Abstract

Rapid Thermal Annealing has been used to study the electrical activation of a range of donor and acceptor species in ion-implanted GaAs. By varying the time and temperature of the post implant anneal, it was found that the activation processes for most implants can be characterised in terms of two distinct regions. The first of these occurs at short annealing times, where the electrical activity is seen to follow a time-dependent behaviour. At longer annealing times, however, a time-independent saturation value is reached, this value being dependent on the annealing temperature.

By analysing the data from Be, Mg, S and Se implants in GaAs, a comprehensive model has been evolved for the time and temperature dependence of the sheet electrical properties. Application of this model to each of the ions studied suggests that the activation processes may be dominated by the extent to which ions form impurity-vacancy complexes. An analysis of the time-dependent regime also shows that, at short annealing times, the mobile species is more likely to be the substrate atoms (or vacancies) rather than the implanted impurities. In the time-dependent region, the values of diffusion energy were found to be between 2.3 to 3.0 eV for all ions, these values corresponding to a diffusion of Ga or As vacancies (or atoms). In the saturation region, activation energies of 0.3 to 0.4 eV and 1.0 to 1.2 eV were obtained for the activation processes of interstitial or complexed impurities respectively.
Acknowledgements

I would like to take this opportunity to express my sincere gratitude to my project supervisor, Dr B J Sealy for his advice and encouragement throughout the duration of this project. Particular thanks must also go to Miss Karen Bray, for having the patience and skill to type this manuscript, and to Mr J Mynard and the staff of the Ion Beam Laboratory for their assistance with the ion implantation. I would also like to thank my colleagues in the SSD and IBT Group for their comments, suggestions and numerous discussions. I would also like to thank the SERC and Dr S S Gill of MOD for providing financial support.

Finally, I wish to express my respect and appreciation to my family and loved ones, for their patience and understanding and for the inspiration they have provided throughout all the time spent away from them.

To them I endearingly present this work: may it reflect my gratitude for their untiring encouragement and moral support.
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CHAPTER 1

Introduction

The growing importance of III-V compounds has been emphasised in recent years by the introduction of compound semiconductor IC's whose operating frequencies are far greater than their silicon based equivalents\(^1,2\). The inherent advantages of using GaAs as a substrate material have long been appreciated, since GaAs substrates can be easily fabricated in semi-insulating form. This property, coupled with an intrinsically high electron mobility (typically 9000 cm\(^2\)/vs\(^2\))\(^2\) has made GaAs the preferred substrate material for most III-V device applications. In addition, the improvements in current GaAs technology have also given the material enormous potential in the field of integrated optics and opto-electronics. However, despite these advantages, there are a number of technological constraints which have served to confine the use of GaAs integrated circuits to a relatively small area of specialised applications. Foremost among these difficulties is the dissociation of the substrate elements at relatively low temperatures, thereby complicating the use of a diffusion-based technology for impurity doping. Secondly, because the material suffers from the lack of a stable native oxide, the traditional metal oxide semiconductor (MOS) structure used in a silicon based technology has been replaced with a metal-semiconductor (Schottky
barrier) technology for the GaAs system. The most important
device structure for GaAs is therefore the metal semiconductor
field effect transistor or MESFET.

As a fabrication step in MESFET technology, ion implantation is
now a well established method for achieving finely controlled
doping in III-V semiconductors, offering many advantages over
alternative doping methods such as diffusion(3). However, since
the process of ion implantation introduces significant lattice
disorder in the substrate, a post-implant annealing stage is
usually required to repair the damaged crystal structure and
simultaneously cause the implanted species to become electrically
active.

Of the wide range of annealing methods developed, the technique of
Rapid Thermal Annealing (RTA) is the most attractive for GaAs,
since it allows accurate control over both the time and
temperature of the annealing stage, thereby offering improved
control over impurity diffusion. In conjunction with the
development of RTA techniques, significant improvements have also
been made in the use of dielectric encapsulants such as Si₃N₄ and
AlN, which prevent the decomposition of GaAs during the anneal. As
a result of these new encapsulants, annealing at temperatures in
excess of 1000°C can now be achieved without any serious
degradation of the GaAs surface(4).
1.1 Research Objectives

Although ion-implantation techniques are now widely employed in GaAs processing, a commonly recurring, and technologically important problem is the apparent inability to fully activate high-dose implants in GaAs\(^5\). The solution to this problem is made more difficult by the apparent lack of detailed information on the mechanisms by which implanted ions achieve electrical activation.\(^1\) By using RTA to study the annealing kinetics of various implanted ions in GaAs, this work is involved with a characterisation of the mechanisms involved for each ion and with the development of a theoretical model for the diffusion and activation processes in ion implanted GaAs.

The importance of this work is of particular relevance to devices fabricated using an ion implantation stage, since the activation mechanisms which occur during the post-implant anneal have a significant effect on the distribution of active carriers in the implanted layer. Thus, by accurately modelling the time and temperature dependence of the activation process for both donors and acceptors, it should be possible to obtain a measure of

\(^1\) Footnote, the electrical activity is defined as the fraction of the implanted dose that has become activated, expressed as a percentage. Hence, electrical activity:

\[
\text{Sheet Carrier Concentration} \times 100\% = \frac{a_t}{\text{Implant Dose}}
\]
the carrier concentration in the implanted layer and also propose a detailed activation mechanism for each ion species. The model developed during the course of this work provides a means of analysing the experimental results presented in this thesis and can also be applied to a wide range of published data on ion implanted GaAs.

1.2 Structure of the Thesis

Following the introduction, Chapter 2 of the thesis provides a background to the project by summarising the recent trends and data relating specifically to rapid thermal annealing of ion implanted GaAs. In this literature survey, sections on ion implantation, encapsulation, donor implants, acceptor implants and RTA techniques are all included, though references to the more conventional studies on furnace annealing have been minimised wherever possible. Chapter 3 provides a description of the experimental techniques and the measurement procedures which were adopted during the research work, discussing both their theoretical concepts and the actual procedures involved in each case. A summary of the experimental results obtained from these techniques is given in Chapter 4, in which the data obtained from a number of studies on both donor and acceptor implants is presented.

Chapter 5 then provides a discussion and interpretation of the experimental results from each of the ions studied. Following an extensive analysis of these results a theoretical model for the activation and diffusion mechanisms in ion implanted GaAs is introduced, along with applications of the model to work reported
elsewhere in the literature. Finally, Chapter 6 presents an overall summary of the research work and includes a number of recommendations for further study.
CHAPTER 2

Literature Survey

2.1 Introduction

In this chapter, a brief summary of the published data relating to the encapsulation and rapid thermal annealing of ion implanted GaAs is presented. No account is made, therefore, of the conventional furnace annealing studies on GaAs, since a number of review articles currently exist in the literature\(^\text{(6,7)}\). Rather, this chapter is initially concerned with a discussion of the various material aspects of GaAs and the techniques used to prevent dissociation of the material during annealing. Following a discussion of these topics, the chapter also provides a description of the various rapid thermal annealing techniques which have been applied to GaAs in recent years. Finally, the results from a number of studies on both donor and acceptor implants in GaAs are summarised.

2.2 Material Properties of GaAs

The technological importance of the GaAs compound stems from a combination of its intrinsic physical and electrical properties. As previously mentioned, one of the important advantages of GaAs over silicon is its ability to provide good quality semi-insulating substrates, which have high resistivity values.
(typically $10^8 \ \Omega/cm$). This property is highly desirable in a substrate material, since it allows direct electrical isolation of component devices fabricated in the material, with the additional advantage of low capacitance interconnections.

In order to achieve these material properties, several growth techniques have been developed to produce good quality GaAs substrates which can retain their semi-insulating properties during subsequent high-temperature processing. Of these, the Liquid Encapsulated Czochralski (LEC) technique has proved to be the most successful method of growing GaAs, resulting in the current availability of 2 - 3" GaAs wafers which have relatively low dislocation densities (typically $10^4 - 10^5/cm^2$) and which remain thermally stable during annealing.

In addition to the material aspects of the semiconductor, a further advantage of GaAs lies in its relatively large direct bandgap, typically 1.43 eV at room temperature. In semiconductor materials which have smaller bandgaps, the thermal ionisation of electrons at room temperature can lead to an increased conductivity which may be undesirable in some device applications. The larger bandgap of GaAs therefore implies that GaAs devices should be capable of operating at much higher temperatures than their silicon-based equivalents. Furthermore, because the bandgap of GaAs allows direct electron-hole recombination to occur, the material also provides an excellent candidate for the fabrication of semiconductor lasers and LED's. The potential applications in the field of optical communications are therefore enormous, since many of the optical devices currently fabricated can now be directly coupled to conventional
GaAs structures, thereby forming a completely integrated semiconductor system. However, since the majority of these devices utilise an ion implantation and annealing stage during their fabrication, much work remains in optimising the processing steps required to electrically activate the implanted region. These procedures are also made more complicated when the properties of any additional devices (which may exist on the same wafer) have to be preserved. The various techniques used to address these problems are described in the following sections.

2.3 Prevention of GaAs Surface Dissociation

The majority of the techniques used for annealing implantation-induced damage in GaAs are directed towards achieving solid-phase epitaxial regrowth of the damaged layer\(^{(10)}\). In most cases,\(^{2}\) the temperatures required for this process are well in excess of the incongruent evaporation temperature of the material (typically 640°C), above which arsenic is preferentially lost from the GaAs surface\(^{(11)}\). Historically, two approaches to this problem have been proposed:

(i) the use of a dielectric encapsulation layer deposited on the GaAs surface.

(ii) annealing in an arsenic/arsine overpressure, thereby preventing the loss of the group V element.

\(^{2}\) Note that, depending on the amount of damage introduced by the implant, anneals can sometimes be performed at temperatures of between 500 - 600°C\(^{(12)}\).
The relative advantages and disadvantages of each annealing technique are discussed below.

2.3.1 Encapsulation

Several methods of encapsulating GaAs have been studied and reported in the literature. Of these, the most widely used encapsulants are: sputtered or plasma-deposited SiO₂(13–17), sputtered, plasma-deposited or CVD Si₃N₄(18–29), reactively evaporated(30,31) or sputtered AlN (or Al₂O₃Ny)(32–34), or various combinations of these materials.

As an ideal encapsulant, the chosen material should satisfy a number of criteria:

(1) it should be easily deposited at low temperatures, as a uniform layer.

(2) it should be capable of withstanding the desired annealing temperature without allowing decomposition of the GaAs surface or outdiffusion of the dopant.

(3) it must not act as a diffusion source for impurities at the GaAs surface.

(4) it should have a thermal expansion co-efficient which closely matches that of GaAs.

(5) it should possess excellent adhesion to the substrate and yet be easily removed after annealing.

Historically, one of the first encapsulants reported for GaAs was a layer of pyrolytically deposited SiO₂(13). However, further studies on this encapsulant showed that, during the anneal,
significant amounts of gallium and arsenic diffused into the SiO₂ layer and that, at annealing temperatures above 800°C, indiffusion of silicon from the encapsulant also occurred(35). Similar problems have also been encountered when using Si₃N₄(18) and SiO₂Nₓ(16) encapsulants, though a study by Inada et al(22) has shown that the main cause of gallium and arsenic outdiffusion can be attributed to a high oxygen content in the encapsulating layer. Thus, although SiO₂ is generally regarded as being unsuitable for GaAs encapsulation, low-oxygen content Si₃N₄ films have proved to be satisfactory encapsulants for ion implanted GaAs(36) and are now widely used in device fabrication. Si₃N₄ itself can be easily deposited from a vapour of silane and ammonia onto a hot substrate(36), or from a plasma of silane and nitrogen at lower temperatures (below 340°C)(37). However, since its quality as an encapsulant depends strongly on the growth method employed, results obtained with Si₃N₄ encapsulants have shown a strong dependence on the deposition parameters used in growing these films. Furthermore, because of the difference in thermal expansion co-efficients between Si₃N₄ and GaAs, the surface strain induced at high temperatures can have a significant effect on dopant redistribution and electrical activation. These effects are generally manifested by a broadening of the implant profile, and may also give rise to regions where impurity accumulation has occurred(38).

The effects of these strain-induced phenomena can be somewhat alleviated by using an encapsulant with a thermal expansion co-efficient which closely matches that of GaAs(28). Recently, for example, several papers have reported the use of AlN as an encapsulant for high temperature annealing(30,31). AlN films,
which can be deposited by reactive sputtering or reactive evaporation, appear to inhibit gallium and arsenic outdiffusion successfully, while maintaining good adhesion to the GaAs surface. Furthermore, the fact that the thermal expansion co-efficient of AlN \( (6.3 \times 10^{-6} \, \text{deg}^{-1}) \) is very close to that of GaAs \( (6.9 \times 10^{-6} \, \text{deg}^{-1}) \) serves to minimise the effects of stress-induced profile broadening\(^{34}\). The resulting influence on the shape of the implant profile is demonstrated by Figure 2.1, where annealing at 850°C for twenty minutes under a SiO\(_2\) cap produced significant profile broadening when compared to a similar anneal using an AlN encapsulant\(^{34}\).

More recently, Bensalem et al\(^{(4)}\) have used reactively evaporated AlN encapsulants to anneal n\(^+\) layers formed by various ion species implanted into GaAs. Although anneals up to 1000°C were successfully performed under an AlN encapsulant, the authors conclude that a double-layer encapsulant of 300 Å Si\(_3\)N\(_4\) + 1000 Å AlN yields more reproducible results. This type of double-layer encapsulant has been used to successfully anneal high dose tin and selenium implants \((1 \times 10^{15} \, \text{ions/cm}^2)\) up to temperatures of 1100°C and has also been used to anneal all the donor implanted samples presented in this thesis.
Figure 2.1. Carrier profiles obtained by AlN-capped annealing (solid line) and SiO₂-capped annealing (dashed line) of Si implanted in GaAs at 150 keV to a dose of $2.4 \times 10^{12}/\text{cm}^2$, followed by annealing at 850°C for twenty minutes (from Reference 34).
Various other double-layer encapsulants have also been reported in the literature. Lidow et al.\(^{(39)}\) used a Si\(_3\)N\(_4\)/SiO\(_2\) combination to anneal GaAs samples up to 1100°C without any surface degradation and Chapman et al.\(^{(40)}\) have used a similar encapsulant to anneal a \(1 \times 10^{15}\) Se\(^+/\text{cm}^2\) implant up to 1140°C for ten seconds. The conclusions to all these studies show that a double-layer encapsulant is an extremely effective method of protecting the GaAs surface, while simultaneously preventing significant dopant redistribution.

2.3.2 Overpressure Annealing Techniques

In contrast to the use of dielectric films, the general technique of "capless" annealing relies on suppressing arsenic outdiffusion by providing an excess of arsenic above the surface of the GaAs.

In Proximity Annealing\(^{(41)}\), for example, the excess arsenic overpressure is achieved by placing two GaAs samples face-to-face during heat treatment. The partial pressure of arsenic in the small gap separating the samples is sufficient to prevent excessive surface decomposition in most cases, though separation of the two samples is sometimes difficult after a high temperature anneal has been performed. A partial solution to this problem can be achieved by annealing in an arsenic vapour overpressure\(^{(42)}\), though any variations in the overpressure atmosphere can cause serious degradation of the material surface, with a possible effect on electrical activation\(^{(43)}\). Due to these difficulties, and because of the high pressure of arsenic required at high annealing temperatures, capless annealing is usually limited to temperatures below 900°C.
As a comparison of the various annealing methods, Table 2.1 summarises the techniques used to prevent decomposition of the GaAs surface, together with the maximum useful annealing temperature associated with each technique.

<table>
<thead>
<tr>
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<th>PROBLEMS</th>
<th>MAX. USEFUL TEMPERATURE</th>
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<td>ENCAPSULATION</td>
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<td>SiO$_2$</td>
<td>CVD (Silox)</td>
<td>Ga Outdiffusion 750°C</td>
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<td>Si$_3$N$_4$</td>
<td>CVD</td>
<td>Strain 900-950°C</td>
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<td></td>
<td>Plasma</td>
<td>Pinholes 1050°C</td>
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<td></td>
<td>Sputtered</td>
<td>Blisters 700-750°C</td>
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<tr>
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<tr>
<td>Al</td>
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<td>AlN</td>
<td>Sputtered 1000-1050°C</td>
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<tr>
<td></td>
<td>Evaporated 1000-1050°C</td>
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<tr>
<td>A1O$_2$N$_x$</td>
<td>Sputtered 900°C</td>
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<td>COMBINATION</td>
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<td>CVD SiO$_2$/Plasma Si$_3$N$_4$</td>
<td>1100°C</td>
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<tr>
<td>CVD Si$_3$N$_4$/Evap. AlN</td>
<td>1140°C</td>
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Table 2.1. Comparison of various encapsulation methods showing the problems associated with them and their maximum useful temperatures.
2.4 Rapid Thermal Annealing of Ion Implanted GaAs

In contrast to conventional furnace annealing techniques, Rapid Thermal Annealing (RTA) offers a number of distinct advantages for processing ion-implanted GaAs. Firstly, due to the relatively short times at high temperatures, good electrical activities and mobilities can be achieved without significant dopant redistribution\(^4\)). Secondly, the performance specifications of encapsulants and substrates may be less critical when using RTA techniques because the time at temperature is kept short. Significant improvements in wafer throughput are also obtained as a result of the short processing times involved.

As indicated by Figure 2.2, these factors have contributed to the growing importance of transient annealing in the past ten years, with particular emphasis being placed on the use of Incoherent Light Annealing techniques and Graphite Strip Heaters. Additional methods of transient annealing, using either Lasers or Electron Beams, have also been examined, but both to a somewhat lesser degree.
Figure 2.2. Number of papers published per annum on transient annealing of III-V compounds (excluding reviews). [ILA - Incoherent Light Annealer; GSH - Graphite Strip Heater and EBA - Electron Beam Annealer] (Reference 45).

Historically, the first study of short-time (transient) annealing of GaAs was performed by Surridge et al(46), who demonstrated that, for a given annealing temperature, the percentage of ions which become electrically active increased with time up to a maximum "saturation" value. As the annealing temperature was increased, this maximum "saturation" value also increased, but the time taken to reach saturation became less (see Figure 2.3).
Figure 2.3. The dependence of Sheet Electron Concentration and Mobility on Annealing Time and Temperature for Se (ΔΔ) and Sn (○○) - implanted GaAs. The data shows that electrical activity increases with annealing time. Implants were $2 \times 10^{14}$ Sn/cm$^2$ and $2 \times 10^{14}$ Se/cm$^2$ at energies of 300 keV and 390 keV, respectively (Reference 46).
During the same period, a number of other workers(47,48) reported an alternative rapid thermal annealing technique, which used high-power lasers to anneal ion-implanted material. The aim here was to achieve very short anneal times, of the order of $10^{-9}$ seconds. However, due to the problems of poor surface morphology and the inability to activate low implant doses, laser annealing of GaAs has not been pursued in recent years(49).

The use of a scanning electron beam as a method of annealing GaAs was first reported by Shah et al(50). In this study, an electron beam was used to anneal GaAs samples which had been implanted with $6 \times 10^{12} \text{ Si}^+/\text{cm}^2$ at 160 keV. Electrical activities of 50% - 60% were obtained from the uncapped samples used in this work, though subsequent improvements in electron beam annealing of silicon implants has been obtained by using a dielectric encapsulating layer(51). In more recent studies, electron beam annealing has also been used to obtain high carrier concentrations from both selenium(52) and zinc(53) implanted GaAs. However, due to persistent problems with control and reproducibility, this technique is now regarded as being unsuitable for most device applications.

Of all the annealing systems developed, only the Incoherent Light Furnace and the Graphite Strip Heater allow a high degree of accuracy and control over both annealing temperature and annealing time. As an example, Sealy et al(54) have used a graphite strip heater (based on an earlier design by Donnelly(55)) to obtain high electrical activities (86%) from a 300 keV implant of $5 \times 10^{12} \text{ Se}^+/\text{cm}^2$. This was achieved by annealing at 1000°C for twenty seconds. Higher dose ($1 \times 10^{15}/\text{cm}^2$) selenium implants were
studied by Chapman et al\textsuperscript{(40)}, who obtained activities in the region of 15 - 20\% from Si$_3$N$_4$/SiO$_2$ encapsulated samples annealed at 1140°C for ten seconds. The annealing apparatus in this study was a graphite strip heater, similar to those used by Donnelly and Sealy.

More recently, Patel et al\textsuperscript{(56)} and Blunt et al\textsuperscript{(72)} have applied RTA to the study of both tin and selenium implants, obtaining carrier concentrations around $1 \times 10^{19}$/cm$^3$ by annealing at temperatures in the range 1050 - 1090°C. As a continuation of this work, Bensalem et al\textsuperscript{(58,59)} made preliminary studies on the activation mechanisms for both tin and selenium implants in GaAs, using a graphite strip heater to investigate the changes in electrical activity which occur as a result of different annealing conditions (see Figure 2.4).
Figure 2.4. Sheet Electron Concentration versus Annealing Time and Temperature for a $1 \times 10^{14}$ Sn/cm$^2$, 300 keV implant annealed using a Double Graphite Strip Heater (Reference 58).
The results from these studies, which will be further discussed in Chapter 5, illustrate that the graphite strip heater is a useful tool for studying short-time annealing effects. However, despite its successful use at research level, the graphite strip heater has been greatly overshadowed by the use of the incoherent light furnaces for most industrial applications.

In the case of Optical Furnace Annealing, rapid heating rates are achieved by non-focussed radiation from banks of quartz-halogen lamps, placed in various geometries around the implanted wafer. Arai et al.(60) were the first to introduce this method in their investigation of low dose \(3 \times 10^{12} \text{ ions/cm}^2\) silicon implants in GaAs. The results of this study, which showed that profile broadening was significantly reduced by using RTA, led to a profusion of further experiments using incoherent lamp furnaces(61,62). In addition to studies on silicon, excellent results have also been obtained for a range of ion species(63,64), as reflected by the growth in the number of publications which use incoherent light annealing as a processing stage. Further details of these publications, as well as a general introduction to RTA techniques, are extensively covered in a number of excellent review articles by Sealy et al.(54,65).

2.5 Donor Implants in GaAs

(1) Silicon Implantation

Due to its relatively low mass and widespread use as an n-type impurity, silicon is probably the most thoroughly investigated donor species in GaAs. Many workers have reported that RTA
techniques are superior to furnace annealing techniques, for both low and high dose silicon implants$^{(66,67)}$. Studies have also been made on the time and temperature dependence of the electrical activity, indicating that short times at high temperatures are all that are necessary to achieve good levels of activity$^{(68)}$. However, for doses greater than $1 \times 10^{13}$ Si$^+/\text{cm}^2$, annealing at temperatures above 950°C can lead to an apparent degradation of activity, either due to the amphoteric nature of silicon in GaAs$^{(69,70)}$, or to failure of the encapsulant$^{(71)}$. In Figure 2.5, the optimum annealing conditions are shown for a number of implant doses and energies$^{(72)}$. For higher doses, further studies$^{(73)}$ indicate that much higher annealing temperatures (in the range of 1100°C) are required to obtain the maximum levels of activity. For example, Kuzuhara et al.$^{(73)}$ obtained a doping concentration of $9 \times 10^{18}/\text{cm}^3$ from a 200 keV, $5 \times 10^{14}$ Si$^+/\text{cm}^2$ implant by annealing at 1140°C for five seconds.
Figure 2.5. Optimum Annealing Conditions for maximum electron concentration in Si-implanted GaAs. Annealing conditions are 0 - 5 s at 950 - 1100°C. $T_{opt}$ = optimum temperature (Reference 72).

Since the optimum annealing conditions are seen to be different for low and high doses of silicon, difficulties can arise in the fabrication of GaAs MESFETs, where the low dose (channel) implants and high dose (source/drain) implants are annealed simultaneously. A compromise in annealing temperature is therefore required to achieve optimum device performance; though this too will be subject to the effects of an optimised encapsulant and a carefully chosen annealing schedule.
(2) Other Donor Species

With such widespread interest being generated in the field of rapid thermal annealing, other donor ions, notably selenium, tin and sulphur, have also received attention, though all to a much lesser extent than silicon.

Selenium implants have been investigated over a range of doses and energies, with low dose implants being successfully activated to approximately 80% \(^{(54)}\). In fact, a comprehensive comparison \(^{(74)}\) of transiently annealed selenium and silicon implanted samples has shown that, for the same annealing conditions, selenium yields similar electrical results to silicon when the implant dose is less than \(1 \times 10^{14} \text{ ions/cm}^2\).

For larger selenium doses however, much higher annealing temperatures are required to yield significant electrical activity. As an example Chapman et al \(^{(40)}\) showed that an activation of 18%, (with a corresponding sheet resistivity of 25 \(\Omega/\square\)), could be obtained from a hot (300°C) implant of \(1 \times 10^{15} \text{ Se/cm}^2\) by annealing at 1140°C for ten seconds.

Further studies \(^{(52,57)}\) have yielded sheet resistivities as low as 37 \(\Omega/\square\) and 22 \(\Omega/\square\) from room temperature and 200°C selenium implants respectively, with corresponding electron concentrations in excess of \(1 \times 10^{19}/\text{cm}^3\) being achieved after a 1050°C anneal for ten seconds \(^{(57)}\).
Selenium ions have also been studied in detail by Bensalem et al.(59), who concentrated on the annealing kinetics of a $1 \times 10^{14}$ Se/cm$^2$ implant and proposed a model for the activation mechanisms of selenium in GaAs. This model will be presented and discussed during a later chapter, as will the results from Bensalem's study of a 300 keV, $1 \times 10^{14}$ Sn$^+$/cm$^2$ tin implant in GaAs(58).

Aside from a number of publications arising directly from Bensalem's work, only two other publications have reported the use of tin as an "n" type dopant in GaAs. The results from these studies also conclude that very high temperatures are required to anneal out the significant damage caused by heavy-ion implantation. Nevertheless, electrical activities as high as 71% and 29% have been reported for doses of $1 \times 10^{14}$ Sn/cm$^2$ and $1 \times 10^{15}$ Sn/cm$^2$ following high temperature annealing at $1090^\circ$C(58,52). However, in order to reach the required annealing temperature, the previously mentioned double-layer encapsulant of Si$_3$N$_4$ and AlN had to be developed. The complications of this process therefore limit the use of high dose tin implants for device applications.

As an alternative candidate, the activation of sulphur ions have recently been studied using an incoherent light furnace(75). In this work, low dose (<$3 \times 10^{13}$/cm$^2$) sulphur implants were annealed at temperatures in the range 900°C - 1000°C for two seconds, yielding peak electron concentrations in excess of $5 \times 10^{18}$/cm$^3$ with no profile broadening. The behaviour of higher dose (>1 x $10^{14}$ ions/cm$^2$) sulphur implants was, however, quite different, with profiles suffering from both in and outdiffusion
during a two second anneal at 1000°C(75). Even though RTA can reduce the effects of diffusional broadening, there are still a number of additional factors which need to be considered in annealing sulphur implants in GaAs (e.g. the type of encapsulant, the annealing temperature and the annealing time). The effects of all these parameters, and the conclusions drawn from them, will be discussed further in Chapter 5.

2.6 Acceptor Implants in GaAs

In studies on acceptor implants, beryllium, magnesium, zinc and cadmium ions have all been investigated as potential candidates for the formation of p⁺ layers. In contrast to "n" type implants in GaAs, an important difference between acceptors and donors is the ease with which the former become electrically active. Thus, depending on the exact implant conditions used, it is possible to achieve hole concentrations around $1 \times 10^{18}/\text{cm}^3$ by annealing at temperatures as low as 700°C for short times(12). A summary of the results obtained for a variety of ions is presented below:

(1) Zinc Implantation

For zinc-implanted GaAs, the first significant RTA result was the achievement of 80 – 90% activity from a $1 \times 10^{15}$ ion/cm² zinc implant, annealed at 900°C for thirty seconds(76). Since then, rapid thermal annealing of zinc implants have been studied by numerous workers(53,77,78), the general conclusion being that very short annealing times (<5 seconds) are required to prevent excessive dopant redistribution. As an example, Barrett and
Sealy(53) obtained a peak hole concentration of $8 \times 10^{19}$/cm$^3$, with very little diffusional broadening, by annealing at times of between one and three seconds. Further studies by Barrett et al(77) and Tiwari et al(78) have also shown that high levels of hole concentration can be readily obtained by annealing at very high temperatures (>1000°C) for estimated dwell times of less than one second.

(2) **Beryllium Implantation**

Because of its light mass and greater implant range, beryllium is a widely used "p" type dopant for GaAs. Despite its high toxicity, several studies have been made on rapid thermal annealing of Be-implanted GaAs. In one of the earliest reports, Tabatabei-Alavi et al(79) annealed a dual implant of $4.4 \times 10^{14}$ Be/cm$^2$ (at 50 keV) plus $5.1 \times 10^{14}$ Be/cm$^2$ (at 150 keV) at 950°C for ten seconds, yielding a peak hole concentration of about $2 \times 10^{19}$/cm$^3$. Banerjee et al(80) have also achieved high carrier concentrations by using an electron beam heater to achieve 90% activity from a $1 \times 10^{14}$ Be/cm$^2$ dose. This was obtained from an anneal at 900°C for approximately half a second. By comparing the RTA results with results from a thirty minute furnace anneal, they concluded that RTA was a superior technique in that it achieved much higher hole concentrations and allowed much better control over dopant redistribution. Such observations have since been confirmed by a number of other workers(81,82). Liu and Narayan(81), for example, annealed a dose of $3.8 \times 10^{14}$ Be/cm$^2$ at 720°C for short times of five to ten seconds and showed that the post-anneal beryllium distribution was very similar to the as-implanted atomic profile.
Pearton et al\textsuperscript{(82)} have investigated low ($1 \times 10^{13}$/cm\textsuperscript{2}) and high ($1 \times 10^{15}$/cm\textsuperscript{2}) doses of beryllium, both implanted at an energy of 40 keV. Sheet activities of 100\% and 70\%, respectively, were measured following three second anneals in the temperature range 800\textdegree C - 1000\textdegree C. From a Secondary Ion Mass Spectrometry (SIMS) analysis of the higher dose implant, they concluded that the 30\% reduction in activity from the high dose was due to outdiffusion of beryllium, so that, in fact, the net activation for both implants was close to 100\%.

Further studies of beryllium implanted GaAs have been performed by Barrett et al\textsuperscript{(83,84)} and Vaidynathan and Dunlap\textsuperscript{(85)}. In the former case, implant doses of $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ Be/cm\textsuperscript{2} were implanted at energies of 25, 40, 75 and 360 keV. By using an incoherent light furnace to anneal at 950\textdegree C for one second, a maximum peak hole concentration of $2 \times 10^{19}$/cm\textsuperscript{3} was measured for the $1 \times 10^{15}$ Be\textsuperscript{+}/cm\textsuperscript{2} implant at 40 keV. The authors also observed that annealing for longer times (eg twenty minutes) caused significant broadening of the implant profile, accompanied by a significant loss of beryllium from the surface.

More recently, Vaidynathan and Dunlap\textsuperscript{(85)} have studied doses of $1 \times 10^{13}$ Be/cm\textsuperscript{2} and $1 \times 10^{14}$ Be/cm\textsuperscript{2} annealed at much lower temperatures. The authors concluded that, for a 550\textdegree C anneal, the electrical activity increased with increasing annealing time in the range 2 to 30 seconds. For the $1 \times 10^{14}$ Be/cm\textsuperscript{2} implant, a maximum activity of 60\% was obtained by annealing at 550\textdegree C for thirty seconds.
Magnesium Implantation

The use of rapid thermal annealing to activate magnesium implants was first reported by Blunt et al. (86), who used an incoherent light furnace to anneal a $1 \times 10^{14}$ Mg/cm$^2$ implant at 150 keV. A peak hole concentration of $5 \times 10^{18}$/cm$^3$ was obtained after an 800°C anneal for five seconds. Kuzuhara et al. (62) have studied a higher dose ($2 \times 10^{14}$ Mg/cm$^2$) implant and showed that the percentage of ions which become electrically active increases as the annealing temperature is increased from 700°C to 900°C. At the highest anneal temperature (900°C), a dual peak was observed in the carrier profile which was attributed to the combined effects of outdiffusion and accumulation of magnesium.

Implant doses in the range $5 \times 10^{13}$ Mg/cm$^2$ to $1 \times 10^{15}$ Mg/cm$^2$ (all at an energy of 100 keV) have been studied by Patel and Sealy (64), who observed that, in contrast to the above results, the levels of activity remained essentially constant over the temperature range 700°C - 900°C. In addition, their results also indicate that, at high annealing temperatures, no change in activity occurred when the annealing time was increased from ten to thirty seconds. For the highest implant doses, however, annealing at longer times caused the depth profiles to broaden considerably, resulting in significant accumulation of magnesium at the surface.

Tiwari et al. (78) have also shown that, for an implant dose of $1 \times 10^{15}$ Mg/cm$^2$, the electrical activity also remains virtually constant in the annealing temperature range 800°C - 950°C. The conclusions drawn here are that optimum electrical activation is
obtained by annealing at 900°C and that, at temperatures greater than this, the electrical activity decreases due to a loss of magnesium into the encapsulating layer.

2.7 Dual Implants in GaAs

Recent attempts to enhance the electrical activity obtained from a given implant have utilised combinations of ions, which are co-implanted and subjected to RTA treatment. The concept of dual implantation is based on maintaining a balance in the composition of the substrate lattice, thereby reducing the effects of dopant compensation due to vacancy-complex formation(87). Among the ion combinations that have been studied are (Se + Ga)(88), (Se + Sn)(89), (Zn + As)(90), (Mg + As)(91) and (Si + P)(92) - all of which have led to an increase in carrier concentration when compared to a single implant. In addition, a further advantage is obtained in the case of the amphoteric ions, silicon and germanium, since the use of a dual implant significantly increases the probability of these ions occupying the desired lattice site (therefore reducing the probability of any amphoteric behaviour).

2.8 Annealing Kinetics

Since the early work by Surridge et al(46), a number of workers(58,59) have shown that the electrical activity of implanted ions in GaAs is a function of both the annealing time and the annealing temperature (as previously indicated by 2.4). These results indicate that the annealing process is divided into two distinct regions, (1) a time dependent regime, where the
activity increases with annealing time, and (2) a saturation region, in which the electrical activity remains virtually constant.

With the advent of RTA, such effects have been studied more extensively, so that a number of models currently exist to describe the activation mechanisms for ions in GaAs\(^{58}\). As an example, various groups\(^ {93,94} \) have proposed the formation of vacancy-dopant complexes to account for implanted ions which remain electrically inactive. The model developed by Hurle\(^ {95,96} \), for bulk and epitaxially grown material, also proposes that inactive impurities (tin and tellurium) exist in the form of vacancy complexes.

Bensalem and Sealy have extended this concept and used it as a basis for their model of the activation mechanisms for Sn\(^ {58} \), Se\(^ {59} \) and Zn\(^ {97} \) ions in GaAs. By analysing the time-dependent and saturated annealing behaviour of these ions, they propose that the time-dependent regime arises from a diffusion of the implanted atoms from complex sites to suitable lattice vacancies. However, to date, none of the work reported in the literature has succeeded in proposing a model which can describe the activation process over the entire time-temperature regime - and which can be readily applied to the activation mechanisms for both donors and acceptors.

With this objective in mind the following chapter provides a description of the experimental methods used in developing such a model, followed by an extended discussion and analysis of the various experimental results.
Experimental Techniques

3.1 Introduction

This chapter describes the major experimental and measurement techniques employed during the course of this study. The chapter itself is divided into six sections, each of which relates the basic theoretical concepts involved in each of the techniques, followed by a description of the actual procedures adopted during the experimental work.

The chapter follows the sequence of experimental methods in the order:

(1) Material characterisation
(2) Ion implantation
(3) Dielectric encapsulation
(4) Rapid Thermal Annealing
(5) Sample preparation
(6) Electrical measurements using the Hall effect technique.
3.2 Material Characterisation

All of the substrate material used in this work consisted of undoped semi-insulating GaAs layers which were grown in the (100) direction by the liquid encapsulated Czochralski (LEC) technique. Typically, the material has an initial resistivity of the order of $10^9$ Ω.cm and was initially supplied in the form of 2" diameter wafers which had been polished on one side by the manufacturer.

In order to determine the thermal stability of the as-received GaAs, a sample from each of the as-received substrates was first encapsulated with approximately 1000 Å of Si$_3$N$_4$, then subjected to an anneal at 850°C for between ten and fifteen minutes. The GaAs material which preserved its semi-insulating properties following such an anneal was deemed satisfactory for the purposes of this study. However, in cases where the resistivity of the material dropped considerably after heat treatment (ie to less than $10^{-2}$ Ω.cm), this material was considered to be of inferior quality and was therefore omitted from any further processing. Good quality GaAs wafers were first cleaved into two halves, then subjected to a solvent clean before loading into the implantation chamber.

3.3 Ion Implantation

3.3.1 Advantages of Ion Implantation

As stated previously, the use of ion implantation as a method of doping semiconductor material is now well established and the topic has therefore been the subject of a number of review
articles and texts(98,99). For the purposes of this study however, the more important advantages of ion implantation may be summarised as follows:

(1) The total implanted dose of a given impurity may be accurately monitored and controlled.

(2) The concentration of dopant as a function of depth may be accurately predicted, by a suitable choice of ion energy and dose.

(3) The process is relatively free of contamination since, at the low temperatures involved, the diffusion of unwanted impurities is minimised.

(4) The range of possible dopants is greater than that of a diffusion based technology, since ion implantation does not rely solely on dopants which exist in gaseous form.

In addition, by employing a suitable lithographic patterning stage, selective area implants can be performed with a high degree of lateral definition and a relatively small lateral spread. This has the important consequence of reducing the variations in device characteristics fabricated by ion implantation(99).

3.3.2 Physics of Ion Implantation

Ion implantation involves the direct injection of a positively charged ion species into a target substrate. The ions are initially produced by heating the dopant material in the presence of a plasma, which is contained in a source held at a high dc voltage. The ionised impurities are then accelerated through a
fixed potential (the ion "energy") and pass through a mass analysis stage before striking the target substrate (at ground potential).

On entering the target material the ions lose energy, either by interacting with the target electrons (electronic stopping) or by collisions with the target nuclei (nuclear stopping), before eventually coming to rest beneath the target surface. The classical theory developed by Lindhard et al (LSS)(100) is based on a relationship between the energy (and mass) of the incident ion and the mass of the target atoms. The theory predicts that the implanted ions will assume a Gaussian distribution on entering an amorphous target.

In practice the two parameters most commonly used to describe this distribution are the (mean) Projected Range normal to the surface ($R_P$), and its standard deviation ($\Delta R_P$). The required relationship between the implant dose, $N_D$, and the impurity concentration $N(x)$ as a function of depth ($x$) is:

$$N(x) = \frac{N_D}{\sqrt{2\pi} \Delta R_P} \exp\left(-\frac{(x - R_P)^2}{2 \Delta R_P^2}\right)$$

Atoms/Cm$^3$

where $x$ is the depth perpendicular to the target surface.

Since the early work of LSS, a number of theoretical models have been proposed for determining more accurate values of $R_P$ and $\Delta R_P$ (for example, Gibbons(101), Ziegler(102), Biersack(103)). Of these, the recently developed Project Range Algorithm (PRAL) proposed by Biersack(103) has been used to predict values of $R_P$ and $\Delta R_P$ for the ions used in this study. This algorithm, in the
form of a commercially available SUSPRE\textsuperscript{(104)} package, has also been used to calculate the amount of energy lost by the ion due to the combined effects of nuclear and electronic stopping. The values of $R_p$, $\Delta R_p$, nuclear energy loss $E_n$ and electronic energy loss $E_e$ have been calculated for each of the ions studied, and the results presented in Table 3.1(b).

It should be stated that, in this model, no account is made for the more complicated effects of thermal diffusion\textsuperscript{(99)} or channelling of the implanted ions along a major crystallographic plane or axis\textsuperscript{(105)} - both of which may contribute to a deeper experimental implant profile. However, in most cases, the effects of at least one of these variables, (ie channelling) can be reduced by tilting the target crystal axis at an angle of approximately $7^\circ$ to the ion beam axis, thereby presenting a pseudo-random crystal target to the incoming ion beam.

3.3.3 Ion Implantation Procedure

In this study, ion implantation was performed on either complete GaAs wafers or on parts of a wafer. In either case, all the samples were cleaned by boiling in hot toluene for approximately five minutes, followed by a further five minutes in hot methanol. Samples were then rinsed in distilled water and dried thoroughly before being loaded into the target chamber.
With the exception of the Be⁺ implant (see Table 3.1) all the material used in this study was implanted using the 500 keV heavy ion accelerator at the University of Surrey. Details of the ion species used, along with their respective doses and energies, are given in Table 3.1(a).
### Table 3.1

#### (a) Ion Implantation Schedule

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ion Dose (cm(^{-2}))</th>
<th>Ion Energy (keV)</th>
<th>Ion Beam Current (μA)</th>
<th>Implant Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be(^{(1)})</td>
<td>5 x 10(^{14})</td>
<td>75</td>
<td>-</td>
<td>RT</td>
</tr>
<tr>
<td>Mg</td>
<td>5 x 10(^{14})</td>
<td>100</td>
<td>2 - 3</td>
<td>RT</td>
</tr>
<tr>
<td>Mg</td>
<td>1 x 10(^{14})</td>
<td>100</td>
<td>2 - 3</td>
<td>RT</td>
</tr>
<tr>
<td>S</td>
<td>1 x 10(^{14})</td>
<td>120</td>
<td>1 - 2</td>
<td>RT</td>
</tr>
<tr>
<td>Se</td>
<td>1 x 10(^{13})</td>
<td>300</td>
<td>3 - 4</td>
<td>RT</td>
</tr>
</tbody>
</table>

\(^{(1)}\) Be implantation was performed at the GEC Hirst Research Centre.

#### (b) Ion Implantation Parameters

<table>
<thead>
<tr>
<th>Ion</th>
<th>Implant Energy (keV)</th>
<th>Projected Range (R_p) (Å)</th>
<th>Standard Deviation (\Delta R_p) (Å)</th>
<th>Nuclear* Energy Loss (E_n) keV</th>
<th>Electronic* Energy Loss (E_e) keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>75</td>
<td>2262</td>
<td>1185</td>
<td>17</td>
<td>58</td>
</tr>
<tr>
<td>Mg</td>
<td>100</td>
<td>1196</td>
<td>737</td>
<td>67.4</td>
<td>37.6</td>
</tr>
<tr>
<td>Se</td>
<td>300</td>
<td>1193</td>
<td>506</td>
<td>258</td>
<td>42</td>
</tr>
<tr>
<td>S</td>
<td>120</td>
<td>995</td>
<td>556</td>
<td>81.4</td>
<td>38.6</td>
</tr>
</tbody>
</table>

* Calculated from SUSPRE(104).
In order to facilitate ease of loading, the GaAs samples were mounted onto aluminium sample plates which were then suspended from a carousel-type sample holder. The geometry of the sample plates was such that the ion beam was aligned at an angle of about 7° to the <100> surface normal. When full, the carousel itself was capable of holding 18 pairs of 2" diameter wafers.

After loading the carousel into the target chamber, the chamber was evacuated to approximately $10^{-6}$ torr before implantation commenced. For all samples, the effective implantation area was determined by the size of an earthed aperture plate which was mounted directly above the GaAs substrates. Emission of secondary electrons from the sample was significantly reduced by using a 300 V suppression electrode, placed in close proximity to the sample surface. Measurement of the ion beam current was achieved by measuring the equivalent electron current which flowed between the sample and earth. This current was displayed instantaneously by a multi-range ammeter and was also linked to a current integrator which, in conjunction with the known implant area, gave a measure of the total implant dose.

Raster Scanning of the ion beam was achieved by applying variable frequency triangular waveforms to two sets of orthogonal electrostatic deflection plates. The ac potential applied to these plates was varied in accordance with the ion energy, so that the ion beam scanned an area which was greater than the actual area of the aperture used.
Since the process itself involves the displacement of target atoms, a considerable amount of crystalline damage is present after the implantation stage. The total amount of damage may be reduced by implanting the ions into a heated substrate\(^\text{(57)}\). However, in the majority of cases, ion implantation is performed at room temperature so that a subsequent high temperature annealing stage is required. The following section describes the encapsulation techniques used to inhibit GaAs dissociation during the annealing cycle.

### 3.4 Encapsulation Techniques

As mentioned in Chapter 2, the correct choice of encapsulant is of paramount importance in preventing the outdiffusion of dopant atoms and the decomposition of the GaAs surface.

A previous study by Sealy et al\(^\text{(4)}\) has demonstrated the superiority of a double layer encapsulant which consists of a thin film of pyrolitically deposited Si\(_3\)N\(_4\) (typically 300 Å) on which is deposited a thicker layer (~ 600 Å) of evaporated AlN. The results show that this combination of thin films provides a suitable encapsulant for annealing ion implanted GaAs at temperatures up to about 1100°C. For the purposes of this work therefore, the study of selenium and sulphur implants utilised a combination of Si\(_3\)N\(_4\) and evaporated AlN, which was deposited in accordance with the earlier work\(^\text{(4)}\). For the acceptor implants (Be and Mg) however, annealing took place at much lower temperatures (typically < 800°C). For these samples, earlier work has demonstrated that, at such low annealing temperatures, only a single layer of 1000 Å evaporated AlN is required\(^\text{(85)}\).
3.4.1 Experimental Apparatus for Si₃N₄ Deposition

The design of the apparatus used for depositing Si₃N₄ is similar to an earlier design proposed by Donnelly [55]. A schematic diagram of the apparatus is shown in Figure 3.1, in which the samples to be encapsulated are placed on a rectangular graphite strip heater (approximately 160 x 5 x ≈1 mm), which is capable of reaching a temperature of 635°C in approximately five seconds.

Prior to deposition, the reaction chamber is evacuated to a pressure of 10⁻⁴ Torr and subsequently purged with nitrogen gas for approximately five minutes. Silane (5% SiH₄ in N₂) and ammonia (NH₃) gases are then introduced into the chamber, along with the nitrogen, in a preset flow ratio of 100 N₂:40 NH₃:60 SiH₄ (in N₂). The flow rates of these gases, together with the sample temperature, determines the rate at which the Si₃N₄ is deposited (as discussed further in Chapter 4).

After allowing the flow of gases to reach a steady state condition, Si₃N₄ growth was performed at the time and temperature required to yield the desired thickness.
Figure 3.1. Experimental apparatus for Si₃N₄ deposition.
The fundamental process which governs the chemical vapour deposition of Si$_3$N$_4$ under these conditions is determined by the pyrolytic decomposition and reaction rates of the silane and ammonia gases, according to the following chemical reaction (106).

$$3 \text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12 \text{H}_2$$

Subsequent to their removal from the reaction chamber, the thickness of the Si$_3$N$_4$ films was determined from the colour reference chart shown in Table 3.2. Typically, growth at 625°C for thirty seconds produced a film thickness of 300 Å. However, in order to further study the effects of Si$_3$N$_4$ growth rate, a number of samples were encapsulated with Si$_3$N$_4$ films grown under different temperature and time conditions. The results of this study, which served to improve the overall reproducibility of the deposition process, are presented in Chapter 4.

<table>
<thead>
<tr>
<th>Order</th>
<th>Colour</th>
<th>Si$_3$N$_4$ Thickness Range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silicon</td>
<td>0-0.020</td>
</tr>
<tr>
<td></td>
<td>Brown</td>
<td>0.020-0.040</td>
</tr>
<tr>
<td></td>
<td>Golden Brown</td>
<td>0.040-0.055</td>
</tr>
<tr>
<td></td>
<td>Red</td>
<td>0.055-0.073</td>
</tr>
<tr>
<td></td>
<td>Deep Blue</td>
<td>0.073-0.077</td>
</tr>
<tr>
<td>First</td>
<td>Blue</td>
<td>0.077-0.093</td>
</tr>
<tr>
<td></td>
<td>Pale Blue</td>
<td>0.093-0.100</td>
</tr>
<tr>
<td></td>
<td>Very Pale Blue</td>
<td>0.100-0.110</td>
</tr>
<tr>
<td></td>
<td>Silicon</td>
<td>0.110-0.120</td>
</tr>
<tr>
<td></td>
<td>Light Yellow</td>
<td>0.120-0.130</td>
</tr>
<tr>
<td></td>
<td>Yellow</td>
<td>0.130-0.150</td>
</tr>
<tr>
<td></td>
<td>Orange-red</td>
<td>0.150-0.180</td>
</tr>
<tr>
<td>First</td>
<td>Red</td>
<td>0.180-0.190</td>
</tr>
<tr>
<td></td>
<td>Dark Red</td>
<td>0.190-0.210</td>
</tr>
<tr>
<td></td>
<td>First Blue</td>
<td>0.210-0.230</td>
</tr>
<tr>
<td></td>
<td>Blue-Green</td>
<td>0.230-0.250</td>
</tr>
<tr>
<td></td>
<td>Light-Green</td>
<td>0.250-0.280</td>
</tr>
<tr>
<td></td>
<td>Orange-Yellow</td>
<td>0.280-0.300</td>
</tr>
<tr>
<td></td>
<td>Second Red</td>
<td>0.300-0.330</td>
</tr>
</tbody>
</table>

Table 3.2. Colour/Thickness Relationship for CVD Si$_3$N$_4$ (Ref 106).
3.4.2 Experimental Apparatus for AlN Deposition

The experimental apparatus used for the deposition of evaporated AlN is shown in Figure 3.2. In its current form, the apparatus consists of a standard metal evaporator which has been modified to allow a flow of ammonia (NH$_3$) into the evaporation chamber. Initially, the ammonia was transported into the chamber by bubbling nitrogen through an aqueous ammonia solution. However, the system has now been modified such that NH$_3$ gas can now be introduced into the chamber.

![Figure 3.2. Schematic diagram of the apparatus used to deposit evaporated AlN. [A - Gauge; B - Aqueous NH$_3$; C - Flow Meter; D - Tungsten Filament; E - Shutter; F - Sample Holder; G - Gas Inlet; V - Valve; DP - Diffusion Pump and RP - Rotary Pump].](image-url)
Prior to loading the samples, aluminium wire was first degreased by boiling in hot solvent and then mounted onto the evaporator filament. The GaAs samples were then placed in close proximity to the filament and the entire chamber evacuated to a pressure of $5 \times 10^{-5}$ torr. With the chamber being continuously pumped, a mixture of $N_2/NH_3$ gas was allowed to enter the chamber and, simultaneously, the aluminium wire was slowly melted onto the evaporator filament.

After allowing the gas flow to reach a steady value, the aluminium was heated to evaporation temperature and allowed to react with the ammonia gas according to the following reaction.

$$2\ Al + 2\ NH_3 \rightarrow 2AlN + 3H_2$$

It should be noted that, in order to allow this reaction to take place successfully, the distance between the samples and the filament was made greater than the mean free path of the Al vapour (typically <5 cm).

This process was allowed to continue until approximately 1000 Å of AlN has been deposited, at which time the filament temperature was reduced and the reaction stopped.

Subsequent to AlN deposition, the GaAs samples were removed from the evaporation chamber and cleaved into 5 mm x 5 mm squares in preparation for the annealing stage. The experimental apparatus used to achieve rapid thermal annealing of the samples is described in the following section.
3.5 Annealing Techniques

3.5.1 The Double Graphite Strip Heater (GSH)

Annealing of the implanted samples was performed in a graphite strip heater, based on an earlier design by Donnelly(55). Recently however, Gwilliam et al(107) have shown that an improved performance may be obtained by using two graphite strips in place of the original one. A schematic diagram of the double graphite strip heater used in this project is shown in Figure 3.3.

Figure 3.3. Schematic of the Dual Graphite Strip Heater.
The apparatus is seen to consist of two thin sheets of graphite (typically 120 mm x 40 mm x 0.5 mm) which form a bridge between two pillar electrodes. The strips themselves are separated by a gap of approximately 1.5 mm, into which the 5 mm$^2$ GaAs samples are placed. The entire system itself is housed in a vacuum bell-jar which allows annealing to be performed in a nitrogen atmosphere. Temperature measurement and control are achieved by means of a closed feedback loop from the two thermocouples, $T_1$ and $T_2$, which are embedded within each of the graphite strips. $T_3$ is an additional thermocouple which is mounted between the graphite strips, thereby representing the sample temperature. In practice, however, the difference in temperature recorded by the thermocouples $T_1$, $T_2$ and $T_3$ was very small, typically less than 4°C at annealing temperatures between 900°C and 1000°C. Heating of the graphite is achieved by passing currents of up to 100 A through the strips, thereby enabling the system to reach temperatures of approximately 1000°C in five to six seconds. Figure 3.4 (overleaf) shows a typical time temperature response obtained from the graphite strip heater, in which three annealing parameters are identified.
Figure 3.4. Typical Temperature - Time Response of GSH.

The parameters defined in this figure are:

(1) The rise time ($t_r$) from room temperature to the annealing temperature.

(2) The dwell time ($t_d$) at temperature, and

(3) The annealing temperature itself ($T_a$).

Thus, all samples can be designated according to their annealing schedule by using the format $T_a/t_r/t_d$ (eg 1000/8/10).

A further point to note from Figure 3.4 is that the sample temperature (denoted by $T_3$) is seen to lag the strip temperature by approximately one second. Consequently, there is no overshoot of the sample temperature in this system, though the one second lag may introduce some error in the recorded value of the dwell time, $t_d$. 
Prior to annealing, the sample and control thermocouples $T_1$, $T_2$ and $T_3$ were calibrated by using the melting points of silver (963°C) and gold (1062°C) as references. The response of the thermocouples was then assumed to be linear over the range 500°C - 1100°C. These assumptions lead to combined uncertainties in the annealing time and annealing temperature of ±1 second and ±2°C, respectively.

3.5.2 Annealing Procedure

After encapsulation with AIN or a Si$_3$N$_4$/AIN combination, 5 mm x 5 mm square samples of implanted GaAs were placed in the centre of the lower graphite strip, in close proximity to the sample thermocouple, $T_3$. The enclosed system was evacuated to a pressure of $10^{-1}$ torr before annealing was performed in a nitrogen atmosphere. Annealing temperatures used in this study were in the range 480°C - 1000°C and the annealing times were varied between two seconds and 120 seconds, depending on the anneal temperature used.

Subsequent to annealing, the samples were allowed to cool to a temperature of between 70°C - 80°C before being removed from the apparatus. During the annealing stage, values of the three annealing parameters $T_a$, $t_r$ and $t_d$ were recorded, as was the post annealing condition of the encapsulant.

Under extreme annealing conditions, (ie high temperatures at long times) the encapsulant showed signs of possible failure (eg peeling or cracking). These samples were therefore excluded
from any further processing. In the majority of cases, however, successfully annealed samples were immediately prepared for differential Hall effect measurements, as described in the next section.

3.6 Differential Hall Effect Measurements

This section describes the various processing and measurement techniques involved in measuring the sheet and volume electrical properties of the ion implanted layers. These measurements, which were obtained from a combination of Hall effect and layer removal techniques, form the basis for all the experimental results generated during this study.

3.6.1 Preparation of Samples

In order to satisfy the criteria for accurate measurements using the Hall technique\(^{108}\), the samples were initially cut into a clover-leaf shape before the encapsulant was removed (Figure 3.5). The required shape was obtained by fixing a metal mask to the GaAs samples using dental wax. The unmasked portions of the samples were then cut away by using a jet of nitrogen which contained an abrasive alumina powder. Once completed, the sample and mask were separated by immersion in hot toluene for five minutes. The samples were then cleaned in hot methanol and rinsed in distilled water, prior to dissolution of the encapsulant in hydrofluoric (HF) acid. Once the encapsulant had been fully removed, the samples were again rinsed in distilled water and cleaned in boiling methanol, in preparation for the formation of electrical contacts.
3.6.2 Alloyed Contact Formation

Alloyed electrical contacts were formed by using tin dots for the sulphur and selenium implanted layers and a 95%In/5%Zn compound for the magnesium and beryllium implants.

In all cases, the samples were placed onto a small electrical heater and four pieces of the contact material positioned near the edge of each clover-leaf (as indicated in Figure 3.5). A mixed H₂/N₂ gas (5% H₂ in N₂) was then allowed to flow over the sample in order to absorb any moisture from within the system and to provide a reducing atmosphere. Alloying of the contacts was performed at 300°C for four minutes, during which time the H₂/N₂ gas was allowed to bubble through a solution of hydrofluoric acid for approximately one and a half minutes, thereby preventing oxide formation. In preparation for Hall effect measurements, the linearity of the contacts was checked by measurement of I-V characteristics using a standard transistor curve tracer.
3.6.3 The Hall Effect and Van Der Pauw Technique

Consider the shape of the sample (shown previously in Figure 3.5), in which a constant current \( I \) is flowing between two contacts (1 and 3) in the \( x \) direction. Application of a magnetic field \( B \) at right angles to the current flow (i.e., in the \( z \) direction) causes an electric field to be induced between the contacts (2 and 4) in the \( y \)-plane — a phenomenon first discovered by Hall\(^{108b}\). The resulting change in voltage, known as the Hall voltage, \( V_H \), can be expressed in terms of the sheet Hall coefficient, \( R_{HS} \), such that:

\[
R_{HS} = 10^8 \frac{V_H}{B \cdot I} = \frac{R_H}{d} \text{(cm}^2\text{/Coulomb)}
\]

where \( B \) is the applied magnetic field in Gauss.

An analysis technique proposed by Van der Pauw\(^{108a}\) can be suitably applied to Hall effect measurements providing the following criteria are satisfied:

1. That the electrical contacts are positioned at the periphery of the sample and are as small as possible.
2. That the sample is of uniform thickness, and
3. That the surface of the sample is continuous over its entire area.

Fulfillment of these criteria, by using a clover-leaf sample, allows the following parameters to be measured directly.
Sheet Resistivity

If the resistance \( \frac{V_H}{I} \) between adjacent contacts is denoted by:

\[
\begin{align*}
R_2 &= \frac{V_{3,4}}{I_{1,2}} \quad \text{and} \quad R_2 = \frac{V_{4,1}}{I_{2,3}} \quad \text{and} \quad \frac{R_1}{R_2} < 5
\end{align*}
\]

the specific sheet resistivity, \( \rho_s \), of the material may be expressed as:

\[
\rho_s = \frac{\pi}{\ln 2} \left( \frac{R_1 + R_2}{2} \right) F \left[ \frac{R_1}{R_2} \right] \Omega/\square
\]

where \( F \) is a function of the contact symmetry and is given by:

\[
F = 1 - \frac{(R_1 - R_2)^2}{(R_1 + R_2)^2} \left( \frac{\ln 2}{2} - \frac{(R_1 - R_2)^4}{(R_1 + R_2)^4} \right) \left[ \frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12} \right]
\]

or

\[
F = 1 - 0.3466 \frac{(R_1 - R_2)^2}{R_1 + R_2} - 0.0924 \left( \frac{R_1 - R_2}{R_1 + R_2} \right)^4
\]

Hence, for a perfectly symmetrical sample, \( R_1 = R_2 \) and \( F = 1 \)
(2) **The Sheet Hall Mobility** ($\mu_{HS}$)

This is easily calculated from the equations for $\rho_s$ and $R_{HS}$ and is given by:

$$\mu_{HS} = \frac{R_{HS}}{\rho_s} \text{ (cm}^2\text{/vs)}$$

(3) **Sheet Carrier Concentration, $N_S$**

The sheet carrier concentration, which gives a measure of the free carrier activation in an implanted layer, is given by:

$$N_S = \frac{r}{e R_{HS}} \text{ (carriers/cm}^2)$$

where $e$ is the electronic charge ($e = 1.602 \times 10^{-19} \text{ C}$) and $r$, the Hall scattering factor, is the ratio between the Hall mobility $\mu_H = \frac{R_{HS}}{\rho_s}$ and the conductivity mobility $\mu$. In general, the magnitude of $r$, which depends on the impurity concentration and a number of scattering mechanisms within the material, is assumed to equal unity. Depending on the dominant transport mechanism (i.e., holes or electrons), this assumption can lead to an uncertainty margin of 20% in the value of $N_S(110)$.

3.6.4 **The Hall Apparatus**

A schematic diagram of the experimental Hall apparatus, used to obtain the above parameters, is shown in Figure 3.6. Samples to be measured are first mounted onto a custom made ceramic circuit board, where electrical connections are made to the contacts.
using a highly conductive silver paint. The mounted sample is then positioned between the pole pieces of an electromagnet in preparation for resistivity and Hall effect measurements.

![Diagram of Hall Apparatus](image)

**Figure 3.6. Schematic Layout of the Hall Apparatus.**

Allowance is made for slight non-linearities in the electrical contacts by performing two sets of measurements, the sample current being reversed in the second set. In addition, the direction of the magnetic field (currently 5 K gauss) is also reversed to reduce the effects of sample misalignment. In order to implement these changes effectively, the system utilises a computer controlled switching sequence which enables twelve separate measurements to be performed. Details of the actual measurements are given in Table 3.3. The voltage readings obtained from the measurement cycle are then fed into a computer, which calculates the required values of $R_{hs}$, $\rho_s$, $N_s$, $\mu_s$ and $F$, using the equations stated above.
Table 3.3

Sequence of Steps Used in Hall Measurements

<table>
<thead>
<tr>
<th>Measurement Number</th>
<th>Current</th>
<th>Measured Voltage</th>
<th>Magnetic Field</th>
<th>Measurement Performed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+ IAB</td>
<td>VCD</td>
<td>0</td>
<td>Resistivity</td>
</tr>
<tr>
<td>2</td>
<td>+ IBC</td>
<td>VAD</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>+ IBD</td>
<td>VAC</td>
<td>0</td>
<td>Hall</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>+B</td>
<td>&quot;</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-B</td>
<td>&quot;</td>
</tr>
<tr>
<td>7</td>
<td>- IAB</td>
<td>VDC</td>
<td>0</td>
<td>Resistivity</td>
</tr>
<tr>
<td>8</td>
<td>- IBC</td>
<td>VDA</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>9</td>
<td>- IBD</td>
<td>VCA</td>
<td>0</td>
<td>Hall</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>&quot;</td>
<td>+B</td>
<td>&quot;</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-B</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

As indicated in Figure 3.6, the additional equipment consists of a Keithley constant current source, which supplied sample currents with an accuracy of ±0.5%, and a digital voltmeter which, in this case, was a Solartron A200 series.
3.6.5 Depth Profiling of Implanted Layers

Since both the carrier concentration and mobility of an implanted layer are functions of depth, then it is desirable to measure their distribution as a depth profile. This is achieved by initially measuring the sheet parameters, removing a thin surface layer (typically 300 Å) by chemical etching, and then remeasuring the sheet values. For the purposes of this study, the etch solution consisted of a mixture of H$_2$SO$_4$:H$_2$O$_2$:H$_2$O in a volume ratio of 1:1:125. During etching, the solution was continuously agitated by means of a magnetic stirrer and the electrical contacts were protected from the etch by a coating of Apiezon wax. After etching for the required time (e.g., thirty seconds), the sample was rinsed in de-ionised water to prevent any further etching, and the next set of measurements performed. The volume values of carrier concentration $N_V$ and mobility, $\mu_V$, obtained for the $n$th layer (of thickness $d_n$) are given by:

$$N_V = \left[ \frac{1}{(\rho_s)_{n}} - \frac{1}{(\rho_s)_{n} + 1} \right] \frac{1}{ed_n \mu_n} \text{(carriers/cm}^3\text{)}$$

and

$$\mu_V = \left[ \frac{(R_{HS})_n}{(\rho_s)_{n}^2} - \frac{(R_{HS})_{n + 1}}{(\rho_s)_{n + 1}^2} \right] \frac{1}{(\rho_s)_{n}} - \frac{1}{(\rho_s)_{n+1}} \text{cm}^2/\text{vs}$$

The measuring and etching procedures are repeated until the entire implant layer has been consumed, or until the voltage readings from the sample become too unstable to measure accurately.
At the end of the final etching sequence, the actual etch rate of the solution is determined by measuring the step height of the etched layer on a Rank–Taylor Hobson Talystep. The volume values of carrier concentration were then adjusted using the corrected etch rate.

Thus, by using a combination of the encapsulation, annealing and measurement techniques described in this section, it was possible to study the changes in electrical activation which occur when samples of ion implanted GaAs are annealed at different times and temperatures. The results obtained from a number of studies on both donor and acceptor implants are presented in the following chapter.
4.1 Introduction

This chapter presents the experimental results obtained from a number of investigations on donor and acceptor ions in GaAs. The chapter itself is divided into two main sections, the first of which contains information on the electrical properties of the acceptors, beryllium and magnesium. The second section, which concentrates on a study of donors in GaAs, is initially concerned with a characterisation of the Si$_3$N$_4$ apparatus (Section 4.4). This was performed in order to make significant improvements to the quality and reproducibility of the Si$_3$N$_4$ layers used in this study. As a result of the optimised encapsulation process, the electrical properties of the donor ions, sulphur and selenium, could be investigated more extensively.

In all cases, the emphasis has been placed on studying the time and temperature dependence of the electrical properties of these ions, with a view to developing a model for the activation mechanisms involved in each case. Thus, following implantation and encapsulation, the samples were annealed at various temperatures and times using the double graphite strip heater.
During each annealing sequence, an accurate record was made of the annealing temperature ($T_A$), the dwell time at temperature ($t_d$) and the rise time, ($t_r$).

As discussed in the previous chapter, after annealing, the samples were cut into the required clover-leaf pattern before the encapsulant was removed in hydrofluoric (HF) acid. Electrical contacts were then made to the samples in preparation for Hall effect measurements of sheet carrier concentration ($N_S$, $P_S$), sheet mobility, $\mu_S$, and sheet resistivity $\rho_S$. In order to determine the electrical properties as a function of implant depth selected samples were also subjected to depth profiling as described in Section 3.6.

As a final point it should be noted that, although a number of discussion areas are raised during this chapter, a detailed explanation of these points is reserved until Chapter 5. The emphasis in this chapter is therefore placed solely on presenting the experimental data and identifying those areas which require further discussion.

4.2 Beryllium Implantation

4.2.1 Sheet Electrical Properties of Be Implanted GaAs

In order to study the activation mechanisms for beryllium in GaAs, a 2" wafer of semi-insulating GaAs was implanted with $5 \times 10^{14}$ Be/cm$^2$ at an energy of 75 keV. Following implantation, the wafer was encapsulated with approximately 1000 Å of reactively evaporated AlN and then cleaved into 5 mm x 5 mm square samples.
Rapid thermal annealing was performed using the double graphite strip heater, for annealing times of two to sixty seconds, at temperatures in the range 485°C to 650°C. Subsequent to annealing, the samples were examined for any indication of encapsulant failure and, when suitable, mounted for Hall effect measurements.

Figure 4.1 shows the variation in sheet hole concentration as a function of annealing time and temperature for the $5 \times 10^{14}$ Be$^+/\text{cm}^2$ implant. The error bars on the data points correspond to an estimated uncertainty of ±1 second in annealing time and ±10% in the measured values of sheet carrier concentration (as discussed in Section 3.5).

As shown by the diagram, the electrical activity is seen to increase rapidly with both annealing time and temperature, reaching a maximum sheet concentration of approximately $3.4 \times 10^{14}/\text{cm}^2$ after an anneal at 630°C for ten seconds. In addition, as the annealing temperature is increased, the levels of activity are seen to saturate at increasingly shorter annealing times. Hence, for each annealing temperature, two distinct regions of activation can be identified:

(1) A time dependent region, in which the activity increases with annealing time, and

(2) a time independent (saturation) region in which the sheet electrical activity remains virtually constant.
Figure 4.1. Sheet hole concentration versus annealing temperature and time for the 75 keV, $5 \times 10^{14}$ Be/cm$^2$ implant. Annealing was performed in the double graphite strip heater using 1000 Å of reactively evaporated AlN as an encapsulant. Error bars on the data represent uncertainties in annealing time and $P_s$. Solid lines are predicted by the theory presented in Chapter 5.
It should be noted that, at sufficiently high temperatures (i.e., >620°C), the time dependent region becomes too short to measure accurately. In this region, the changes in activity then become a function of annealing temperature only. Following an analysis by Bensalem et al.\textsuperscript{(58)}, it is possible to re-plot the saturated activity values in the form of an Arrhenius plot (ln $P_s$ versus $1/T$), from which a characteristic activation energy may be deduced. The resulting graph (Figure 4.2(a)) yields an activation energy ($E_a$) of $(0.32 \pm 0.05)$ eV for beryllium in GaAs, the interpretation of which is reserved for discussion in a later chapter.

With regard to the sheet resistivity, annealing at temperatures below 485°C yielded highly resistive samples which were unsuitable for accurate Hall effect measurements. However, as the temperature (and time) of the anneal was increased, the sheet resistivity decreased by over two orders of magnitude, in inverse proportion to the sheet hole concentration (Figure 4.3). As an example of the rapid decrease in resistivity, Figure 4.3 indicates that an anneal at 485°C for ten seconds yielded a sheet resistivity in excess of $5 \times 10^3 \Omega/\square$. By keeping the time constant and increasing the annealing temperature to 630°C, the sheet resistivity is seen to decrease by nearly two orders of magnitude, to approximately 140 $\Omega/\square$. It must be stated at this point that, although lower resistivity values would undoubtedly have been obtained by annealing at higher temperatures, the main purpose of the experiment was to study the changes in activity as a function of both temperature and time. Since the time dependent region decreased at the higher annealing temperatures, this limited the useful temperature range to between 485°C and 650°C.
Figure 4.2. Calculation of Activation Energy (Ea) and Diffusion Energy (Ed) for the 75 keV, $5 \times 10^{14}$ Be/cm$^2$ implant, (curves (a) and (b) respectively).

(Ed values will be referred to in Chapter 5).
Figure 4.3. Sheet Resistivity versus Annealing Time and Temperature for the 75 keV, $5 \times 10^{14}$ Be/cm$^2$ implant.
Figure 4.4 shows the variation in sheet hole mobility as a function of the average hole concentration in the implanted region, which is calculated from the formula:

\[
\text{Average Hole Concentration (cm}^{-3}) = \frac{\text{Sheet Carrier Conc (cm}^{-2})}{3\Delta R_p}
\]

As a comparison, the maximum reported hole mobilities(111) for the same carrier concentration are plotted on the same axis. The results show that, after annealing, the hole mobility in the implanted layer compares favourably with the values obtained from good quality "p" type GaAs. The indication here is that, for this beryllium implant, much of the implant damage has been removed by annealing at temperatures as low as 485°C. The limiting factor on the hole mobility in these samples is therefore the doping level in the implanted layer.
Figure 4.4. Comparison of experimental and theoretical hole mobilities versus carrier concentration. Implant was $5 \times 10^{14}$ Be/cm$^2$ at 75 keV.
4.2.2 Carrier and Atomic Distributions in Be Implanted GaAs

In order to assess the changes in carrier concentration and mobility as a function of implant depth, a number of samples were subjected to depth profiling, as discussed in Chapter 3.6. Figure 4.5 shows carrier concentration and mobility profiles obtained from samples annealed at temperatures in the range 580°C to 650°C for an anneal time of thirty seconds. In agreement with the sheet results, the figures indicate that the peak hole concentration increases with annealing temperature, up to the predicted theoretical maximum of $1 \times 10^{19}$ carriers/cm$^3$. All the carrier concentration profiles are seen to lie within the limits of the theoretical PRAL(103) distributions, indicating that no significant redistribution of implanted beryllium has occurred. Furthermore, since the carrier concentration profiles closely follow the predicted atomic distribution and contain no anomalous peaks or troughs, this would indicate an absence of electrical compensation from such effects as unannealed implant damage($^{54,56}$). This statement is further supported by the values of hole mobility throughout the implanted layer, which are comparable to those expected from good quality "p" type GaAs(111).
Figure 4.5. Carrier concentration and mobility profiles for the $5 \times 10^{14}$ Be/cm$^2$ implant, as a function of annealing temperature. Annealing was performed in a Double Graphite Strip Heater for thirty seconds. Curve (a) - 580°C Anneal, (b) - 650°C Anneal.
4.2.3 Summary of Be Results

It has been demonstrated that the electrical activity of a $5 \times 10^{14}/\text{cm}^2$, 75 keV Be$^+$ implant is governed by the combined factors of annealing temperature and time (Figure 4.1). The electrical activation process can be conveniently split into two distinct regimes.

1. A time dependent region, and
2. A saturation region, in which the sheet electrical activity remains constant with annealing time.

By plotting the saturated activity values as a function of inverse temperature, an activation energy of $(0.32 \pm 0.05)$ eV was measured for Be in GaAs (Figure 4.2(a)). Depth profiling of the samples (Figure 4.5) showed that peak hole concentrations of around $1 \times 10^{19}/\text{cm}^3$ can be obtained without any measurable impurity diffusion. The profiles also indicated that much of the implant damage had been removed after annealing above 500°C. This statement was confirmed by the sheet and volume mobility values, which were in close agreement to the values reported for good quality GaAs.
4.3 Magnesium Implantation

4.3.1 Introduction

In order to study magnesium activation, individual implant doses of $5 \times 10^{14}$ Mg/cm$^2$ and $1 \times 10^{14}$ Mg/cm$^2$ were implanted at an energy of 100 keV into samples of semi-insulating GaAs. Both implants were performed at room temperature, with the GaAs substrates aligned in a non-channelling direction to the ion beam.

Following implantation, the implanted samples were encapsulated with approximately 1000 Å of reactively evaporated AlN and cleaved into 5 mm x 5 mm squares. In the case of the $5 \times 10^{14}$ Mg/cm$^2$ implant, the large amount of material available allowed a comprehensive study of the electrical properties as a function of both annealing time and temperature. For the $1 \times 10^{14}$ Mg/cm$^2$ implant, however, the electrical activity was measured predominantly as a function of annealing temperature only, thereby allowing a direct comparison of activation energies to be made between the two implant doses.
4.3.2 Sheet Electrical Properties of $5 \times 10^{14}$ Mg/cm$^2$ Implant

Directly following the implantation and encapsulation stages, samples were annealed in the double graphite strip heater at temperatures in the range 630°C to 750°C, for times of between four and thirty seconds. After annealing, the integrity of the encapsulant was inspected visually and was found to be suitable for annealing at 750°C for up to thirty seconds. Following encapsulant removal, the samples were mounted for Hall effect measurements of the sheet electrical properties.

In Figure 4.6 the sheet hole concentration, $P_s$, is plotted as a function of annealing time at various anneal temperatures. In a similar manner to the beryllium results (Figure 4.1), the electrical activity is seen to increase with time at a given temperature until, at the longer annealing times, a saturation value is reached. The electrical results show that an activation level of approximately 40% can be achieved by annealing at 740°C for ten seconds, and indicate that, at temperatures above 710°C, the time dependent activation process occurs in less than two seconds. Further comments on the likely diffusion mechanisms which can occur during this time period are given in Chapter 5. However, in the saturation region itself, notice should be given to the actual values of sheet carrier concentration (Table 4.1), as reference will be made to these values during the discussion chapter.
Figure 4.6. Sheet hole concentration versus annealing time and temperature for the $5 \times 10^{14}$ Mg/cm$^2$ implant. Solid lines are predicted by the theory presented in Chapter 5.
Table 4.1

Sheet Electrical Properties of $5 \times 10^{14}$ Mg/cm$^2$ Implant

Versus Anneal Temperature (Saturated Values)

<table>
<thead>
<tr>
<th>Anneal Temperature</th>
<th>Sheet Hole Concentration (Carrier/cm$^2$)</th>
<th>Sheet Hole Mobility (cm$^2$/vs)</th>
<th>Sheet Resistivity ($\Omega$/$\square$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>640°C</td>
<td>$5.6 \times 10^{13}$</td>
<td>63</td>
<td>1900</td>
</tr>
<tr>
<td>650°C</td>
<td>$6.3 \times 10^{13}$</td>
<td>75</td>
<td>1330</td>
</tr>
<tr>
<td>660°C</td>
<td>$7.0 \times 10^{13}$</td>
<td>82</td>
<td>1100</td>
</tr>
<tr>
<td>675°C</td>
<td>$8.2 \times 10^{13}$</td>
<td>89</td>
<td>830</td>
</tr>
<tr>
<td>685°C</td>
<td>$9.6 \times 10^{13}$</td>
<td>92</td>
<td>740</td>
</tr>
<tr>
<td>710°C</td>
<td>$1.3 \times 10^{14}$</td>
<td>96</td>
<td>540</td>
</tr>
<tr>
<td>740°C</td>
<td>$1.86 \times 10^{14}$</td>
<td>102</td>
<td>360</td>
</tr>
</tbody>
</table>

The Arrhenius plot of the saturated activity values is shown in Figure 4.7(a), in which an activation energy of $(1.0 \pm 0.1)$ eV is measured for magnesium in GaAs. Since this value of $E_a$ is approximately three times larger than that of the beryllium activation energy ($E_a = 0.32$ eV), this would imply that the activation mechanisms for these acceptors are significantly different. Further comments on the difference in activation energies will be discussed in Chapter 5.
Figure 4.7. Calculation of Activation Energy \((E_a)\) and Diffusion Energy \((E_d)\) for the \(5 \times 10^{14} \text{ Mg/cm}^2\) implant, (curves \((a)\) and \((c)\) respectively). Also included is the Activation Energy plot for the \(1 \times 10^{14} \text{ Mg/cm}^2\) implant (curve \((b)\)).
The changes in sheet resistivity as a function of annealing temperature and time are shown in Figure 4.8. Here, annealing at 630°C for five seconds produces a sheet resistivity of approximately 6500 Ω/□ at a sheet hole concentration of 1.3 x 10^{13}/cm^{2}. By increasing the anneal temperature to 685°C, the electrical activity increases to 18% (P_s = 9 x 10^{13}/cm^{2}) and the corresponding sheet resistivity decreases by over an order of magnitude. A sheet resistivity value of 700 Ω/□ was obtained after a five second anneal at 685°C, with a minimum of 362 Ω/□ being reached after 740°C for thirty seconds.

The apparent difference in the ratios of sheet carrier concentration and sheet resistivity can be explained by the variation in hole mobility, which is normally expected to decrease as the carrier concentration increases. However, Figure 4.9 shows that, for these samples, the sheet mobilities themselves are significantly less than those predicted for good quality GaAs of the same doping levels, and increase as the carrier concentration increases. In the worst case, the hole mobility is degraded by over 60% from its predicted value of 150 cm^{2}/vs (at a sheet concentration of P_s = 1.3 x 10^{13}/cm^{2}). However, as the carrier concentration increases, the mobility values are seen to improve significantly.
Figure 4.8. Sheet resistivity versus annealing time and temperature for the $5 \times 10^{14}$ Mg/cm$^2$ implant.
Figure 4.9. Comparison of experimental and theoretical hole mobilities for the $5 \times 10^{14}$ Mg/cm$^2$ implant, (curves (a) and (b) respectively).
Although this behaviour is in direct contradiction to the theoretical curve of Figure 4.9, similar trends have also been observed for other ions in GaAs\(^{(46)}\). In accordance with this earlier work, it is proposed that:

(1) The mobility in these samples is being degraded by the effects of residual implant damage, and
(2) These effects reduce as the anneal temperature (and hence the carrier concentration) is increased.

For the same dose beryllium implant, however, the hole mobilities showed no signs of degradation and were limited only by the carrier concentration in the implanted layer (Figure 4.4). Therefore, in addition to the differences in activation energies (1.0 eV for magnesium and 0.32 eV for beryllium) the behaviour of the hole mobility in these samples also indicates that the annealing mechanisms are different for each ion. As previously stated, a detailed discussion of all these points will be presented in a later chapter.

### 4.3.3 Sheet Electrical Properties of 1 x 10\(^{14}\) Mg/cm\(^2\) Implant

In addition to the 5 x 10\(^{14}\) Mg/cm\(^2\) implant, 100 keV Mg\(^{+}\) ions were also implanted to a dose of 1 x 10\(^{14}\) Mg/cm\(^2\). AlN encapsulated samples were annealed in the double graphite strip heater for the same annealing times and temperatures as the 5 x 10\(^{14}\) Mg/cm\(^2\) implant, in order to ensure that the interpretation of results from each implant would be equally affected by any variations in the annealing conditions. Thus, a direct comparison could be made between the activation energies obtained for the two doses, and
any changes in the encapsulant would affect both sets of samples equally. The variation in sheet hole concentration as a function of annealing time and temperature is shown in Figure 4.10 for the $1 \times 10^{14}$ Mg/cm$^2$ implant.

In a similar manner to the higher dose magnesium implant, the levels of activity are seen to increase with annealing temperature, reaching a sheet concentration value of $6.1 \times 10^{13}$/cm$^2$ at 750°C. However, a difference in the two cases is that, for the $5 \times 10^{14}$ Mg/cm$^2$ implant, a time dependent activation region was still in evidence at annealing temperatures from 630°C to 675°C (Figure 4.6). The behaviour of the $1 \times 10^{14}$ Mg/cm$^2$ implant is, however, quite different. For the same annealing temperatures, the activity levels are all seen to have reached their saturation values and no measurable time-dependence is observed. Thus, for magnesium implanted GaAs, these results suggest that the annealing times required to reach saturation become shorter as the implant dose is reduced. In the saturation region itself, the activation energy of 1.0 eV (Figure 4.7(b)) is the same as that measured for the $5 \times 10^{14}$ Mg/cm$^2$ implant. Thus, although the diffusion mechanisms in magnesium implanted GaAs would seem to be dose dependent, the activation process which occurs in the saturation region is shown to be independent of implant dose.
Figure 4.10. Sheet Hole Concentration versus Annealing Time and Temperature for the $1 \times 10^{14}$ Mg/cm$^2$ implant.
The actual values of the saturated sheet electrical properties are
given in Table 4.2 as a function of annealing temperature, for an
anneal time of thirty seconds.

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>Sheet Hole Concentration (Carrier/cm⁻²)</th>
<th>Sheet Resistivity Ω/Ω</th>
<th>Sheet Hole Mobility cm²/VS</th>
</tr>
</thead>
<tbody>
<tr>
<td>640</td>
<td>4.5 x 10¹²</td>
<td>9980</td>
<td>136</td>
</tr>
<tr>
<td>650</td>
<td>7.5 x 10¹²</td>
<td>5470</td>
<td>160</td>
</tr>
<tr>
<td>675</td>
<td>1.3 x 10¹³</td>
<td>3000</td>
<td>157</td>
</tr>
<tr>
<td>685</td>
<td>2.2 x 10¹³</td>
<td>1900</td>
<td>154</td>
</tr>
<tr>
<td>720</td>
<td>3.7 x 10¹³</td>
<td>1200</td>
<td>139</td>
</tr>
<tr>
<td>740</td>
<td>5 x 10¹³</td>
<td>920</td>
<td>135</td>
</tr>
<tr>
<td>750</td>
<td>6.2 x 10¹³</td>
<td>750</td>
<td>134</td>
</tr>
</tbody>
</table>

In a similar manner to the results from the 5 x 10¹⁴ Mg/cm²
implant, the mobility values of Table 4.2 are plotted in
Figure 4.11 as a function of the average carrier concentration in
the implanted layer. As in the case of the higher dose implant,
the hole mobility is again degraded by the effects of residual
implant damage, increasing only when the anneal temperature is
increased. A difference in the amount of damage introduced by the
two implants is reflected by the experimental values of
Figure 4.11, which indicate that, above a certain annealing
temperature, the compensating effects of the lower dose implant
damage start to decrease. Above this critical temperature, the
mobility values then follow their predicted dependence on the
carrier concentration(111).
Figure 4.11. Comparison of Theoretical and Experimental Hole Mobilities for the $1 \times 10^{14}$ Mg/cm$^2$ implant.
4.3.4 Carrier Concentration and Mobility Profiles in Magnesium Implanted GaAs

Figure 4.12 shows the variation in the carrier concentration and mobility profiles from the $5 \times 10^{14} \text{Mg/cm}^2$ implant as a function of annealing temperature, at an anneal time of thirty seconds. For the lowest temperature anneal of 640°C, Figure 4.12(a) shows that electrical activity does not occur in the tail region of the implanted layer, indicating that a significant amount of electrical compensation still exists due to residual implant damage. As the annealing temperature is increased (Figures 4.12(b) and 4.12(c)) the peak carrier concentration increases and, since the damage related compensation is being removed, electrical activity also begins to occur in the tail of the implant profile.

For the highest temperature anneal (700°C) the carrier concentration reaches a peak of approximately $5 \times 10^{18}$ carriers/cm$^3$, with a mobility profile which is commensurate with this level of doping and which shows no signs of degradation.

An important point to note is that, in all cases, no sign of magnesium in- or out-diffusion is observed in these profiles, so that the time/temperature dependence of Figure 4.6 is due to a mechanism which occurs within the boundaries of the as-implanted profile. The possible mechanisms which could give rise to this time-dependent behaviour are discussed further in the latter section of Chapter 5.
Figure 4.12. Carrier concentration and Mobility profiles as a function of Annealing Temperature for the $5 \times 10^{14}$ Mg/cm$^2$ implant. Annealing was performed at 640°C (curve (a)), 680°C (curve (b)) and 700°C (curve (c)) for thirty seconds.
4.3.5 Summary of Magnesium Results

As in the earlier beryllium case, the results from the 100 keV, $5 \times 10^{14}$ Mg/cm$^2$ implant show that the electrical activity is a function of both annealing time and temperature (Figure 4.6). At the longer annealing times the electrical activity reaches a saturation value, which itself is temperature dependent. From an Arrhenius plot of these saturated values an activation energy ($E_a$) of $1.0 \pm 0.1$ eV was calculated for the $5 \times 10^{14}$ Mg/cm$^2$ implant (Figure 4.7(a)). This value was in close agreement with the value obtained from a similar analysis of the $1 \times 10^{14}$ Mg/cm$^2$ implant (Figure 4.7(b)). However, a significant difference exists between these two implant doses in that the sheet electrical properties of the $1 \times 10^{14}$ Mg/cm$^2$ implant show no evidence of a time-dependent behaviour in the temperature range 630 - 675°C (Figure 4.10), whereas, for the $5 \times 10^{14}$ Mg/cm$^2$ case, a time dependent region is still observable at these temperatures (Figure 4.6).

The results of Figure 4.9 indicate that annealing of the $5 \times 10^{14}$ Mg/cm$^2$ implant at such low temperatures also causes severe degradation of the hole mobility. As the annealing temperature increases, so the mobility values gradually improve until, at approximately 700°C, the hole mobility reaches a value commensurate with the hole concentration in the implanted layer. Such trends are in accordance with results obtained from other studies of ion-implanted GaAs, which indicate that the hole mobility is being seriously affected by the presence of residual implant damage(46).
For the $1 \times 10^{14}$ Mg/cm$^2$ implant, similar effects were in evidence at annealing temperatures from 630°C - 685°C (Figure 4.11). However, above this temperature range, the hole mobility began to follow its predicted dependence on carrier concentration. This effect is further evidence that the mobility is being affected by residual damage, since, for a lower dose implant this damage can be annealed out at lower temperatures.

From the depth profiles of Figure 4.12, the results indicate that a peak hole concentration of around $5 \times 10^{18}$ carriers/cm$^3$ can be achieved by annealing a $5 \times 10^{14}$ Mg/cm$^2$ implant at 700°C for short times (<30 seconds). An important point to note is that none of these profiles showed signs of magnesium in- or out-diffusion, so that the time and temperature dependence of Figure 4.6 arises from a process which occurs within the boundaries of the as-implanted profile itself.

4.4 Characterisation of Si$_3$N$_4$ Growth

4.4.1 Introduction

Before proceeding with an extensive investigation of selenium and sulphur implanted GaAs (sections 4.5 and 4.6) it was first deemed necessary to characterise the growth of the Si$_3$N$_4$ encapsulant used in annealing these samples. As previously stated, a study by Sealy et al(4) demonstrated the superiority of a double-layer encapsulant, which consisted of a thin film of Si$_3$N$_4$ (typically 300 Å) on which was deposited a 1000 Å layer of reactively
evaporated AlN. The reason that this combination of layers was successful becomes evident when one considers the thermal expansion co-efficients of the materials involved, ie:

\[
\begin{align*}
\text{GaAs} & : 6.9 \times 10^{-6} \text{ K}^{-1} \text{ (at 200°C)} \\
\text{AlN} & : 6.3 \times 10^{-6} \text{ K}^{-1} \text{ (at 200°C)} \\
\text{Si}_3\text{N}_4 & : 2.8 \times 10^{-6} \text{ K}^{-1} \text{ (at 200°C)}
\end{align*}
\]

Evidently, the use of AlN as an encapsulant is highly desirable, since the effects of any interfacial strain will be reduced due to the close match in thermal expansion co-efficients. However, early studies have shown that, because the quality of the AlN layers was so variable, its performance as an encapsulant was quite unpredictable\(^{30,31}\). Alternately, since good-quality \(\text{Si}_3\text{N}_4\) layers could be easily and reproducibly deposited, the concept of a double-layer encapsulant was proposed\(^4\). Although less critical than the quality of a single AlN encapsulant, the success of the double-layer encapsulant does depend on the thickness of the \(\text{Si}_3\text{N}_4\) layer, since this must be thin enough to allow the AlN to have an effect on the induced strain, yet thick enough to ensure a uniform film over the GaAs surface. Thus, in order to achieve reproducible control over the thickness of the \(\text{Si}_3\text{N}_4\) layer used in these studies, the deposition rate of \(\text{Si}_3\text{N}_4\) has been studied as a function of growth temperature and time.
4.4.2 Time/Temperature Dependence of Si$_3$N$_4$ Growth

The samples used in this study were formed by cleaving segments of GaAs into approximately 1 cm x 1 cm squares. Layers of Si$_3$N$_4$ were then deposited at temperatures of 550°C, 575°C, 600°C and 625°C, by the method described in Chapter 3. At each temperature the growth rate (as a function of time) was determined from the thickness reference chart of Table 3.2 and plotted as Figure 4.13.

It should be noted that, throughout this study, the gas flow rates were maintained at the following values:

- NH$_3$ : 600 cc/min
- 5% SiH$_4$ : 400 cc/min
- N$_2$ : 1500 cc/min

Figure 4.13 shows that, for each of the four temperatures studied, a linear relationship is obtained between the Si$_3$N$_4$ film thickness and growth time. This indicates that the governing reaction for the process \(3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2\) takes place at a constant rate for each growth temperature.
Figure 4.13. Si$_3$N$_4$ film thickness as a function of Growth Time and Temperature. Intercept is at $t = 4.5$ seconds.

Although providing a useful reference for subsequent Si$_3$N$_4$ growth operations, this data also indicates the minimum temperature at which the reaction begins to take place. From measurements of temperature rise-time, the heating rate of the graphite strip within the Si$_3$N$_4$ apparatus is approximately 110°C/second. Since the x-axis intercept of Figure 4.13 is at $t = 4.5$ seconds, this would indicate that the minimum temperature for the onset of Si$_3$N$_4$ growth is approximately 500°C. This is further justified by plotting the gradients of the curves from Figure 4.13 as a function of growth temperature. The resulting graph (Figure 4.14) is approximately linear within the temperature range 550°C - 625°C and has an intercept on the x-axis at a temperature of 525°C-530°C which is in good agreement with the value measured above.
Figure 4.14. $\text{Si}_3\text{N}_4$ Growth Rate versus Growth Temperature. Onset of $\text{Si}_3\text{N}_4$ growth occurs at the intercept value of 530°C.

Furthermore, since this graph is in the form: $y = mx + c$, then $\text{Si}_3\text{N}_4$ growth in the current system may be described by the following expression:

$\text{Si}_3\text{N}_4$ growth rate ($\text{Å/s}$) $= 0.06 \times$ Growth Temperature (for $T > 525°C$)

The most effective $\text{Si}_3\text{N}_4$ layers for use with the double-layer encapsulant were found, by experiment, to be those with thicknesses of between 300 Å and 500 Å. Thus, for the donor implanted samples described in the following sections, all $\text{Si}_3\text{N}_4$ growth operations performed at 625°C for times of between eight to ten seconds, thereby yielding an average film thickness of 400 Å. Use of these layers, in conjunction with the evaporated AlN films, allowed annealing to be performed at temperatures in excess of 1000°C without significant encapsulant failure.
4.5 Selenium Implantation

A previous study by Sealy et al.\textsuperscript{[59]} showed that, as in the Be\textsuperscript{+} and Mg\textsuperscript{+} cases, the electrical activity obtained from a 300 keV $1 \times 10^{13}$ Se/cm\textsuperscript{2} implant was also a function of both annealing time and temperature. For the purposes of this study, Se\textsuperscript{+} implantation was again performed at an energy of 300 keV, though in this case the dose was reduced to $1 \times 10^{13}$ Se\textsuperscript{+}/cm\textsuperscript{2}. Ion implantation was performed at room temperature, with the samples aligned in a non-channelling direction to the Se\textsuperscript{+} ion beam. Following implantation, the Se\textsuperscript{+} implanted samples were encapsulated with 400 Å of Si\textsubscript{3}N\textsubscript{4} plus 1000 Å of reactively evaporated AlN and annealed in the double graphite strip heater for times of five to forty seconds, at temperatures in the range 800°C - 975°C. Subsequent to annealing the samples were prepared for Hall effect measurements in the manner described in Section 3.4.

The variation in sheet electron concentration with annealing time and temperature is shown in Figure 4.15, in which the electrical activity of a $1 \times 10^{13}$ Se\textsuperscript{+}/cm\textsuperscript{2}, 300 keV implant is again seen to be a function of both the annealing time and temperature. For this dose an activation efficiency of 11\% was obtained after annealing at 800°C for thirty seconds, rising to 75\% when the annealing temperature was increased to 975°C.
Figure 4.15. Sheet Electron Concentration versus Annealing Time and Temperature for the 300 keV, $1 \times 10^{13}$ Se/cm$^2$ implant. Solid lines are predicted by theory (Chapter 5).
As in the case of the magnesium and beryllium implants, each of the annealing temperatures has a saturation value associated with it, the actual values of which are listed in Table 4.3 below. From an Arrhenius plot of these saturated values (Figure 4.16(a)) the activation energy for selenium in GaAs was measured as $(1.2 \pm 0.1 \text{ eV})$, a value which is in agreement with the earlier work of Sealy et al(59) and with other studies of Se-implanted GaAs(112,113) performed at different implant doses and energies.

In addition to the sheet electron concentration, the sheet resistivity and Hall mobility were also measured, the results being summarised in Table 4.3. It should be noted that, since this was a relatively low dose implant, no degradation of the electron mobility was observed in the samples annealed between 800°C and 975°C. This is also in agreement with the results obtained from a previous study(114).

**Table 4.3**

Sheet Electrical Properties of $1 \times 10^{13} \text{ Se/cm}^2$ Implant versus Anneal Temperature (Saturated Activity Values)

<table>
<thead>
<tr>
<th>Anneal Temperature</th>
<th>Sheet Electron Concentration (Carriers/cm$^2$)</th>
<th>Sheet Mobility (cm$^2$/vs)</th>
<th>Sheet Resistivity Ωcm</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>$1.12 \times 10^{12}$</td>
<td>3060</td>
<td>1813</td>
</tr>
<tr>
<td>825°C</td>
<td>$1.72 \times 10^{12}$</td>
<td>2970</td>
<td>1224</td>
</tr>
<tr>
<td>850°C</td>
<td>$2.27 \times 10^{12}$</td>
<td>2740</td>
<td>1000</td>
</tr>
<tr>
<td>875°C</td>
<td>$3.0 \times 10^{12}$</td>
<td>2590</td>
<td>802</td>
</tr>
<tr>
<td>900°C</td>
<td>$3.35 \times 10^{12}$</td>
<td>2830</td>
<td>658</td>
</tr>
<tr>
<td>950°C</td>
<td>$4.4 \times 10^{12}$</td>
<td>2600</td>
<td>537</td>
</tr>
<tr>
<td>975°C</td>
<td>$8.12 \times 10^{12}$</td>
<td>1850</td>
<td>415</td>
</tr>
</tbody>
</table>
Figure 4.16. Calculation of Activation and Diffusion energies \( (E_{a} \text{ and } E_{d}) \) for the \( 1 \times 10^{13} \text{ Se/cm}^{2} \) implant (curves \( (a) \) and \( (b) \) respectively).
4.6 Sulphur Implantation

For this study, a set of room temperature samples implanted with $1 \times 10^{14}$/cm$^2$ 120 keV sulphur ions were encapsulated with 400 Å of Si$_3$N$_4$ plus 1000 Å of AlN and annealed in the double graphite strip heater. Using the Hall effect apparatus, the sheet electrical properties were then measured as a function of annealing times from five to sixty seconds, in a temperature range of 800°C - 975°C.

4.6.1 Sheet Electrical Properties of Sulphur Implanted GaAs

Figure 4.17 indicates that, as in the $1 \times 10^{14}$ Mg/cm$^2$ case, the sheet electron concentration of the $1 \times 10^{14}$ sulphur implant increases with annealing temperature, but remains essentially independent of the annealing time (up to sixty seconds). For an 800°C anneal, the activation level remains constant at approximately 3.5%, but rises to 33% when the annealing temperature is increased to 975°C. The corresponding sheet resistivities (Table 4.4) decrease from 372 Ω/□ at 800°C to 79 Ω/□ at 975°C, with corresponding mobility values which show no signs of being affected by implant damage (Figure 4.19). As stated previously, higher values of carrier concentration (and lower resistivities values) could undoubtedly have been achieved by annealing at higher temperatures, but the main aim of the work was to study the mechanisms of activation rather than to achieve high values of carrier concentration.
Figure 4.17. Sheet Electron Concentration versus Annealing Time and Temperature for the $1 \times 10^{14}$ S/cm$^2$ implant.
From the data in Figure 4.17, an activation energy of 1.1 ± 0.1 eV was calculated for sulphur in GaAs (Figure 4.18), this value being close to the activation energies of both magnesium (1.0 ± 0.1 eV) and selenium (1.2 ± 0.1 eV). The complete range of carrier concentration, resistivity and mobility values are given in Table 4.4.

**Table 4.4**

Sheet Electrical Properties of 1 x 10^14 S/cm² Implant

versus Anneal Temperature

<table>
<thead>
<tr>
<th>Anneal Temperature</th>
<th>Sheet Electron Concentration (Carriers/cm²)</th>
<th>Sheet Mobility (cm²/Vs)</th>
<th>Sheet Resistivity Ω/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>4.0 x 10^12</td>
<td>4160</td>
<td>370</td>
</tr>
<tr>
<td>850°C</td>
<td>6.4 x 10^12</td>
<td>3360</td>
<td>300</td>
</tr>
<tr>
<td>875°C</td>
<td>1.1 x 10^13</td>
<td>2980</td>
<td>290</td>
</tr>
<tr>
<td>900°C</td>
<td>1.7 x 10^13</td>
<td>2460</td>
<td>150</td>
</tr>
<tr>
<td>925°C</td>
<td>2.1 x 10^13</td>
<td>2370</td>
<td>120</td>
</tr>
<tr>
<td>950°C</td>
<td>2.7 x 10^13</td>
<td>2150</td>
<td>90</td>
</tr>
<tr>
<td>975°C</td>
<td>4.2 x 10^13</td>
<td>1950</td>
<td>80</td>
</tr>
</tbody>
</table>

A further, and perhaps important point to note is that the sheet mobility values of Figure 4.19 are in close agreement with the electron mobility values obtained from good quality "n"-type GaAs(111).
Figure 4.18. Calculation of Activation Energy (Ea) for the $1 \times 10^{14}$ S/cm$^2$ implant. Saturation values are given in Table 4.4.
Figure 4.19. Comparison of experimental and theoretical electron mobilities for the 120 keV, $1 \times 10^{14} S/cm^2$ implant.
From this data it can be deduced that, although the changes in electrical activity are governed by a temperature dependent activation process (with $E_a \approx 1.1$ eV), the mobility values are not themselves part of this temperature dependence, but are predominantly governed by a combination of the carrier concentration in the implanted layer and the quality of the material after annealing. As in the case of the high-temperature annealed magnesium samples the inactive fraction of the implanted sulphur dose is not, therefore, being compensated by the effects of residual crystalline damage (since this would be annealed out at these temperatures and, if present, would have a more serious affect on the mobility in the implanted layer).

4.6.2 Carrier and Atomic Distributions in Sulphur Implanted GaAs

A number of the samples from Figure 4.17 have been profiled to assess the distribution of carrier concentration and mobility with depth. Figure 4.20 illustrates that, in accordance with the sheet results, the peak carrier concentration in the implanted layer increases with annealing temperature, reaching a value of $6 \times 10^{18}$ carriers/cm$^3$ after an anneal at 950°C for twenty seconds. At relatively short annealing times such as this, the profiles do not show signs of the extensive profile broadening normally assumed with a fast-diffusing impurity such as sulphur(75), thereby reflecting one of the advantages of RTA over furnace annealing. However, Figure 4.21 illustrates that the dwell time at temperature does have a significant effect on the profile shape, with evidence of sulphur indiffusion being observed as the annealing time at 900°C is increased from ten to sixty seconds.
Figure 4.20. Electron Concentration and Mobility Profiles for the $1 \times 10^{14}$ S/cm$^2$ implant. Annealing was performed for the times and temperatures indicated.
Figure 4.21. Influence of dwell time ($t_d$) on profile shape for the $1 \times 10^{14}$ S/cm$^2$ implant. Annealing time increased from ten to sixty seconds at 900°C.
An interesting point to note is that this change in the profile shape is not reflected in the sheet electrical properties (Figure 4.17), which were seen to remain virtually constant as the annealing time was increased. Thus, the implication is that, for short times, time-dependence of the sulphur in-diffusion process is not reflected as a time-dependence in the sheet electrical properties. As stated previously these points, and the other issues raised in this chapter, will be further discussed in Chapter 5.

4.7 Conclusions

As a conclusion to this chapter, it has been demonstrated that the activation levels in ion-implanted GaAs are strongly dependent on the post-implant annealing conditions. From the saturation regions associated with each ion species, a characteristic activation energy has been measured, this energy being independent of implant dose (or implant energy).

However, as yet, no attempt has been made to characterise the time-dependent regions associated with each ion, nor to develop a comprehensive model for the activation processes in ion-implanted GaAs.

With these objectives in mind, the analysis of the data is presented in the following chapter.
5.1 Introduction

The aim of this chapter is to present a detailed interpretation of the various experimental data and, from a knowledge of the processes involved, develop a model for the activation mechanisms in ion-implanted GaAs.

In the previous chapter, the electrical activation of Be$^+$, Mg$^+$, Se$^+$ and S$^+$ ions was studied as a function of annealing temperature and time, (the experimental results being presented in Sections 4.1 to 4.4 respectively). From these results, the activation process for the majority of these ions was shown to be divided into two distinct regions, ie:

(1) a time dependent regime, in which a diffusion energy is likely to dominate in the activation process, and

(2) a saturation region, in which a characteristic activation energy exists for each of the ions studied.
Before assigning these energies to a particular diffusion or activation process, it is first necessary to discuss the possible mechanisms which can occur in ion-implanted GaAs and also develop an expression which can be used to model the experimental data in a comprehensive way.

5.2 Development of Activation Model

The basic equations used in constructing this model (which are presented in detail in the next section) have been generally applied to a number of annealing mechanisms, such as defect annealing\(^{(95)}\), impurity incorporation\(^{(96)}\) or precipitate dissolution. Furthermore, since each of these processes may involve mechanisms of diffusion or complex formation and dissociation, it is also possible to define a characteristic energy for each of the mechanisms involved, and hence model each process in terms of these energies. However, before establishing which of the above processes have a significant effect on the number of implanted impurities which become electrically active, it is first necessary to identify the various types of activation mechanism which can occur for each of the ions studied.

As a crystal, the structure of GaAs can be viewed as being composed of two interleaved sublattices of Ga and As. Thus, in order for an impurity to act as a donor or acceptor, it must first locate itself as a substitutional dopant on one of these sublattices\(^{(115)}\). The donors Se and S for example, have been shown to preferentially occupy As sites\(^{(96)}\) whereas atoms such as Be, Mg
and Sn are predominantly found to occupy sites in the Ga sublattice \cite{87}. (This is true, despite the fact that Sn is a group IV ion like Si and Ge, both of which are amphoteric in GaAs)

After implantation, the implanted region is considerably damaged and the implanted impurities are distributed at random positions within the implanted layer. Following a post-implant anneal, the crystallinity of the damaged layer is restored and the implanted species is then incorporated into the lattice in one of four possible configurations \cite{116}:

(1) as electrically inactive interstitials,
(2) as substitutional donors or acceptors,
(3) as impurities which form complex defects (e.g., impurity-vacancy complexes), or
(4) in the form of precipitates.

For GaAs, various models have been put forward to explain the behaviour of the different impurities used as dopants, although most of the work has been performed on crystalline (as opposed to ion implanted) material. In some cases the electrically inactive fraction of the implanted impurity has been linked to the presence of precipitates, while others have proposed that the inactive fraction of the dose arises from impurity atoms forming complex defects with Ga or As vacancies. As an example, a detailed description of the incorporation of Te and Sn in GaAs has been presented by Hurle \cite{95,96}, in which the presence of complex defects is used to explain impurity compensation in doped GaAs. Although ion implanted layers have not been analysed to the same degree, several authors \cite{117,118} have tentatively explained the
lack of electrical activity in ion-implanted GaAs as being due to the presence of point defects and/or the formation of impurity-vacancy complexes.

As a comparison, Table 5.1 provides a summary of the various reasons proposed to explain electrical inactivity in ion-implanted GaAs.

Table 5.1

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Inactive State</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>Interstitial</td>
<td>119</td>
</tr>
<tr>
<td>Zn</td>
<td>Interstitial</td>
<td>120</td>
</tr>
<tr>
<td>Mg</td>
<td>Complex Defect</td>
<td>121</td>
</tr>
<tr>
<td>Sn</td>
<td>Complex Defect</td>
<td>96</td>
</tr>
<tr>
<td>Se</td>
<td>Complex Defect (Se$<em>{AS}$ - V$</em>{Ga}$)</td>
<td>59</td>
</tr>
<tr>
<td>S</td>
<td>Complex Defect (S$<em>{AS}$ - V$</em>{AS}$)</td>
<td>122</td>
</tr>
<tr>
<td>Si</td>
<td>Complex</td>
<td>(Si$<em>{AS}$ - Si$</em>{Ga}$) 123, 124</td>
</tr>
</tbody>
</table>

For the ions studied in this work, Table 5.1 shows that the types of inactive state can be split into two major groups, i.e:

(1) Ions such as Be and Zn for which the inactive fraction exists in the form of interstitials.
(2) Ions such as Se, S, Mg (and Sn) for which the inactive fraction exists in the form of impurity-vacancy complexes.
Thus, in order to achieve electrical activity from these impurities, it may be possible that either an interstitial atom, a complex or a host atom (or vacancy) migrates until a suitable site is found.

However, before trying to establish which of these mechanisms may apply to the ions studied in this work, it is first necessary to develop a theory which can be applied to model the time and temperature dependence for each ion. Such a model would then allow the experimental data to be interpreted in terms of the actual physical processes involved.

5.3 Theoretical Modelling of Implanted GaAs

In developing a theoretical model for the data, it is first necessary to consider a number of points arising from the experimental work.

Firstly, because the activation process contains a time-dependent regime, it is desirable to model this region in terms of a diffusion energy which can then be linked to the mobile species. Secondly, the model should allow a saturation region to be predicted at long annealing times and, thirdly, the model should be universally applicable to all ions.

In the general case, for a given number of implanted impurities (N), the number of impurities which can become active at a given time (N(t)) is proportional to the number of impurities available for activation at that time. This can be expressed in terms of a first-order rate equation of the form:
where $K$ is a rate constant for the process, and is a function of the diffusion coefficient ($D$) in ion-implanted material. Hence, we define:

$$K = K'D = K'D \exp\left(-\frac{E_d}{kT}\right) \quad \ldots \quad (5.2)$$

where $K'$ is a constant which, in this case, corresponds to the average distance that an atom has to diffuse in order to become electrically active. The other terms are: $D_0$, which is a pre-exponential factor for the process, $k$, which is the Boltzmann constant, $T$, the absolute temperature, and $E_d$, the energy of diffusion in ion implanted material.

As mentioned above, this type of equation has been used extensively in describing mechanisms of diffusion and migration, and has also been used as the basis of an earlier model for activation in ion-implanted GaAs\(^{58,59}\). Unfortunately though, the use of Equation 5.1 in describing the time and temperature dependence of electrical activation is inaccurate in most cases, since the form of this equation implies a process which can continue at the same rate ($K$) for all values of time.

The presence of a saturated activity region in ion-implanted GaAs means, therefore, that this equation must be modified to allow for the presence of a temperature-dependent saturation term, which is
defined as $\Gamma(T)$. $\Gamma(T)$ is therefore the maximum activity which occurs at a given temperature, and is proportional to the implanted dose. Hence $\Gamma(T)$ can be expressed in the form:

$$
\Gamma(T) \propto N_D \exp\left(-\frac{E_a}{kT}\right) \quad \ldots (5.3)
$$

where $N_D$ is the implant dose (ions/cm$^2$) and $E_a$ is a characteristic activation energy which describes the activation process for each ion species. Thus, in order to fully describe the activation process, the $\Gamma(T)$ term must be included in the original rate equation (5.1). The required modification to include this term is,

$$\frac{dN(t,T)}{dt} = -K(N(t) - \Gamma(T)) \quad \ldots (5.4)$$

which, following integration, yields,

$$N(t,T) = \Gamma(T) \left[1 - \exp\left(-Kt\right)\right] \quad \ldots (5.5)$$

Hence, by substitution of Equations 5.2 and 5.3 into Equation 5.5, the entire time-temperature dependence of electrical activity can be described by:

$$N(t,T) \propto N_D \exp\left(-\frac{E_a}{kT}\right) \left[1 - \exp\left(-K'D_0 t \exp\left(-\frac{E_d}{kT}\right)\right)\right] \quad \ldots (5.6)$$
In order to calculate the respective values of \( E_a \) and \( E_d \) in this equation, it is necessary to analyse the time and temperature dependence in two distinct regimes. At the longer annealing times (i.e., in saturation), Equation 5.6 reduces to Equation 5.3, so that the slope of an Arrhenius plot of \( \ln \Sigma(T) \) versus \( \frac{1}{T} \) yields a value for \( E_a \) (as shown previously in Figures 4.2, 4.7, 4.16 and 4.22). The intercept value of such a plot (at \( x = 0 \)) also yields a proportionality constant for use in Equation 5.6, since this intercept is, itself, proportional to \( \ln N_0 \). Calculation of the intercept constant is an important factor, since it allows additional values in the saturation region to be predicted from the equation for a straight line graph:

\[
\ln \Sigma(T) = \ln \text{Intercept} - \frac{E_a}{kT}
\]

In the time-dependent region, values of diffusion energy are calculated by re-arranging Equation 5.6 to yield an expression of the form:

\[
\ln \left[ \frac{1}{1 - \frac{N(t,T)}{\Sigma(T)}} \right] = \ln (f(t,T)) = \ln K'D_0 - \frac{E_d}{kT} \quad \text{.... (5.7)}
\]

so that a plot of \( \ln (f(t,T)) \) versus \( \frac{1}{T} \) yields a slope proportional to \( E_d \) and an intercept corresponding to \( K'D_0 \).
5.4 Interpretation of Experimental Data

5.4.1 Activation Energy Values

As shown in Chapter 4, from the Arrhenius plots of $\ln E(T)$ versus $1/T$, the values of activation energy have been calculated from the saturation regions associated with each ion studied. These values are listed in Table 5.2, in conjunction with other values of $E_a$ reported in the literature.

With the exception of the 0.7 eV reported for the $1 \times 10^{15}$ Be/cm$^2$ implant (which has a significant error attached to it), the values of $E_a$ in Table 5.2 are seen to fall into two distinct groups, i.e.

1. $E_a$ values of 0.3 - 0.5 eV (for Zn, Be), and
2. $E_a$ values of 1.0 - 1.2 eV (for Mg, Sn, Se and S).

With reference to Table 5.1, the main causes of electrical inactivity in GaAs were also divided into two distinct categories (i.e., interstitials or complexes). Thus, at this stage, it is proposed that the activation energy in the saturation region corresponds to the net energy required to allow an inactive impurity to become electrically active. In the case of Be and Zn, the low $E_a$ values (0.3 - 0.5 eV) correspond to the energy required to activate an interstitial impurity, whereas for Se, Sn, Mg and S the energy of 1.0 - 1.2 eV is thought to be the energy required to split up an impurity-vacancy complex, thereby allowing the impurity to become electrically active. This explanation is in agreement with existing literature on Se(59), Sn(96) and Si(123,124) incorporation in GaAs (in which similar explanations...
have been proposed) and is also consistent with work in which the presence of point defects in ion implanted material is related to the presence of electrically inactive complex defects(125). As previously mentioned, the values of Ea in Table 5.2 are found to be independent of ion energy, ion dose and implant temperature(112,113,126). These conclusions are consistent with the magnesium results obtained in this work, and support the value obtained from the $1 \times 10^{13}$/cm$^2$ selenium implant, which is in good agreement with other Ea values for selenium in GaAs. Additional reference to all these Ea values will be made at a later stage in this discussion.

Table 5.2

Activation Energies in Ion-Implanted GaAs

<table>
<thead>
<tr>
<th>Ion Species</th>
<th>Implant Dose (ions/cm$^2$)</th>
<th>Activation Energy (Ea)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>$5 \times 10^{14}$</td>
<td>0.3 - 0.45 eV</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{15}$</td>
<td>0.7 eV$^*$</td>
<td>123</td>
</tr>
<tr>
<td>Zn</td>
<td>$1 \times 10^{15}$</td>
<td>0.3 - 0.45 eV</td>
<td>97</td>
</tr>
<tr>
<td>Mg</td>
<td>$5 \times 10^{14}$</td>
<td>1.0 ± 0.1 eV</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{14}$</td>
<td>1.0 ± 0.1 eV</td>
<td>This work</td>
</tr>
<tr>
<td>Se</td>
<td>$1 \times 10^{14}$</td>
<td>1.2 ± 0.1 eV</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{13}$</td>
<td>1.2 ± 0.1 eV</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{15}$</td>
<td>1.3$^*$ eV</td>
<td>112</td>
</tr>
<tr>
<td>Sn</td>
<td>$1 \times 10^{14}$</td>
<td>1.2 ± 0.1 eV</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{15}$</td>
<td>1.2 eV</td>
<td>127</td>
</tr>
<tr>
<td>S</td>
<td>$1 \times 10^{14}$</td>
<td>1.1 ± 0.1 eV</td>
<td>This work</td>
</tr>
</tbody>
</table>

* Note that for some of the values in the Table, the electrical activities may not all be in the saturation region (so that a large error in Ea will result).
5.4.2 Analysis of Time Dependent Regions

In order to assign a diffusion energy to the time-dependent regions of the beryllium, magnesium and selenium activation processes (Figures 4.1, 4.6 and 4.15 respectively), it is first necessary to re-plot the experimental data in the manner defined by Equation 5.7. The resulting graphs (Figures 4.2(b), 4.7(c) and 4.16(b)) yield Ed values of $2.3 \pm 0.1$ eV, $2.45 \pm 0.1$ eV and $2.5 \pm 0.1$ eV for beryllium, magnesium and selenium, respectively. By comparing these values of Ed with those obtained from other impurities in ion implanted GaAs (Table 5.3), we see that, in general, the values of diffusion energy are similar for all the ions studied.

Table 5.3

Diffusion Energies for Crystalline and Ion-Implanted GaAs

(For values marked * see text)

<table>
<thead>
<tr>
<th>Implanted Species</th>
<th>Diffusion Energy in Implanted GaAs (eV)</th>
<th>Reference</th>
<th>Diffusion Energy in Crystalline GaAs (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>2.45 *</td>
<td>This work (128)</td>
<td>2.7</td>
<td>(129)</td>
</tr>
<tr>
<td>Be</td>
<td>2.32 *</td>
<td>This work (130)</td>
<td>1.2</td>
<td>(129)</td>
</tr>
<tr>
<td>Se</td>
<td>2.5 * ± 0.1</td>
<td>This work (59)</td>
<td>4.16</td>
<td>(131)</td>
</tr>
<tr>
<td>S</td>
<td>3.0 *</td>
<td>(132)</td>
<td>2.6</td>
<td>(129)</td>
</tr>
<tr>
<td>Sn</td>
<td>2.5 * ± 0.1</td>
<td>(58)</td>
<td>2.0 - 2.7</td>
<td>(133), (134)</td>
</tr>
</tbody>
</table>
With reference to some of the above values, the diffusion energies marked with an asterisk (*) were obtained from experiments on profile broadening of the implanted layer (as opposed to the annealing time dependence values studied in this work). Care must therefore be taken in drawing any comparisons between these sets of values, since the magnitude of $E_d$ may be altered by the type of mechanism involved in each case. In the present study, for example, the aim of the work is to analyse the time-dependence of the electrical activation process, an effect which occurs at relatively short annealing times, where no significant profile broadening is observed. Since this time-dependent behaviour arises from a mechanism which occurs within the boundaries of the as-implanted profile, it may be erroneous to draw strict comparisons to processes which occur outside the profile boundary (as in the diffusional broadening type of experiments). Furthermore, the presence of a time independent saturation region, (in which the sheet values remain constant), implies that small changes in the profile shape (which may occur at the longer annealing times) are not reflected by a significant change in the sheet concentration values. It is unlikely therefore, that the time-dependent activation regime can be attributed solely to a process which involves a diffusion of the implanted impurity.

A possible exception to the $E_d$ values obtained from profile broadening studies is the value of 4.3 eV for Se implanted GaAs, which was obtained from an annealing time-dependence by Sealy et al\(^\text{(59)}\). This value of $E_d$ is also in good agreement with an earlier value of 4.16 eV\(^\text{(131)}\) obtained from tracer diffusion

* Note that in some cases a change in the profile shape is reflected by a change in the sheet carrier concentration.
studies of selenium in GaAs. However, by using the more refined theory of Section 5.2 to re-analyse the data from Sealy's publication, a value of $E_d \approx 2.5 - 3.0$ eV was obtained for the $1 \times 10^{14}$ Se/cm$^2$ implant reported in this work.

In the various early studies of annealing kinetics in ion-implanted GaAs, all the measured $E_d$ values were interpreted as being the diffusion energies of the implanted species; mainly because the values of $E_d$ appeared to be similar to published diffusion energies in single-crystal GaAs. However, it must be stated that, by excluding the effects of a saturation region in the analysis, the equations used in these studies do not result in an accurate value for $E_d$. By applying the more detailed theory of Section 5.2 to the available data, it seems that, in fact, the $E_d$ values are similar for all ions and lie in the range 2.3 - 2.5 eV.

Before proposing a mechanism which corresponds to these values of diffusion energy, it is necessary to consider a number of points from Table 5.3 and from the experimental results of Chapter 4. These factors may be summarised as follows:

(a) the diffusion energy in ion implanted GaAs is seen to be virtually independent of the ion species;

(b) within the time-dependent regions of Figures 4.1, 4.6 and 4.15, no signs of impurity diffusion are observed in the depth profiles of the samples, and
Although the sulphur depth profiles of Figure 4.21 show signs of impurity diffusion, these effects are not significantly reflected in the sheet values of Figure 4.19.

The conclusion to be drawn from points (b) and (c) is that any diffusion of the implanted species is not observable from the sheet electrical properties and that, as previously stated, the time-dependent region therefore arises from a mechanism which occurs within the boundaries of the as-implanted profile. Furthermore, since it appears that the diffusion energy values do not necessarily correspond to those of the implanted impurity, then the only other mobile species in the implanted layer are the substrate atoms (or vacancies) or, in the case of a complexed ion, the impurity-vacancy complex itself. In GaAs, the diffusion energies of the substrate atoms (Ga and As) and their respective vacancies $V_Ga$ and $V_{as}$ have been measured by a number of workers. The reported $Ed$ values for both Ga and $V_Ga$ are within the range $2.5 \pm 0.4 \text{ ev}(135,136)$, whereas for As and $V_{as}$, the published values are between $3.0 - 3.5 \text{ ev}(137,138,139)$.

By comparing these values to the $Ed$ values of Table 5.3, and considering the fact that there is no significant impurity diffusion in these samples, the results suggest that the diffusion energies measured for the various ions correspond more closely to a diffusion of the substrate atoms (or vacancies) and not to a diffusion of the implanted impurity itself.
The complete model for the activation processes in ion-implanted GaAs can therefore be described in terms of two possible mechanisms, each one depending on whether the inactive fraction of the implanted dose exists in the form of complexes or interstitials.

5.5 Activation Mechanisms in Ion Implanted GaAs

5.5.1 Mechanism for Interstitial Impurities (Mechanism A)

This model assumes that, prior to becoming electrically active, all the implanted atoms occupy interstitial positions. During low temperature/short time annealing, no significant diffusion of these impurities takes place (no profile broadening) but a re-ordering of the damaged layer occurs from a simultaneous diffusion of substrate atoms and vacancies. In the Ga sublattice, the diffusion energy for this process is approximately 2.3 eV - 2.5 eV. Electrical activation can then occur by considering the following process: If we assume that V_{Ga} is the diffusing species, then as the gallium vacancy approaches an interstitial atom, the interstitial transfers itself to the (diffusing) vacancy, where it can then become electrically active. The energy required for this activation process, as determined in Section 4.2, is of the order of 0.3 eV - 0.4 eV. Thus, using Be as an example, this type of activation mechanism can be summarised by the reversible reaction:

\[ \text{Be}_i + V_{Ga} \rightleftharpoons \text{Be}_{Ga} \]

where Be\(_i\) represents a beryllium atom occupying an interstitial
site, and $V_{Ga}$ represents the gallium vacancy.

5.5.2 Mechanism for Complexed Impurities (Mechanism B)

In this case, the precise mechanism which occurs in activating a complexed impurity is dependent on two additional factors, (1) the type of vacancy involved in the complex (ie $V_{As}$ or $V_{Ga}$) and (2) which sublattice site the impurity must occupy in order to become electrically active. For the selenium case, the inactive fraction is thought to be in the form of a complex with a gallium vacancy (ie $Se_{As} - V_{Ga}$)(59). Thus, the time-dependence in this case could be dominated by either (1) a diffusion of Ga atoms to the complex site ($E_d \approx 2.5$ eV), thereby allowing the complex to split up by annihilation of the $V_{Ga}$, or (2) a diffusion of the complex to a gallium atom (the energy for this process also being approximately 2.5 eV).

In the analysis of the $1 \times 10^{13}$ Se/cm$^2$ implant (Figure 4.16) the diffusion energy of $2.5 \pm 0.1$ eV would appear to correspond to a diffusion of Ga atoms to the complex site. The work by Sealy et al(59) also yields an $E_d$ value of between 2.5 - 3.0 eV for an implant dose of $1 \times 10^{14}$ Se/cm$^2$, which would tend to agree with the above hypothesis.
In the saturation region, the individual activation energies of 1.0 - 1.2 eV are independent of this diffusion process and can be attributed to the energy required to split the impurity-vacancy complex and activate the implanted species. The activation mechanism for complexed ions can therefore be summarised as follows:

\[(\text{Ga(As)} - \text{VGa(As)}) + \text{Ga(As)} \xrightarrow{\text{GaGa(AsAs)}} \text{Ga(As)} + \text{GaGa(AsAs)}\]

where \((\text{Ga(As)} - \text{VGa(As)})\) corresponds to an impurity on a gallium (or arsenic) site, complexed with a gallium (or arsenic) vacancy. However, the exact form of the complex will depend on the ion species and the type of vacancy with which it complexes.

It should be noted that both of the above models are also fully applicable to the activation of other ions, given that the inactive fraction of the implanted dose exists in the form of complexes or interstitials. However, in its current form, there are some limitations to the model, since, for example, the effects of profile broadening cannot be fully predicted from the sheet electrical properties. This is especially true of the sulphur data (Figure 4.17) in which the sheet values at the longer annealing times do not change significantly, even though some broadening of the electrical profile is occurring (Figure 4.21). Although the Be and Mg profiles of Figures 4.5 and 4.12 do not show signs of impurity diffusion, this may occur if the annealing time is extended considerably. Additional work is therefore required before a full prediction of the active carrier profile can be obtained.
Table 5.4 summarises the values of activation and diffusion energies for the four ions studied in this work, along with the relative intercept values obtained from the respective plots of $E_a$ and $E_d$.

**Table 5.4**

<table>
<thead>
<tr>
<th>Ion Species</th>
<th>Ion Dose cm$^{-2}$</th>
<th>Activation Energy $E_a$(eV)</th>
<th>Intercept Constant (cm$^{-2}$)</th>
<th>Diffusion Energy $E_d$(eV)</th>
<th>$K'D_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>$5 \times 10^{14}$</td>
<td>0.32 ± 0.1</td>
<td>5.2 x $10^{16}$</td>
<td>2.3 ± 0.1</td>
<td>5 x $10^{12}$</td>
</tr>
<tr>
<td>Mg</td>
<td>$5 \times 10^{14}$</td>
<td>0.98 ± 0.1</td>
<td>3.4 x $10^{17}$</td>
<td>2.45 ± 0.1</td>
<td>3 x $10^{12}$</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{14}$</td>
<td>0.98 ± 0.1</td>
<td>1.76 x $10^{17}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>$1 \times 10^{13}$</td>
<td>1.2 ± 0.1</td>
<td>1.35 x $10^{16}$</td>
<td>2.5 ± 0.1</td>
<td>4 x $10^{11}$</td>
</tr>
<tr>
<td>S</td>
<td>$1 \times 10^{14}$</td>
<td>1.1 ± 0.1</td>
<td>3.65 x $10^{16}$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In this table, the intercept constants (at $1/T = 0$) have been determined by applying a linear regression analysis to the Arrhenius plots of $\ln \frac{f(t, T)}{T}$ v $\frac{1}{T}$. The values of $K'D_0$ are obtained in a similar manner from the plots of $\ln f(t, T)$ v $\frac{1}{T}$.

As previously stated, calculation of the intercept constants (from the saturated activity values) is an important step in determining the actual concentration values in the saturation region, since this intercept is itself defined by $E_a$. An interesting point to note from this table is that the intercept values are two to three orders of magnitude greater than the implant dose, an observation which is discussed further in the following sections. However, with regard to the $E_a$ values themselves, the activation energy of
1.2 eV for the $1 \times 10^{13}$ Se/cm$^2$ implant is identical to that previously measured for a higher dose implant of $1 \times 10^{14}$ Se/cm$^2$ in GaAs$^{(59)}$. Identical $E_a$ values have also been obtained from a hot (200°C) implant of $1 \times 10^{15}$ Sn/cm$^2$ at 300 keV$^{(57)}$, and from doses of $1 \times 10^{14}$ Sn/cm$^2$ and $1 \times 10^{15}$ Sn/cm$^2$ annealed in an optical furnace$^{(58,52)}$. These results therefore support the conclusions from the magnesium data of Figure 4.7, and re-confirm observations which show that the magnitude of $E_a$ is independent of ion dose, implant energy and implant temperature.

A much more important point to note from this study is that, by substituting the above values of $E_a$, $E_d$, Intercept and $K'D_0$ into Equation 5.6, it was possible to generate a complete family of activation curves for each of the ions studied (as shown in Figures 4.1, 4.6 and 4.15). The model developed in this thesis is therefore much more accurate than those reported previously$^{(58,59,97)}$, since it is capable of describing the diffusion and activation processes over the entire range of times and temperatures. For each of the ions studied, the accuracy of fit is within ±10% of the experimental values.

5.6 Applications to Published Data

As an example of the application of this model to published data, Figure 5.1 shows the results obtained from an earlier study by Bensalem et al$^{(58)}$, in which the variation in sheet electron concentration from a 300 keV, $1 \times 10^{14}$ Sn/cm$^2$ implant is plotted as a function of annealing time and temperature. At the time of publication, no accurate theory was available to predict these
Figure 5.1. Sheet Carrier Concentration versus Anneal Time for 1 x 10^{14} \text{ Sn/cm}^2 (300 \text{ keV RT}). Solid lines are predicted by the current theory when values of $E_d = 2.5 \text{ eV}$ and $E_a = 1.2 \text{ eV}$ are used.
results, but, by selecting appropriate values of $E_d = 2.5$ eV and $E_a = 1.2$ eV, all of the experimental values from Bensalem's work can be fitted to the current model (as indicated by the solid lines of Figure 5.1). Again, the accuracy of fit in this case is within $\pm 10\%$ of the experimental values.

The annealing kinetics of zinc$^{97}$ and selenium$^{59}$ ions have also been studied by Bensalem et al, yielding $E_d$ values of 1.0 eV and 4.3 eV, respectively. However, the insufficient data in the time-dependent regions of these studies, coupled with a less accurate method of analysis, means that these values are considerably in error.

As previously stated, however, the refined theory of Section 5.2 has been applied to the Se data from Bensalem's work in an attempt to rationalise this data with the current model. The results (shown previously in Table 5.3), yield a diffusion energy value which lies in the range 2.5 - 3.0 eV, (as opposed to the reported value of 4.3 eV). This result is therefore consistent with the activation model for complexed ions, as discussed in Section 5.3.

5.7 Determination of Intercept Constants

With reference to the intercept values of Table 5.5, determination of these constants allows the proportionality sign in Equation 5.3 to be replaced by an equality sign. In saturation, therefore, the temperature dependent values are given by,

$$\Gamma(T) = \text{INTERCEPT CONSTANT} \times \exp \left[ -\frac{E_a}{kT} \right] \quad \text{... (5.8)}$$
where the intercept constant is itself a function of the implant dose. Although these intercept values can be deduced experimentally, it should also be possible to predict them from a knowledge of the activation mechanisms involved for each ion. In order to do this, it is first necessary to re-examine the basis of the current model.

In Section 5.2, the basic theory used in the model was developed from a source of "N" implanted impurities diffusing to active sites. Previously, therefore, N has been implicitly defined as the concentration of implanted impurities (since it was assumed that these were the mobile species). However, if, as proposed in this work, the diffusion process is actually due to a movement of gallium or arsenic vacancies (or atoms), then "N" should correspond to the initial concentration of vacancies (or atoms) available for diffusion at \( t = 0 \), (and is therefore a function of the implanted dose, but not the actual dose itself). This concept could also be used to explain the intercept values of Table 5.4, which are seen to be much higher than the implant dose. Thus, if it can be shown that the intercept values correspond to the sheet vacancy concentration after implantation, then this would (a) act as evidence to support the activation mechanisms proposed in this study, and (b) allow a prediction of the saturated activity levels to be made for a wide range of implant energies and doses. It is proposed, therefore, that the saturated activity levels are given by,

\[
\eta(T) = V \text{DOSE} \exp \left(-\frac{E_a}{kT}\right)
\]

\[\ldots (5.9)\]
where $V_{\text{DOSE}}$ is the initial concentration of vacancies generated by the implant dose (and is measured in the same units).

For calculation purposes, this concentration of vacancies can be estimated if (1) the energy deposited due to nuclear collisions ($E_n$) can be calculated, and (2) the energy required to displace an atom from its lattice site ($E_{\text{dis}}$) is known.

In a single element target such as silicon, the number of vacancies produced by an ion (whose mass is unequal to that of the target atoms) is given by the modified Kinchin-Pease formula (101,104):

$$\text{Number of vacancies per ion} = \frac{0.42 \times E_n}{E_{\text{dis}}}$$  \hspace{1cm} (5.10)

So that, for a wide range of implant conditions (i.e., those below which an amorphous layer is formed), the number of vacancies generated is given by:

$$\text{No of vacancies (cm}^{-2}\text{)} = V_{\text{DOSE}} = \frac{\text{DOSE} \times 0.42 \times E_n}{E_{\text{dis}}}$$ \hspace{1cm} (5.11)

(where $V_{\text{DOSE}}$ and DOSE are both measured in units of cm$^{-2}$).

In a compound semiconductor such as GaAs, however, the situation is slightly more complex, because the energy deposited by nuclear interactions is divided into forming both gallium and arsenic vacancies (though the relative displacement energies, and hence the total number of each type of vacancies, may be different in
each case). To a first approximation, this effect can be incorporated into the model by effectively dividing the value of $E_n$ by two, thereby assuming that the number of gallium vacancies is equal to the number of arsenic vacancies. Hence, for a compound such as GaAs it is proposed that:

$$\text{Number of gallium vacancies} = \text{Number of arsenic vacancies.}$$

Therefore

$$V = \frac{0.42 \times \text{DOSE} \times E_n}{2E_d} \text{ cm}^{-2} \quad \ldots \quad (5.12)$$

As stated previously, by comparing this value to the intercept constants for each ion, it should be possible to predict the saturated activity levels for a wide range of implant conditions. However, before making such a comparison, it is first necessary to discuss a number of possible errors in the above calculation.

The first of these is that, unfortunately, no accurate values of $E_d$ in GaAs are available in the literature. Typical values of $E_d$, in the range 20 eV to 60 eV, have been reported for a number of materials$^{99}$ and it is expected that the $E_d$ values for Ga or As should lie in this range. However, because of this uncertainty, a possible 50% error may arise in calculating the sheet vacancy concentration from Equation 5.12. Secondly, and more importantly, a large source of error arises from the fact that the experimentally determined intercept values are strongly dependent on the slopes of the individual Arrhenius plots and, therefore, on the precise values of $E_a$. Any errors which arise in the measurements of annealing temperature, or which occur in the Hall effect apparatus will therefore have a significant effect on the experimentally determined intercept values.
A further point to note is that the vacancy concentration predicted by Equation 5.12 is at best only an estimate, since the exact vacancy concentration will be a complex function of (1) the homogeneity and efficiency of the encapsulant, (2) the strain induced at the encapsulant/substrate interface, (3) the ability of the encapsulant to prevent outdiffusion of Ga or As, and (4) the quality of the substrate material itself.

In order to solve the first of these problems (i.e., obtaining a value for $E_{Ds}$), the method adopted has been to measure the experimental intercept value from the Be data (Table 5.4) and then compare this to Equation 5.12, thereby allowing an estimation of $E_{Ds}$ to be made. The value of $E_n$ for the 75 keV beryllium implant was calculated from a commercially available SUSPRE(104) package as being 17.2 keV, (the same package being used to calculate values of $E_n$ for all implants in this work). By assuming a value of $E_{Ds} = 40$ eV, the sheet vacancy concentration predicted by Equation 5.12 was calculated as $4.5 \times 10^{16}$/cm$^2$, which compares favourably with the intercept value of Table 5.4 ($5.2 \times 10^{16}$/cm$^2$).

Since this $E_{Ds}$ value is within the estimated range of 20 eV - 60 eV it is proposed therefore, that in the beryllium case, the intercept value does in fact give a measure of the implantation-induced vacancy concentration.

Furthermore, since an amorphous layer has not been produced by this implant (because the concentration of vacancies is too low), this value of $E_{Ds}$ can also be used to predict the intercept values
for any other beryllium implant, and should also be applicable to the study of Zn activation in GaAs (since the activation mechanisms are the same in both cases).

5.7.1 Analysis for Interstitial Impurities

In order to demonstrate the above ideas (Section 5.7) using published data, an analysis of several beryllium implants has been performed. The precise method adopted has been to determine the predicted sheet vacancy concentration from Equation 5.12, using $E_n$ values calculated from SUSPRE and a value of $E_{ds} = 40$ eV. By selecting a value of $\Gamma(T)$ (and its corresponding annealing temperature), from the literature, it was then possible to calculate values for the activation energy ($E_a$) by re-arranging Equation 5.9 to give:

$$E_a = \ln \left[ \frac{\Gamma(T)/V_{DOSE} \times kT}{e} \right] \text{ eV} \quad \ldots (5.13)$$

Thus, if the vacancy-concentration hypothesis is correct, the $E_a$ values calculated from the literature should agree well with one another and, in accordance with the value of $0.32 \pm 0.1$ eV already measured, should lie in the range $0.3 - 0.4$ eV. A summary of the results obtained from the various publications is given in Table 5.5.
Table 5.5

Comparison of Intercept Constants and $E_a$ Values from Published Data

<table>
<thead>
<tr>
<th>Ion Dose ($cm^{-2}$)</th>
<th>Implant Energy (keV)</th>
<th>$I(T)$ ($cm^{-2}$)</th>
<th>Anneal Temp (°C)</th>
<th>En (keV)</th>
<th>$V_{DOSE}$ (cm$^{-2}$)</th>
<th>Calculated Value of $E_a$ (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{14}$</td>
<td>75</td>
<td>$3.2 \times 10^{14}$</td>
<td>630</td>
<td>17.2</td>
<td>$4.5 \times 10^{16}$</td>
<td>$0.32 \pm 0.1$</td>
<td>This work</td>
</tr>
<tr>
<td>$2 \times 10^{14}$</td>
<td>10</td>
<td>$1.6 \times 10^{14}$</td>
<td>820</td>
<td>4.93</td>
<td>$5.2 \times 10^{15}$</td>
<td>$0.33$</td>
<td>142</td>
</tr>
<tr>
<td>$2 \times 10^{13}$</td>
<td>50</td>
<td>$1.5 \times 10^{13}$</td>
<td>630</td>
<td>14.21</td>
<td>$1.4 \times 10^{15}$</td>
<td>$0.35$</td>
<td>143</td>
</tr>
<tr>
<td>$5 \times 10^{13}$</td>
<td>250</td>
<td>$4 \times 10^{13}$</td>
<td>600</td>
<td>21.76</td>
<td>$5.7 \times 10^{15}$</td>
<td>$0.37$</td>
<td>144</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>250</td>
<td>7</td>
<td>$1 \times 10^{14}$</td>
<td>600</td>
<td>21.76</td>
<td>$0.37$</td>
<td>144</td>
</tr>
<tr>
<td>$6 \times 10^{15}$</td>
<td>280</td>
<td>$1.12 \times 10^{15}$</td>
<td>475</td>
<td>20.23</td>
<td>$6.3 \times 10^{17}$</td>
<td>$0.4$</td>
<td>130</td>
</tr>
<tr>
<td>$1 \times 10^{14}$</td>
<td>100</td>
<td>$9.7 \times 10^{13}$</td>
<td>900</td>
<td>17.2</td>
<td>$9 \times 10^{15}$</td>
<td>$0.42$</td>
<td>145</td>
</tr>
</tbody>
</table>

As predicted, the calculated $E_a$ values are in good agreement with one another and lie within the expected range. These results therefore reinforce the earlier statements that:

1. The displacement energy ($E_{ds}$) in ion-implanted GaAs has a value of approximately 40 eV;
2. In agreement with the proposed model, the activation of beryllium is governed by the distribution of the post-implant vacancy concentration; and
3. The energy required to electrically activate an interstitial Be impurity is of the order of 0.3 - 0.4 eV.
Furthermore, the results of Table 5.5 also support the earlier statements that, within experimental error, the magnitude of \( E_a \) is independent of implant dose and energy.

These statements act as further evidence for the activation mechanisms described in Section 5.4, and are also consistent with a wide range of publications in which the distribution of vacancies in ion-implanted material is shown to have a marked effect on the distribution of active impurities. As an example, Barrett et al\(^{119}\) have shown that the activation efficiency of zinc in ion-implanted GaAs is directly proportional to the concentration of gallium vacancies in the implanted layer, and further demonstrated that zinc activation is enhanced in regions where an excess of vacancies exist. Davies et al\(^{141}\) have also shown that Zn activation is affected by the changes in vacancy concentration which arise when different encapsulants are used, or when As is co-implanted with zinc. Similar observations have been made for a number of other ions in GaAs, the general conclusion being that the degree of electrical activation is greatly dependent on the number of vacancies present at the time of annealing.

Thus, by considering the activation process in terms of the available vacancy concentration, the current model can, for example, predict how a change in ion energy will affect the sheet electrical properties (since the change in vacancy concentration can be estimated from the change in \( E_n \)). The model predicts that the maximum active carrier concentration increases as the implant energy is increased, which is in accordance with published data\(^{54,65}\).
In predicting carrier concentrations as a function of implant dose however, allowance must be made for the formation of an amorphous layer, above which the vacancy concentration is no longer a linear function of the implant fluence. In such cases, a more accurate means of predicting the vacancy concentration must be evolved before the model can be applied. Nevertheless, in its current form, the model provides a comprehensive means of analysing the time and temperature dependence of electrical activation and, in cases where the impurity occupies an interstitial site, gives a prediction of the activation energy to within ±10% of the experimentally determined value.

5.7.2 Analysis of Complexed Ions (Mg, Se, Sn, S)

In extending the vacancy concentration hypothesis to the analysis of the complexed ions Mg, S, Se and Sn, it should have been possible to use the results from the Be data to calculate the concentration of displaced atoms. However, when this analysis was performed for each of the ions studied, the measured intercept values were found to be over an order of magnitude greater than those calculated from Equation 5.12. Since this degree of mismatch is beyond any of the errors associated with either the calculation or the experiment, then a further explanation is required in order to rationalise the data from complexed ions.

Using the Be data as a starting point, it was shown that, in saturation, the entire range of values could be predicted by an intercept (from Equation 5.12) and a gradient whose slope is
proportional to 0.32 eV (see Figure 4.2(a)). This type of mechanism is therefore an example of the simplest and most direct activation process, ie an interstitial transferring to a vacancy.

For those ions which form complexes, however, it was found that the experimental intercept value did not present a true reflection of the sheet vacancy concentration. The reason for this lack of agreement is due to a number of processes which occur during the formation of the complexes themselves. It has been shown that, during the initial stages of damage regrowth, implanted impurities either remain as interstitials or occupy substitutional sites, the energies in each case being significantly different. Furthermore, an additional energy term must also be accounted for when the substitutional impurities form complexes with gallium (or arsenic) vacancies, so this introduces a further difference in the activation processes. Finally, in order for the complexed impurity to become electrically active, energy must be expended in order to break up the complex. Therefore, as a result of these complications, the number of impurities which become electrically active are no longer directly proportional to the initial vacancy concentration. Since the activation energy for complexed impurities is much higher than that for interstitials, the concept of equating intercept values cannot be applied.

For those ions which have activation energies in the range 1.0 - 1.2 eV, additional work is therefore required before Equation 5.12 can be used to give an accurate prediction of the experimentally determined intercept. The situation is summarised in Figure 5.2, using beryllium and magnesium as examples.
Figure 5.2. Comparison of Activation Energies from Interstitial (Be) and Complexed (Mg) Ions. Intercept values can only be predicted in the interstitial case.
In the absence of a direct means of predicting the intercept values from Equation 5.12, it is still possible to characterise the experimental data from the complexed ions (Mg, Se, Sn and S) by obtaining a ratio between the experimental intercept values and the values predicted by Equation 5.6. Thus, by using a value of Eds = 40 eV, and calculating values of En from SUSPRE, the following table has been constructed (Table 5.6).

**Table 5.6**

<table>
<thead>
<tr>
<th>Ion Species</th>
<th>Ion Energy (keV)</th>
<th>Ion Dose cm(^{-2})</th>
<th>En/eV</th>
<th>(a) Calculated Intercept (=)D(\sigma) cm(^{-2})</th>
<th>(b) Experimental Intercept</th>
<th>Ratio ((b)/(a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>100</td>
<td>1 (\times) 10(^{14})</td>
<td>67.3</td>
<td>3.52 (\times) 10(^{16})</td>
<td>3.4 (\times) 10(^{18})</td>
<td>85.6</td>
</tr>
<tr>
<td>(Mg)</td>
<td>100</td>
<td>5 (\times) 10(^{14})</td>
<td>67.3</td>
<td>1.76 (\times) 10(^{17})</td>
<td>1.34 (\times) 10(^{19})</td>
<td>76.6</td>
</tr>
<tr>
<td>Selenium</td>
<td>300</td>
<td>1 (\times) 10(^{13})</td>
<td>258.4</td>
<td>1.356 (\times) 10(^{16})</td>
<td>5 (\times) 10(^{17})</td>
<td>37.4</td>
</tr>
<tr>
<td>(Se)</td>
<td>200*</td>
<td>1 (\times) 10(^{14})</td>
<td>258.4</td>
<td>1.356 (\times) 10(^{17})</td>
<td>4.22 (\times) 10(^{18})</td>
<td>25.2</td>
</tr>
<tr>
<td>Sulphur</td>
<td>120</td>
<td>1 (\times) 10(^{14})</td>
<td>69.7</td>
<td>3.65 (\times) 10(^{16})</td>
<td>1.14 (\times) 10(^{18})</td>
<td>31.2</td>
</tr>
<tr>
<td>(S)</td>
<td>300*</td>
<td>1 (\times) 10(^{14})</td>
<td>274</td>
<td>1.43 (\times) 10(^{17})</td>
<td>4.1 (\times) 10(^{18})</td>
<td>27.2</td>
</tr>
</tbody>
</table>

* Also included in this table are the results from additional data on Sn(58) and Se(59) implants.
As shown by Table 5.6, the ratio values are seen to fall into two distinct groups, seemingly dependent on whether the impurity is a donor or an acceptor species. The reason for the acceptor intercept ratios being approximately twice that of the donor ratios is unclear at this time, but may be related to the presence of different trapping mechanisms for donors and acceptors respectively. Further work should therefore be performed in order to characterise these effects.

An additional point to note is that the ratios between the experimental vacancy concentrations and the predicted vacancy concentrations are seen to decrease with increasing dose. This result is to be expected when one considers that no corrections have been made for the vacancy concentration limit, which would arise as the ion dose increases towards that required to form an amorphous layer.

Because the ratio values are similar for all the donor ions, this would suggest that a similar activation mechanism occurs in each case (which is consistent with the models described previously in Section 5.6). From the initial results obtained from the magnesium data, the process for a complexed acceptor ion does appear to be somewhat different, but, at this stage, the precise details of the mechanisms must remain the subject of further study.
5.8 Conclusions

As a conclusion to this chapter, it has been shown that, by suitably modifying a first-order rate equation, it is possible to model the entire time and temperature dependence of electrical activation in ion-implanted GaAs. Using this model, the experimental results from Be, Mg, S and Se implants in GaAs have been analysed, the results suggesting that activation of these ions is governed by the post-implant vacancy concentration, and by the degree to which ions occupy interstitial or complex sites.

Furthermore, the model has also shown itself to be applicable to a wide range of published data, the accuracy of fit being within ±10% for interstitial ions such as Be. In the case of the complexed impurities (Mg, Se, S and Sn) the model is also capable of producing an accurate fit to the experimental data, but, in order to fully predict the electrical results from the intercept value, additional work is required.
Conclusions and Suggestions for Future Work

6.1 Introduction

The work presented in this thesis has focussed on the use of rapid thermal annealing to study the activation of implanted ions in GaAs.

By characterising the changes in electrical activity as a function of annealing time and temperature, the activation processes for most ions were seen to be divided into two distinct regions, ie, a time dependent regime - which occurred at short annealing times - followed by a time-independent "saturation" region. These two regions were further characterised in terms of a diffusion energy, $E_d$ (for the time-dependence) and an activation energy, $E_a$ in saturation.

By interpreting the experimental data in terms of these energies, it was possible to develop a model for the activation of ions in implanted GaAs. This model was shown to be consistent with all the results obtained in this study, and was also shown to agree with previously published data.
The following sections therefore present a summary of the major conclusions to be drawn from this work, and also provide a number of suggestions for further study.

6.2 Acceptor Implants in GaAs

6.2.1 Beryllium Implantation

For the 75 keV $5 \times 10^{14}$ Be/cm$^2$ implant studied in this work, the electrical activity was shown to follow a time and temperature dependence in a range of annealing temperature from 450°C to 630°C, for annealing times of five to thirty seconds.

The fact that electrical activity could be observed at annealing temperatures as low as 480°C indicates that very little damage is introduced by Be implantation. This statement was supported by the mobility values in the implanted layer, which were found to be in good agreement with values obtained from good quality "p" type GaAs. For the highest annealing temperature studied in this work (630°C), a maximum hole concentration of $1 \times 10^{19}$ carriers/cm$^3$ was obtained, this value being close to the theoretical maximum predicted by the PRAL distribution.

A further point to note is that, due to the short annealing times employed in this work, no evidence of profile broadening was observed for any of the times and temperatures studied. This was taken as an indication that the time-dependent region arises from a diffusion process occurring within the boundaries of the as-implanted profile. From an analysis of the experimental data,
this process was attributed to a diffusion of gallium vacancies within the implanted layer (the energy for this process being 2.3 - 2.5 eV).

In the saturation region an energy of 0.32 eV was measured for Be in GaAs, this value being in good agreement with additional $E_a$ values obtained from the literature. In terms of the physical processes involved, the energy was thought to be the energy required to allow an interstitial beryllium atom to transfer itself to a gallium vacancy. An activation model for beryllium was proposed in terms of a diffusion of gallium vacancies to interstitial beryllium sites. This process was summarised in the form

$$\text{Be}_i + \text{V}_{\text{Ga}} \rightarrow \text{Be}_{\text{Ga}}$$

As an extension to the activation model, a modified Kinchin-Pease formula was used to estimate the concentration of gallium vacancies formed by the beryllium implantation. By equating this value to an experimentally determined intercept constant, the displacement energy of a gallium or arsenic atom was estimated as 40 eV. This analysis also confirmed that, in agreement with the value of $E_d$, the diffusion process in the time-dependent regime arises from a redistribution of gallium vacancies, and not to a redistribution of the beryllium itself.

In order to confirm these results, future work should concentrate on applying the same analysis to other beryllium implants, and also to the study of Zn in GaAs. If the vacancy-concentration hypothesis is correct, and the values of $E_a$ and $E_d$ are accurate,
then it should be possible to predict saturated activity values for any combination of implant energy and dose. The analysis for Zn can be performed in the same way, but some care should be taken to ensure that an amorphous layer has not been formed. The $E_a$ value for Zn may also be slightly different to that of beryllium, but should still reflect a simple activation mechanism of the form:

$$\text{Zn}_i + V_{\text{Ga}} \rightleftharpoons \text{ZnGa}$$

6.2.2 Magnesium Implantation

100 keV implants of $1 \times 10^{14}$ Mg/cm$^2$ and $5 \times 10^{14}$ Mg/cm$^2$ were annealed in a dual graphite strip heater for a range of temperatures and times. For the $5 \times 10^{14}$ Mg/cm$^2$ implant, a time-dependence was observed at annealing times of between five and thirty seconds, in the temperature range 620°C to 650°C. Above these temperatures and times, the activity levels had either become saturated, or the time dependent region became too short to measure accurately. At the highest annealing temperature of 700°C, the sheet hole concentration reached a value of $2.4 \times 10^{14}$ carriers/cm$^2$, corresponding to a peak hole concentration of $6 \times 10^{18}$/cm$^3$. No profile broadening was observed in any of the samples studied, but at temperatures below 680°C the mobility was severely degraded by the effects of residual damage. Above 680°C, however, the mobility in the implanted layer recovered, and, at higher annealing temperatures, was commensurate with the volume values of carrier concentration.
By analysing the time-dependent region associated with the $5 \times 10^{14} \text{ Mg/cm}^2$ implant, a diffusion energy of 2.4 eV was obtained. In contrast to the Be data, this value of diffusion energy was attributed to a diffusion of gallium atoms within the boundaries of the implant profile. In the saturation region, the activation energy of 1.0 eV was proposed as the net energy required to split up an impurity-vacancy complex and subsequently allow the magnesium to become electrically active.

For the $1 \times 10^{14} \text{ Mg/cm}^2$ implant an $E_a$ value of 1.0 eV was also obtained from the saturation values, but no time-dependence was observable. This was taken as further evidence that the time-dependent region arises from a re-ordering of the damaged layer, since, for a lower dose implant, the process would occur at lower temperatures (and also shorter annealing times).

The activation mechanism for magnesium in ion-implanted GaAs can therefore be presented in terms of a diffusion of gallium atoms to a complex site ($E_d = 2.4 \text{ eV}$) with the subsequent annihilation of the complex and electrical activation of the magnesium. In this case the complex may be of the form (MgGa - VGa) but further work must still be performed in order to determine the precise structure of the defect.

6.3 Si$_3$N$_4$ Encapsulation

In order to improve the uniformity and reproducibility of the encapsulant used in this study, the growth rate of Si$_3$N$_4$ was studied as a function of the film deposition temperature.
In the current Si₃N₄ system, it was found that the minimum temperature for the onset of Si₃N₄ growth was approximately 525°C, with films grown at 625°C exhibiting optimum encapsulant characteristics.

By combining this optimised encapsulant with a reactively evaporated AlN layer, the annealing kinetics of Se and S could be studied at temperatures up to 1000°C, with no apparent degradation of the sample surface.

6.4 Donor Implants in GaAs

6.4.1 Selenium Implantation

The annealing kinetics of a 300 keV, 1 x 10¹³ Se/cm² implant were studied as a function of annealing time and temperature. From an analysis of the time dependent regime, a diffusion energy of 2.5 eV was obtained, this value being attributed to a diffusion of gallium atoms within the implant profile. A similar analysis was also performed on an earlier study of a 300 keV, 1 x 10¹⁴/cm² selenium implant⁵⁹, the Ed value in this case being within the range 2.5 - 3.0 eV.

From the saturation regions associated with these implants, an activation energy of 1.2 eV was obtained, this value being in good agreement with other studies on selenium in GaAs. The proposed mechanism for selenium activation is similar to that already described for magnesium, but is considerably different from the activation mechanisms previously reported in the literature⁵⁹,⁹⁶. In the current work it is proposed that the inactive
Se fraction exists in the form of complexes, e.g. \((\text{Se}_{\text{AS}} - \text{V}_{\text{Ga}})\) which do not diffuse significantly during short time annealing. The time-dependence observed for the selenium implant therefore arises from a diffusion of gallium atoms to the complex sites.

### 6.4.2 Sulphur Implantation

It is perhaps unfortunate that, for the annealing temperatures studied in this work, no time dependence was observed for the 120 keV, \(1 \times 10^{14}/\text{cm}^2\) sulphur implant in GaAs. However, the \(E_a\) value of 1.0 eV obtained from the temperature dependence does indicate that the inactive sulphur atoms exist in the form of complexes. This is in agreement with recent EXAFS data, on sulphur in GaAs which shows that the complex is of the form \((\text{S}_{\text{AS}} - \text{V}_{\text{AS}})\)\(^{122}\). The mobility values for all the sulphur implanted samples were in good agreement with values obtained from single crystal GaAs, indicating that the presence of these complexes does not significantly affect the electron mobility. However, without a detailed knowledge of the diffusion energy value, it is impossible to define a precise mechanism for the activation of sulphur in implanted GaAs. Further work should therefore concentrate on characterising the time dependent regime for sulphur activation, either by annealing at lower temperatures for shorter times, or by increasing the sulphur dose.

The effects of profile broadening should also be studied, in order to establish any differences between the diffusion energy of profile broadening and the diffusion energy in the time dependent regime.
6.5 Theoretical Model

By suitable modification of a first-order rate equation, a theoretical model has been developed for the activation mechanisms in ion-implanted GaAs. This model is unique in that it accurately describes the activation process over the entire range of annealing times and temperatures.

Application of the model to different ions suggests that the electrical activity in an implanted layer is controlled by the extent to which impurities form interstitials or complexes.

Furthermore, from an analysis of the time-dependent region associated with each ion, the dominant diffusion process in ion-implanted GaAs was found to be due to a redistribution of the substrate atoms or vacancies, and not to a diffusion of the implanted species itself.

As previously stated, for ions such as Be and Zn, the implantation induced vacancy concentration can be estimated from an experimentally determined intercept value. By equating this value to a modified Kinchin-Pease formula the displacement energy of a gallium or arsenic atom was found to be approximately 40 eV.

However, in the case of complexed ions (Mg, Se and S) the same type of analysis could not be adopted, mainly because the formation and annihilation of the complexes could not be modelled from the experimental data. Additional work is therefore required to fully characterise the activation processes for complexed ions.
Once a full prediction of the sheet concentration values can be made for interstitial and complexed ions, the model can then be extended to allow a prediction of carrier concentration profiles to be made. However, even in its current form, the model provides a valuable means of analysing the electrical data from studies of ion-implanted GaAs and also gives an indication of the activation mechanisms for a wide range of ion species. This is especially true of the characteristic Ea value for each ion, since, by measuring Ea, it should be possible to predict whether the atoms are occupying interstitial sites, or are complexed. Further studies can then be performed to verify these results, and to investigate the relationship between the electrical and microstructural properties of ion-implanted GaAs.

Finally, once a comprehensive model exists for the more direct "p" and "n" type dopants, the work can be extended to investigate the activation mechanisms of amphoteric ions such as Si and Ge, possibly culminating in the development of a process model for ion-implanted GaAs devices.
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