivity measurements. The solid line represents the theoretical energy dependence for a particle of mass 2 amu, calculated using the Kinchin and Pease theory [116].
the data, evident in figure 52, is believed to be as a consequence of taking only single measurements. In addition there was variability in the elapsed time between the irradiation and the measurement and, thus, different amounts of recovery and change in the surface states was possible (see section 4.3).

For Helium ions, the variation of the carrier removal cross section (derived from sheet conductivity measurements) with the ion energy are shown on figure 53 for the material with an initial carrier concentration of \(5.3 \times 10^{16}\) cm\(^{-3}\).

Figure 54 and 55 show the variation of the carrier removal cross section with ion energy for Protons and Deuterons, respectively. In these experiments the carrier removal cross section has been calculated using the Hall effect data (see section 5.3). The samples used were prepared from materials with initial carrier concentration of \(n_0 = 5.3 \times 10^{16}\) and \(8.4 \times 10^{16}\) cm\(^{-3}\) for the Proton irradiation and \(n_0 = 6.2 \times 10^{16}\) and \(9.2 \times 10^{16}\) cm\(^{-3}\) for the Deuteron irradiations. The error in the cross section is estimated to be about 50%. Again a similar dependence of the cross section on the ion energy can be seen, although the scatter is large. This scatter in the data points is due to the limited number of data points recorded for each sample. As explained in section 4.3.2, the Hall measurements were only possible before and after each irradiation.

As can be seen, the absolute value of the cross section, at all energies, does not correspond with the theoretical predictions. However in the present context the absolute values are not important, since the measured values may be particular to this experimental technique. A comparison of the experimental and the theoretical energy
Figure 53. The carrier removal cross section as a function of energy for Helium irradiated epitaxial samples, with \( n_0 = 5.3 \times 10^{16} \text{ cm}^{-3} \) (Epi II), derived from the sheet conductivity measurements. The solid line represents the theoretical energy dependence for a particle of mass 4 amu, calculated using the Kinchin and Pease theory [116].
Figure 54. The carrier removal cross section as a function of energy for Proton irradiated epitaxial samples, with \( n_0 = 8.4 \times 10^{16} \text{ cm}^{-3} \) (Epi I) and \( 5.3 \times 10^{16} \text{ cm}^{-3} \) (Epi II), derived from the Hall effect measurements. The solid line represents the theoretical energy dependence for a particle of mass 1 amu, calculated using the Kinchin and Pease theory [116].
Figure 55. The carrier removal cross section as a function of energy for Deuteron irradiated epitaxial samples, with $n_0=6.2 \times 10^{16}$ cm$^{-3}$ and $9.2 \times 10^{16}$ cm$^{-3}$ (Epi II), derived from the Hall effect measurements. The solid line represents the theoretical energy dependence for a particle of mass 2 amu, calculated using the Kinchin and Pease theory [116].
dependence can best be achieved by considering the gradient of the best fit lines. It is emphasised that these figures are on a log-log scale and, therefore, the gradients of the best fit lines show the power dependence of carrier removal cross section upon the ion energy.

As discussed in section 2.2.2., Pabst and Palmer [163] used ion channelling/backscattering experiments to determine the experimental values of the defect production cross section, for non-channelled 300 keV Proton and Helium ions. For ions of this energy they found that the cross section for the displacement of Si atoms is eight times greater than the value calculated using the Kinchin and Pease elastic displacement model. Kool et al [122], used similar experimental conditions, and found that the energy dependence of the displacement cross section is not consistent with the elastic collisions theory. He suggested that the discrepancy is due to two processes being active. Palmer [164] discussed this anomaly and gave as a possible explanation, the combination of elastic collisions and inner and outer shell ionization, causing reduction of displacement energy by bond weakening. Titley [197] has carried out similar experiments on GaAs and reported that the defect production rate is significantly in excess of that calculated using the elastic collisions theory. Dearnaley et al [59] have also detected a high defect introduction rate in GaP and suggested models that involve outer-shell ionization induced displacements (see section 2.2.2). Barker and Palmer [5] irradiated Ge with 300 keV Proton and Helium ions and from channelling/backscattering measurements, found a defect introduction rate at a depth of 75 nm that is dependent on the energy as $E^{-0.39}$. These workers compared the experimental defect introduction rates with the binary-elastic
collision defect introduction rates, which are dependent on the ion
energy as $E^{-1}$ [164]. They concluded that when considering defect
introduction rates it is necessary to include defects which are formed
by displacement mechanisms that are dependent upon the ionization
effects. If the carrier removal cross section is considered to be
indicative of the production rate of the electrically active defects
and, therefore, the DIR. Thus it is possible to compare the results
obtained from this experiment with the work of Barker and Palmer.
Although their irradiation energy is lower than in this experiment, but
still, from this experiment no enhanced defect introduction rates is
expected at 300 keV irradiation.

Hemment et al.[103] carried out 1.5 MeV Proton irradiations of
highly doped n-type layers in Si, in non-channelling and channelling
directions, to investigate the effect of inelastic energy loss
processes. By monitoring the sheet conductivity, they found that the
values of carrier removal cross section were similar to the theoretical
values calculated using the Kinchin and Pease theory and, therefore,
concluded that the dominant mechanism for damage creation is elastic
scattering.

From these experiments, the energy dependence of the carrier
removal cross section has been found and the values are shown in table
29, where $x$ is the power dependence of the energy, as $E^x$, and $r$ is the
coefficient of correlation for the best fit lines to the data points.
The dependence on the ion energy is found to closely resemble the K-P
elastic collisions dependence, for Protons and Deuterons. For Helium
the energy dependence ($E^{-1.31}$) is found to be greater than the
theoretical predication. However, because of the large experimental
<table>
<thead>
<tr>
<th>ION</th>
<th>CARRIER CONCENTRATION cm⁻³</th>
<th>DIR ± Eₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sheet Cond. x r</td>
</tr>
<tr>
<td>H⁺</td>
<td>5.3x10¹⁶</td>
<td>-0.66 0.89</td>
</tr>
<tr>
<td></td>
<td>8.4x10¹⁶</td>
<td>-1.03 0.88</td>
</tr>
<tr>
<td>D⁺</td>
<td>6.2x10¹⁶</td>
<td>-0.89 0.41</td>
</tr>
<tr>
<td></td>
<td>9.2x10¹⁶</td>
<td>-0.90 0.69</td>
</tr>
<tr>
<td>He⁺</td>
<td>5.3x10¹⁶</td>
<td>-1.31 0.85</td>
</tr>
<tr>
<td>THEORETICAL K-P</td>
<td>-0.88</td>
<td></td>
</tr>
</tbody>
</table>

Table 29. The gradients of the best fit lines to the data points in figures 52 to 56 for Protons, Deuterons and Helium and the theoretical predication of the K-P elastic displacement model expressed as Eₓ. Where r is the coefficient of correlation for best fit line.
errors, there is a large uncertainty associated with the value for Helium so the dependence of the carrier removal cross section on the ion energy may be similar to the theoretical predictions.

For comparison purposes figure 56 shows the variation of carrier removal cross section with ion energy for materials with \(n_o=5.3 \times 10^{16} \text{ cm}^{-3}\) for Protons and Helium and \(n_o=9.2 \times 10^{16} \text{ cm}^{-3}\) for Deuteron irradiations. Table 30 shows some values for the carrier removal cross section from this experiment, from K-P theoretical considerations and as reported in the literature.

**Mass dependence**

From the best fit lines to the experimental points in figure 56, the ratios of the cross sections for Deuterons and Helium ions relative to Protons has been calculated for ion energies of 2.0, 1.5, 1.0 and 0.5 MeV. However for the Deuteron irradiation the material used had a carrier concentration slightly greater than the material used for the Proton and Helium irradiations. But as can be seen from the next section, the difference between the carrier concentrations is relatively small and the variation in carrier removal cross section, as a result of the change in the carrier concentration, is expected to be less than 15% for 1.5 MeV Deuterons. Since the errors are between 37% to 50%, then the ratio of cross sections for the two ions even in different materials can be used for comparison and as a good estimate of the mass dependence. In table 31, the ratios of the cross sections for Helium and Deuteron are shown with respect to Protons for energies of 2.0, 1.5, 1.0 and 0.5 Mev. As can be seen from the table the relative ratio for deuteron to Protons varies from 2.8 at 2.0 MeV to 3.8
Table 30. Values for Frenkel pair production in GaAs (K-P) for Proton irradiation, with \( E_d = 17.5 \text{ eV} \). Also included are the carrier removal cross section calculated from this experiment \( (n_0 = 5.3 \times 10^{16} \text{ cm}^{-3}) \) and from the carrier removal at the surface estimated by (1) Matsumara et al [143] and (2) Pruniaux et al [168].

<table>
<thead>
<tr>
<th>ENERGY (MeV)</th>
<th>CROSS SECTION x10^{-19} cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>THEORETICAL (Kinchin-Pease)</td>
</tr>
<tr>
<td></td>
<td>CARRIER Removal (this experiment)</td>
</tr>
<tr>
<td></td>
<td>REPORTED</td>
</tr>
<tr>
<td>2.0</td>
<td>1.15</td>
</tr>
<tr>
<td>1.5</td>
<td>1.45</td>
</tr>
<tr>
<td>1.0</td>
<td>2.05</td>
</tr>
<tr>
<td>0.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Figure 56. Comparison of the energy dependence of the carrier removal cross section for Proton, Deuteron and Helium irradiation, as derived from the sheet conductivity measurements. The solid lines represent the theoretical energy dependence calculated using the Kinchin and Pease theory [116].
Table 31. The relative values of carrier removal cross section for Deuterons and Helium with respect to Protons, at various energies. The relative theoretical values are also shown.

<table>
<thead>
<tr>
<th>Energy MeV</th>
<th>ratio D/H</th>
<th>ratio HE/H</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>2.8</td>
<td>15.4</td>
</tr>
<tr>
<td>1.5</td>
<td>2.9</td>
<td>19.5</td>
</tr>
<tr>
<td>1.0</td>
<td>3.2</td>
<td>27.0</td>
</tr>
<tr>
<td>0.5</td>
<td>3.8</td>
<td>47.2</td>
</tr>
<tr>
<td>Theoretical K-P</td>
<td>2.1</td>
<td>18.2</td>
</tr>
</tbody>
</table>

Theoretical K-P
at 0.5 MeV ion energy, thus as the irradiation energy decreases the ratio diverges significantly from the theoretical ratio of 2.2, derived from the elastic displacement cross sections. Blood et al [20] irradiated VPE Si-doped GaAs \(n_o=2 \times 10^{15} \text{ cm}^{-3}\), with 300 keV Deuterons and Protons, at low doses of \(10^{10}-10^{11} \text{ cm}^{-2}\), and found this ratio to be about 2.4. Therefore, concluding that the ratio must follow the isotopic mass dependence. In contrast, if the results in figure 56 are extrapolated to 300 keV energy, the ratio of the Deuteron to Protons carrier removal cross section is found to be 4.1. Therefore indicating that at this energy this ratio does not follow the simple mass dependence. It should be noted that Blood considered the total integrated CRR (see section 2.2.1).

On the other hand, Steeples et al [183], who used Deuteron irradiations of less than 1 MeV for isolation purposes, showed that Deuterons are more effective than Protons by a factor of about 20. Although they did not calculate a carrier removal rate and only monitored the change in the conductance of the irradiated materials, it must be assumed that the ratio of the Deuteron to Proton carrier removal cross sections is about 20, in their experiment. This is in variance with the results obtained from this experiment and the experiment carried out by Blood.

For Helium, the theoretical and the experimental ratios of the carrier removal cross sections show even greater differences. The experimental ratio varies from 15.4 to 47.2 at energies of 2.0 and 0.5 MeV, whereas the theoretical ratio is only about 18.2, agreeing with the ratio of the cross sections at the energy of 1.5 MeV. However care should be excercised in interpreting the results, since the assumptions
validating this experiment (see chapter one) may be violated at low energies. The assumption made, namely that the ion beam in traversing through the material's conductive layer should be mono-energetic, may not be valid for low energy Helium irradiation, with a projected range of the order of few μm.

6.1.2 Molecular species dependence

The energy dependence of the carrier removal cross section for the molecular species of Hydrogen, that is $H_1^+$, $H_2^+$ and $H_3^+$, are shown in figures 57 and 58. The samples used in these experiments were prepared from epitaxial material with $n_0=6.8 \times 10^{16}$ cm$^{-3}$. In figure 57, the carrier removal cross section is calculated assuming single particles of mass 1, 2 and 3 for the irradiated species of $H_1^+$, $H_2^+$ and $H_3^+$. Figure 58, on the other hand, shows the carrier removal cross section corrected for the change in ion dose and energy as the result of the dissociation. In both figures the theoretical Kinchin and Pease cross section for masses 1, 2 and 3 times the Proton's mass have also been drawn. The two graphs clearly confirm the disassociation model discussed earlier and strongly support the contention that elastic scattering is the dominant process in defect production. As discussed in chapter 2, the dissociation of $H_2^+$ and $H_3^+$ ions is well documented [12,48]. It is known that the binding energies of these two species are low, being about 4 eV [89,96], therefore, as the incident ion passes through the first few atomic layers of the target material, the electrons responsible for the binding may be lost by ionization resulting in the disassociation of the molecule into its component Protons. The resultant Protons repel one another via a coulomb
Figure 57. Dependence of carrier removal cross section upon the terminal voltage (=Ion energy) for irradiations with beams of H$_1^+$, H$_2^+$ and H$_3^+$ ions, not corrected for the dissociation and the changes in mass and energy.

Figure 58. Dependence of carrier removal cross section upon the particle energy (=Proton energy) for irradiations using beams of H$_1^+$, H$_2^+$ and H$_3^+$ ions, corrected for the dissociation and the changes in mass and energy.
repulsion. This disassociation results in a modification of the energy, dose and the angular distribution of the incident beam, but these differences do not appear to give rise to a different value for the carrier removal cross section.

Mitchel et al [146] and Moore et al [148] used monoatomic and diatomic heavy ions (As, Sb, Te and Bi) in the keV energy range and found that the damage created by the diatomic implants were about 50 times greater than that of monoatomic ions. In contrast, the molecular effect has been found to be negligible for the light ions [147]. This is believed to be due to the damage cascades created by the light ions being comparatively small. Therefore no significant overlapping is expected to occur between the individual cascades along the particles track. Mitchel et al carried out Protons and Deuteron implants into Ge and Si. Using RBS techniques, they found that the amount of damage produced by equivalent implants of mono or diatomic Protons and Deuteron ions were identical. However Caywood et al [42] reported the RBS/channelled data for 0.8 MeV $H_1^+$, 1.6 MeV $H_2^+$ and 2.4 MeV $H_3^+$ ions incident on Si. They found the RBS spectra for $H_1^+$ and $H_2^+$ ions to be identical but the spectra for $H_3^+$ to be different. This was explained as being due to channelling of Protons produced by the dissociations of $H_3^+$ ions.

Gecim et al [79] reported, similar ion range and carrier removal rates for 0.6-1.5 MeV $H_1^+$, $H_2^+$ and $H_3^+$ implantations, for equivalent doses of ions into GaAs. They further found that this effect was independent of ion energy in the energy range 300 to 500 keV.

In this experiment, both molecular and atomic Deuterons were implanted and the conductivity measurements showed similar values of
carrier removal cross section, after the adjustment of dose and energy. Palmer [164] has also observed the same behaviour for 2D<sup>+</sup> implants.

6.2 Defect introduction

6.2.1 CRR dependence on carrier concentration

The experimental cross section for carrier removal has been found to vary with the initial carrier concentration. Figures 59 and 43 show this dependence for Proton, Deuteron and Helium ions at 1.5 MeV energy. The carrier removal cross sections in figure 59 are derived from sheet conductivity measurements, whilst in figure 43 Hall effect measurements have been used to determine the cross sections.

Protons and Deuterons show an increase in the cross section with doping level of the material, as shown by the solid lines which are drawn to guide the eye. Both cross sections show an increase of about a factor of 3 for an increase of a factor of 100 in the carrier concentration. However, for Helium (figure 59) a very slight dependence of the carrier removal cross section with the materials initial carrier concentration was observed.

The error bars indicated on the figure show the spread in the experimentally determined carrier removal cross section. The random errors encountered in these calculations are +37% for the sheet conductivity measurements and +50% for the Hall effect measurements, respectively.

Kol'chenko and Lomako [121] report that for high energy (up to 28 MeV) electron irradiation into Si, the CRR is independent of the initial carrier concentration (in the range 10<sup>16</sup> to 10<sup>18</sup> cm<sup>-3</sup>) and the
Figure 59. Dependence of the carrier removal cross section upon the irradiated material initial carrier concentrations, for 1.5 MeV Proton, Deuteron and Helium, derived from the sheet conductivity measurements.
chemical nature of the dopant. Hemment et al [103] also found the CRR to be independent of the initial carrier concentration, in highly doped n-type Si \((n_o=10^{26}\ \text{cm}^{-3})\) irradiated with 1.5 MeV Protons. In both cases the Fermi level is above the shallowest defect level \((E_F+0.17\ \text{eV}),\) from table 1) which has been reported for Proton and Electron irradiated Si. It follows therefore, that all of the defect levels are occupied and thus the CRR will be constant (see equation 26 in the next section).

Blood [20] has irradiated lightly doped GaAs \((n_o=2\times10^{15}\ \text{cm}^{-3})\), with 300 keV Protons and Deuterons, and finds a similar dependence of the CRR on the carrier concentration as found in this experiment. As in this experiment, the position of the Fermi level varied from \(E_F+0.14\) to \(E_F+0.01\) eV, for the materials with \(n_o=2\times10^{15}\) to \(3\times10^{17}\ \text{cm}^{-3}\). This range of Fermi level positions spans the shallowest level reported in the literature (see next section) and, therefore, it is thought that the dependence of the CRR on the initial carrier concentration must be due to the movement of the Fermi level through this defect level. In the next section an estimate of the DIR for this level and other deeper levels are made.

6.2.2 Estimates of DIR

In section 2.2 the reported defects and their associated DIR and CRR resulting from Proton, Deuteron and Helium irradiation of GaAs crystal have been discussed. In this section references are made to these defects and estimates of the associated DIR are made using the experimental values of the CRR.

The trapping levels in Proton and Deuteron irradiated GaAs,
determined from DLTS [20,4], have been found to be similar to those created as a result of electron irradiation. Blood [20], Allan [4] and Loualiche [229] report these levels to be:

- $E_1$ 0.12 eV [20]
- $E_2$ 0.18 eV [20]
- $E_3$ 0.41 eV [20]
- $E_4$ 0.71 eV [20]
- $E_5$ 0.84 eV [4]

More recent experiments [228] suggest that the above values for the levels $E_1$ and $E_3$ are too high and it is proposed that the $E_1$ level lies within the range $E_c - 0.04$ eV and $E_c - 0.08$ and the $E_3$ level at $E_c - 0.33$ eV. The levels $E_1$ and $E_2$ have the highest concentrations, but the most frequently reported level is $E_3$, which is thought to be associated with a simple Ga vacancy [20]. Lang [126] reports that levels $E_4$ and $E_5$ are due to impurities or clusters of defects. He reports similar trapping levels in materials irradiated with 1 MeV electrons, confirming that for low fluences both Protons and Electrons irradiations produce similar defects. In a review of the trapping levels in GaAs, he reports a very shallow level at $E_c - 0.02$ eV. He then considers the effect of 400 keV Protons and 1.8 MeV Helium and notes that a broader and deeper DLTS spectrum is obtained as the ion mass is increased, with a general trend towards a relatively larger proportion of the damage leading to the creation of the $E_4$ and $E_5$ levels. For Helium ions he shows that $E_4$ levels dominate the DLTS spectrum.

For Deuterons, where similar initial knock-on damage to Protons are predicted, the traps, again, are very similar to the Electron irradiation traps. However Blood [20] finds that $E_3$ and $E_4$ levels are
in greater abundance in samples irradiated with Deuterons and thus he associates these with the higher CRR reported by Steeples [183]. However, He further reports that in the near surface region, \( \mu m \), (where the CRR was detected in this experiment), Protons and the Deuterons produce similar concentrations of all the levels. This indicates that in these regions the Deuterons and the Protons must create similar types of defects, which confirms the conclusions in section 6.1.1.

The samples prepared from the epitaxial material, as shown on figure 59, fall into two distinct groups, as shown by the two dotted lines, which are the average values for each group. The first group have carrier concentrations between \( 2-3 \times 10^{15} \text{ cm}^{-3} \) with the position of the Fermi level below the \( E_1 \) level by less than \( 2kT \) (0.05 eV). The second group have carrier concentrations \( >5 \times 10^{16} \text{ cm}^{-3} \), with the Fermi level more than \( 2kT \) above \( E_1 \) level. The positions of the Fermi level were calculated using an effective mass of \( 0.067 m_e \) [194], and a value of \( kT \) appropriate to a room temperature of 300 K.

In general the CRR determined experimentally can be expressed as

\[
\text{CRR} = \frac{\Delta n}{\Delta \phi} = \sum_i \xi_i \mathcal{G}_i(E_o, T) f_i(T, n) \quad \text{}(24)
\]

Where \( \xi_i \) is the proportion of the primary defects that are electrically active and \( \mathcal{G}_i \) the generation rate of the primary defects with \( E_o \) as the ion energy and \( T \) as the irradiation temperature, and \( f_i(T, n) \) is the electron occupancy of a localized defect level.
Therefore the DIR can be expressed as $g_i (E_o, T)$. Using the Fermi-Dirac [17] distribution $f_i$, the CRR can be expressed as:

$$\text{CRR} = \text{DIR} f_i (T, n) \quad \text{(25)}$$

Where

$$f_i (T, n) = \left[ 1 + \beta \exp \left( \frac{E_i - E_T}{kT} \right) \right]^{-1}$$

and $\beta$ is the degeneracy factor, with a value of 2, and $E_i$ is the position of the trapping level in the band gap. $\beta$ has a value of 2, as a defect level can accept one electron with either spin. From equations 24 and 25, a CRR can be derived using the two energy level model as proposed by Pegler and Grimshaw [166].

$$\text{CRR} = \text{DIR}_1 \left[ 1 + 2 \exp \left( \frac{E_1 - E_T}{kT} \right) \right]^{-1} + \text{DIR}_2 \quad \text{(26)}$$

With $\text{DIR}_1$ is the DIR for level $E_1$ and $\text{DIR}_2$ is the DIR for all the other levels which are greater than $2kT$ below the Fermi level.

Thus, by using average values of the CRR taken from figure 59 for these two groups of materials, equation 26 can be solved simultaneously for different values of CRR and Fermi level position to give values for $\text{DIR}_1$ and $\text{DIR}_2$. Table 32 shows the values for the defect introduction rate calculated for 1.5 MeV Protons, Deuterons and Helium ions. It is emphasised that these values are only indicative of the DIR for
<table>
<thead>
<tr>
<th>IONS at 1.5 MeV</th>
<th>DIR for E1 (cm⁻¹)</th>
<th>DIR for deeper levels (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROTON</td>
<td>9.6</td>
<td>1.2</td>
</tr>
<tr>
<td>DEUTRON</td>
<td>23.0</td>
<td>2.3</td>
</tr>
<tr>
<td>HELIUM</td>
<td>37.7</td>
<td>60.7</td>
</tr>
</tbody>
</table>

Table 32. Defect introduction rate for levels E1 and for all other deeper levels derived from figure 59, for 1.5 MeV Proton, Deuteron, and Helium.
electrically active defects.

Comparing the estimates of DIR for both level E1 and all other levels, for the Proton and Deuteron irradiated material, confirms the earlier find that the rate at which the ions create defects is proportional to their isotopic mass. For Helium the DIR for E1 level follows isotopic mass ratio, but the DIR for other deeper levels is much greater than expected from the difference in the ion masses.

As discussed in the previous section, for Protons and Deuterons various authors find the same types and abundance of defects, where as for Helium they detect a greater abundance of the deeper levels, that is level E4. This is consistent with high introduction rate found for the deeper levels created by Helium irradiation, in this experiment.

6.3 Deuteron doping effect

It has been demonstrated by Steeples et al [183], that multiple energy implantations of GaAs with Deuteron ions produce high resistance (isolating) layers at doses 20 times smaller than for Protons. These workers, also, reported that at low doses (<1x10^{13} \text{ cm}^{-2}) the carrier removal rate is proportional to the ion mass and, therefore, suggested that it is not the Deuteron ions that are responsible for the enhanced removal rates of the conduction electrons, but it is the defect centers that are decorated by Deuterons.

To investigate these suppositions, it was necessary to study the dependence of the carrier removal cross section, which is assumed to be proportional to the number of defects, the implanted ion dose and the mass and the species of the doping ions. Specifically these experiments were designed to study the effect of Deuteron and Proton
doping on the carrier removal cross section for 1.5 MeV Protons. The details of these implantations are explained in section 5.4. In this section the term "implantation" always refers to the low energy, 30 keV, doping and the term "irradiation" to the 1.5 MeV Proton bombardment.

It was found that for implantation doses greater than $1 \times 10^{12}$ cm$^{-2}$ and $2 \times 10^{12}$ cm$^{-2}$ for Deuterons and Protons, respectively, the materials used ($n_0 = 6.5 \times 10^{16}$ and $9.3 \times 10^{16}$ cm$^{-3}$) were fully compensated. In this context, Deuterons and Protons behave similarly.

The samples that were not fully compensated were irradiated with 1.5 MeV Protons and the effect of Proton and Deuteron dopings on the carrier removal cross section was investigated. Selected samples were also annealed for 10 minutes at a temperature of $325^\circ$C. It has been reported, by Allan [4] that heat treatment at this temperature is sufficient to anneal out the defects created as a result of light ion implantation. Annealing the lattice damage enabled the species dependent effects of Proton and Deuteron dopings of the conductive layer to be explored. Figure 51 (chapter 5) shows the dependence of carrier removal cross section upon the dose and volume concentration of Deuterons and Protons (see section 5.4).

In the Proton implanted samples, the cross section showed no dependence on the implantation dose and had values similar to the un-implanted material. The cross section for the un-implanted material is marked by an arrow on the figure. The annealed samples, however, gave slightly higher values for the cross section than in unannealed samples, but within the experimental errors they were considered to be similar.
In contrast, the carrier removal cross section for the Deuteron implanted samples showed a dependence upon the implantation dose, both for the annealed and unannealed samples, where a difference of a factor of 5 was measured over a dose range of \(4 \times 10^{10}\) to \(1 \times 10^{12}\) cm\(^{-2}\). The errors in the cross section are expected to be +37%, which means that the dose dependence is outside the experimental errors. This is contrary to the conclusion derived from section 6.1.3, which was that the carrier removal cross section decreases with decreasing carrier concentration (that is with an increase in the implanted dose). The cross sections for the unannealed samples were found to be greater than the annealed samples.

The 1.5 MeV cross section for carrier removal has been measured in both annealed and unannealed samples implanted with the same dose \((4.2 \times 10^{11}\) cm\(^{-2}\)) of Proton and Deuteron ions, see figure 51. The ratio of the cross sections in the unannealed Deuteron and Proton implanted samples is 4.7, whilst in the annealed samples this ratio is only 1.3. In the unannealed samples the ratio exceeds unity by an amount which is considered to be still small compared with the difference in the carrier removal rate reported by Steeples et al [183]. It is concluded, therefore, that in this experiment the presence of Deuterons does not cause significantly different carrier trapping to that observed in Proton implanted GaAs. In the annealed samples this ratio, within the experimental uncertainty, is much closer to unity and it is concluded again that the presence of Deuterons does not affect the trapping processes or that the 325°C anneal has caused the Deuterons to diffuse out of the samples [229].

In conclusion, it has been found that Deuterons act as particles
of mass 2 amu and in contrast to the results of Steeples et al, no enhanced effect has been observed, under the conditions set in this experiment. These findings are in agreement with the results of Blood [20], discussed earlier, where no fundamental difference between the defect production processes for Deuterons and Protons was detected.

The carrier removal cross sections calculated from Hall effect measurements also show that the CRR for 1.5 MeV Protons is insensitive to the presence of Deuterons and Protons.
CHAPTER SEVEN

7 CONCLUSIONS AND RECOMMENDATIONS

In this chapter the main conclusions and recommendations for future work are presented.

This study was designed to determine the dominant energy loss process responsible for the production of defects at high energy (~MeV) and for low mass ion (Proton, Deuteron and Helium) irradiation of n-type GaAs. The carrier removal cross section derived was found to show a dependence upon the ion energy and mass similar to the dependence derived from the theoretical Kinchin and Pease elastic displacement cross section [116], within the energy range 0.75-2 MeV. Thus, it was concluded, that the elastic (nuclear) energy loss process is primarily responsible for the creation of defects in the lattice. However, at low energies (<500 keV) it was found that the mass dependence of the cross section diverges from the expected theoretical dependence. This divergence was greater for Helium than for Deuterons.

The molecular species of the hydrogen (H⁺, H₂⁺ and H₃⁺) supported the dissociation models suggested in the literature and the cross section for the resulting Protons show the energy and mass dependences predicted by the Kinchin and Pease model.

The CRR was found to show a dependence upon the initial carrier concentrations of the irradiated material. This was thought to be due to the movement of the Fermi level through the shallowest level reported (E₁=Eₓ,₋0.12 eV). For Deuterons, estimates of the defect introduction rate (DIR) for this level (~23 cm⁻¹) was found to be greater than the sum of the DIR for the deeper levels (~2.3 cm⁻¹).
This was in contrast to the previously reported results [20], where it was found that a deep level (that is $E_3 = E_c - 0.41 \text{ eV}$) was responsible for the removal of the charge carriers. The DIR for Helium, on the other hand, was found to be greater for the deeper levels ($\sim 60.7 \text{ cm}^{-1}$) than level $E_1$ ($\sim 37.7 \text{ cm}^{-1}$), that confirmed the reports that the removal of charge carriers in Helium irradiated samples are due to defects leading to levels $E_3$ and $E_4$ [20]. The relative ratio of the DIR for Deuterons to Protons expectedly followed the mass ratio, for both the level $E_1$ and the other levels. But for Helium this ratio greatly diverged from the simple mass ratio, which may have been due to the insensitivity of this experiment to detect the DIR for the deeper levels.

For doping of Deuterons in GaAs, it was found that cross section value does not appreciably change with the implantation of Deuteron species in the active layer, thus disagreeing with Steeples et al [183], and confirming Blood's results [20].

**Future work**

This work should be extended, in the future to investigate the effect of inelastic energy loss processes, by reducing the effect of elastic energy loss processes. This could be achieved by irradiation of the samples in the channelling directions. For the Deuteron doping, greater range of implantation dose and annealing behaviour need to be studied to fully explain the reported enhanced effect of Deuterons.
**APPENDIX**

**ERROR ANALYSIS**

The uncertainties encountered in the electrical and the dosimmetrical measurements and their propagation through to the final values of CRR and the carrier removal cross section are discussed in this part. The appendix is divided into three sections, with the first section dealing with the errors in the measurements of the sheet conductivity and Hall effect. The second section deals with the dosimmetrical errors, with the final section discussing the propagation of such errors. In all sections the errors discussed are the fractional uncertainties presented in percentage form.

**A.1 Electrical measurements**

The fractional uncertainties in the sheet conductivity measurements can be determined by partially differentiating equation 11, to give:

\[
\frac{\Delta \sigma}{\sigma} = \frac{1}{2} \left( \frac{\Delta V}{V} \pm \frac{\Delta I}{I} \right) \quad (27)
\]

Where \(\Delta V\) and \(\Delta I\) are the small uncertainties in the measurements of \(V\) and \(I\). Here for the sake of generality the subscripts have been omitted. It should be noted that the errors caused by the Van der Pauw's function, \(f(R_1/R_2)\), is considered to be negligible and thus neglected. The factor of 1/2 in the equation is due to the averaging technique of taking four voltage measurements to improve accuracy.
For the Hall coefficient measurements, from equation 12, similarly, the uncertainties become:

\[
\frac{\Delta R_{Hs}}{R_{Hs}} = \frac{1}{2} \left( \frac{\Delta (\Delta V_B/I)}{\Delta V_B/I} + \frac{\Delta B}{B} \right) \quad \text{(28)}
\]

By suitable choice of the sample current the differences between the measured voltages with or without the applied magnetic field, \(\Delta V_B\), can be made sufficiently large, so that the first term in the equation contributes less than 1% to the total error and is, therefore, neglected. Thus:

\[
\frac{\Delta R_{Hs}}{R_{Hs}} \approx \frac{\Delta B}{B} \quad \text{(29)}
\]

From equations 13 and 14, following similar procedures, the uncertainties in the calculation of \(n_s\) and \(\mu_s\) becomes:

\[
\frac{\Delta n_s}{n_s} = \frac{\Delta r}{r} + \frac{\Delta R_{Hs}}{R_{Hs}} \quad \text{(30)}
\]

\[
\frac{\Delta \mu_s}{\mu_s} = \frac{\Delta \rho_s}{\rho_s} + \frac{\Delta R_{Hs}}{R_{Hs}} \quad \text{(31)}
\]

Where \(\frac{\Delta r}{r}\) is the fractional uncertainty in the Hall scattering factor. For the epitaxial material, where it is assumed that the carrier concentration is uniform with depth, the total volume carrier concentration is said to be approximated to:

\[
n = \frac{n_s}{d} \quad \text{(32)}
\]

With the fractional uncertainties of:

\[
\frac{\Delta n}{n} = \frac{\Delta n_s}{n_s} + \frac{\Delta d}{d} \quad \text{(33)}
\]

Where \(d\) is the conductive layer thickness.
Sources of errors in the electrical measurements are discussed below:

(i) Voltage measurements

Typical values of the measured voltages were between 5-10 mV, with the application of a current of between 50-70 μA. The precision in the measurements were determined by the D.V.M, and found to be about ~0.05 mV. Thus the maximum errors introduced by the voltage measurements were in the region of 1.0%, for each reading taken.

(ii) Sample current

The applied current was confined to the conductive layer by using a very high resistivity substrate. Therefore the current flowing between the contacts were either the current flowing through the bulk or the surface leakage current. For the applied currents; the leakage current in the properly cleaned material, were estimated to be negligible and therefore ignored.

The applied current was supplied by a Keithley constant current source, that was capable of supplying digitally selected currents to within 0.5% for long periods, regardless of load variations. This was constantly checked by monitoring the voltage drop across a standard 1 KΩ resistor, and the variation was found to be well within this value.

(iii) Magnetic field

A field of 5 kG was used for all the Hall effect measurements, that corresponds to a D.V.M reading of 126 mV measured across a standard water cooled resistor incorporated in series with the magnet
coils. The reproducibility of the field was found to be good and the fractional uncertainties were assumed to be about 0.5%.

(iv) Hall scattering factor

The main source of error in the Hall effect measurements may be due to the Hall scattering factor, $r$. The considered numerical value of $r$ is in the order of unity [124]. But this is found to be an over-simplification and therefore many estimates of the values for $r$ have been obtained [190]. According to Stillman et al [190], the uncertainties in the precise value of $r$, for GaAs, is estimated to be about 15%.

(v) Conductive layer thickness

The thickness of the conductive layer indicated in table 10 and 11 are as given by the material manufacturer. But from the differential profiling of the samples, the thicknesses obtained varied from the manufacturer's value by about 5-10%. It should be emphasised that the precision in the experimental value is limited by the accuracy of the talystep height measurement technique, which is estimated to be about 5%.

For a typical set of data, for 1.5 MeV Protons or Deuterons irradiations in EII materials, the average maximum fractional uncertainties were as follows:

\[
\frac{\Delta V}{V} = 1.0\% \quad \frac{\Delta I}{I} = 0.5\% \quad \frac{\Delta r}{r} = 15\%
\]

\[
\frac{\Delta d}{d} = 10\% \quad \frac{\Delta \sigma_s}{\sigma_s} = 0.8\% \quad \frac{\Delta R_{Hs}}{R_{Hs}} = 0.5\%
\]
A.2 Dosimetrical errors

The determination of ion dose relies on the integration of the net current flowing from the sample to earth, with respect to time. The current used, has many erroneous components, that can be generalised into two groups. The first group involves the presence of electrons that alter the net positive ion beam current. These electrons usually include secondary, tertiary and Auger electrons ejected from the target material and the electrons trapped in the ion beam potential arriving at the target. The second group includes sputtered and reflected ions from the target, slow positive ions in the ion beam or other impurity atoms, mass analysed similarly to the ions in the beam. Hemment [100] discusses these beam current components and with similar electron suppression geometry and ion beam and target arrangements estimate the fractional uncertainties to be about 2-5%.

The measured ion beam current were in the order of 10-100 nA, and at this low range, the background counts due to leakage currents were found to be about 15% of the ion dose. Thus giving an overall fractional uncertainty in the ion dose of 20%.

A.3 Error propagation

Using standard error analysis equations, the uncertainties in the calculated parameters were found to be as shown in table 33.
<table>
<thead>
<tr>
<th>PARAMETER (x)</th>
<th>FRACTIONAL UNCERTAINTY ($\Delta x/x$)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \sigma_s \over \Delta \phi$</td>
<td>±25</td>
<td>section 5.1.1</td>
</tr>
<tr>
<td>CRR (or cross section)</td>
<td>±37</td>
<td>sheet cond. measurements</td>
</tr>
<tr>
<td>CRR (or cross section)</td>
<td>±50</td>
<td>Hall effect measurements</td>
</tr>
</tbody>
</table>

Table 33. The percentage fractional uncertainties in the calculation of CRR and the cross section from the sheet conductivity and the Hall effect measurements. Also shown is the uncertainties in the calculation of the gradients from section 5.1.
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