UNIVERSITY OF SURREY
DEPARTMENT OF ELECTRICAL & ELECTRONICS ENGINEERING

ACTIVATION AND THERMAL STABILITY
OF ION IMPLANTED GALLIUM ARSENIDE

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Results on the activation characteristics of Be, Be+P, Zn and Zn+P implants in GaAs have been presented. It is found that the in-diffusion of zinc and the out-diffusion of beryllium atoms has been prevented through the co-implantation of phosphorus. High hole concentrations of the order of $6 \times 10^{19}$/cm$^3$ have been obtained for the Zn+P implanted samples. It has also been demonstrated for the first time that by performing the co-implantation of phosphorus and rapid thermal annealing, an effective way of preventing the out-diffusion of beryllium at annealing temperatures up to 950°C for 10s has been achieved.

The influence of heat treatment on the rapid thermally annealed, ion-implanted samples has also been investigated. It is found that the temperature at which the electrical properties change significantly is at 600°C for the Be, Mg and Zn implanted samples and at 700°C for the selenium implanted samples respectively.
These changes in the sheet carrier concentration are observed to be reversible for the selenium and zinc implanted samples after further annealing at high temperatures. This phenomenon is not observed for the beryllium and magnesium implanted samples.

A value in the range of 1.5-2.5eV has been identified as the energy which characterises the rate dependent step for the reversible processes for the zinc and selenium implanted samples. This energy value is thought to correspond to the diffusion of gallium atom/vacancy. Similarly, an energy of about 1eV has been identified for the beryllium implanted samples. It is concluded that the decrease in the sheet hole concentration for the beryllium implanted samples is due to the out-diffusion of the beryllium atoms. The value of 1eV is thought to be the energy which characterises the diffusion of beryllium.
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TO ALL MY MENTORS,
'KNOWLEDGE TO BE GAINED IN THIS WORLD IS OF NO LIMITS.'

— OLD PROVERBS —
CHAPTER 1
INTRODUCTION

1.1 Introduction

This chapter serves as a brief introduction to the topic of ion implantation in gallium arsenide and its associated problems. It also contains the aims of the project and the scope of the thesis.

Gallium Arsenide has long been hailed as the material of the future and it is only in recent years that the technology associated with its growth and processing has matured to the point where IC production can be contemplated at the industrial level. This phenomenon still holds despite inherent problems associated with the material which has to-date restricted the wide scale use of GaAs.

The essential handicap of GaAs stems from the absence of a stable surface oxide and the susceptibility of its surface to decompose during the heat treatment that is essential for device fabrication (especially for the removal of implantation damage and dopant activation). As a result of the inadequate properties of the thermal oxide of GaAs, an alternative approach to circuit fabrication was required. This has been achieved by
using Schottky barrier FETs or MESFETs. Also, a further difficulty is the inability to fabricate high-performance bipolar transistors because of the low minority carrier lifetime. Furthermore, the larger thermal conductivity of silicon over GaAs has enabled silicon devices to operate at higher current densities than GaAs devices as heat can be dissipated about three times faster in silicon than in GaAs.

Ion implantation is a well established method for controlled doping of semiconductors and offers many advantages over other doping methods e.g. diffusion. However, this technique causes crystal lattice disorder which must be removed by subsequent heat treatment at temperatures in the range 500-1000°C in order to electrically activate the implanted dopant species. Various annealing techniques have been developed for this purpose. Rapid thermal annealing (RTA) offers possible solutions to difficulties encountered in conventional furnace annealing and many research groups have demonstrated its use [1-5].

At annealing temperatures higher than 660°C, the evaporation of gallium and arsenic atoms causes the surface of GaAs to decompose and the loss of dopant atoms to become severe. This has led to the development and use of various encapsulation methods. Recent work has focussed on the characterisation of rapid thermally annealed, ion implanted GaAs. These studies have
yielded excellent results which confirmed that rapid thermal annealing in the solid phase is a viable alternative to furnace annealing. A major problem still to be solved before widespread application to device and circuit processing, is to achieve a sufficiently uniform temperature across a wafer to avoid crystallographic slip around the edges.

The behaviour of each ion species implanted into GaAs is different, but more significantly, there are distinct dissimilarities between acceptors and donors. Amongst these dissimilarities is the requirement of high temperature (>900°C) annealing to activate donor-implanted GaAs to any considerable degree. In contrast, acceptor implanted GaAs can be activated at relatively low annealing temperatures. Hence, acceptor implantation followed by annealing has provided a feasible way to reduce the base contact resistance in a heterojunction bipolar transistor (HBT) since degradation of the heterojunction interfaces by high anneal temperatures is avoided. Since the major limitation in the maximum oscillation frequency in a high-performance HBT originates from the parasitic resistance of the base contact region, a reduction in the contact resistance is of paramount importance in order to fabricate such devices. To achieve a low resistance ohmic contact in GaAs, the free carrier concentration at the metal-semiconductor interface must be sufficient to reduce the barrier width to a few tens
of angstroms, hence allowing the majority of the carriers to tunnel across the interfacial region. High surface carrier concentrations can, in principle, be produced by ion implantation at a sufficiently high dose. However, implantation of high doses (>10^{14}/cm^2) can give rise to solid solubility problems and undesirable diffusion effects.

Beryllium ions have generally been used for acceptor implantation in GaAs, the advantages of using this being twofold. Being the lightest acceptor species available, it offers a large range and the lattice disorder caused by implantation is significantly less than that produced by heavier ions. Consequently, electrical activation of beryllium implanted GaAs can be obtained at annealing temperatures as low as 500°C [3]. However, the problem of out-diffusion of the beryllium atoms during annealing has been reported [6-8]; this problem persists when different encapsulants are used and can account for the difficulty in achieving full activation [6]. The use of rapid thermal annealing may solve this problem [3].

In contrast, full electrical activation of zinc implanted GaAs can be obtained at annealing temperatures of about 850°C. However, this is achieved with considerable redistribution of the zinc atoms into the bulk of the material resulting in a decrease in the peak hole concentration and can cause deleterious
effects to device operation. The factors governing the redistribution of zinc atoms are multifold. Various research workers have reported the dependence of the diffusion of zinc atoms on the peak concentration, the annealing time and temperature, the type of encapsulant used and the degree of lattice disorder [9-11,48].

High dose magnesium implanted GaAs has also been the subject of considerable interest [5,12-13] and various research groups have reported the properties of magnesium implanted GaAs that are similar to those observed in the case of the beryllium implants. As mentioned above, a reduction in annealing time results in an increase in the level of activation and also limits the redistribution of acceptors. Moreover, in a detailed study of the solubility effects of zinc in GaAs during growth at a temperature of 1000°C, Panish and Casey [14] showed that the carrier concentration can be made consistently higher if the GaAs is grown under arsenic-rich rather than gallium-rich conditions. Furthermore, Heckingbottom and Ambridge [58] have developed a theory that when the stoichiometry of GaAs is maintained during implantation and annealing then a high percentage electrical activity and a high carrier concentration should be attained. Barrett et al [9] have shown that co-implantation of zinc and arsenic ions results in abrupt electrical profiles with limited in-diffusion after rapid thermal annealing. Co-implantation and rapid thermal annealing may be the
solution to the problem of the relatively low activation efficiency of acceptor-implanted GaAlAs. For example, Morizuka et al [15] have shown that co-implantation of magnesium and phosphorus ions in GaAlAs resulted in a higher peak hole concentration than magnesium implants alone after annealing at 850°C for 2s.

In conclusion, a vast amount of research work has been carried out to overcome the problems associated with ion-implanted GaAs with the aim of realising its full potential for circuit applications. The research work in this area is by no means exhausted and it is hoped that through this work that new grounds may be made.

1.2 Aims of the project

A variety of applications in engine instrumentation, power electronics and satellite communication systems have resulted in the demand and development of solid state components that are capable of operating for sustained periods of time at high temperatures. However, there is little published data that is related to the topic of the thermal stability and hence the deactivation characteristics of ion implanted layers in GaAs. The aims of the project are to form active regions in GaAs by ion implantation and to investigate the influence of heat treatment on the electrical properties and hence the thermal stability of these
layers. It is hoped that through these studies, the physics and possible mechanisms with which dopant atoms are electrically activated and deactivated will be better understood. Preliminary results include the deactivation characteristics of beryllium, magnesium, zinc and selenium implanted layers in GaAs. Moreover, the area of research that is of particular interest here is the formation and thermal stability of P+ regions formed by beryllium and zinc implantation. Furthermore, the effects of co-implantation of phosphorus on the activation efficiency and thermal stability of these layers are investigated. In addition, a study of the deactivation kinetics of beryllium, zinc and selenium implanted GaAs has been undertaken. This has led to the development of a thermodynamic model of the deactivation mechanisms of dopants in GaAs.

1.3 Scope of the Thesis

This thesis begins with a general review in chapter 1 of the development and progress made as well as the difficulties encountered in the field of study — ion implantation as a doping method for GaAs which includes the related topics of encapsulation and annealing. A review of the literature is presented in chapter 2 and also briefly mentioned in this introductory chapter. Chapter 3 presents the experimental and assessment methods used, discussing both the theoretical and
experimental aspects. Chapter 4 presents the experimental results obtained and is presented in a logical sequence rather than chronologically. A discussion of the important points raised in the experimental results is presented in chapter 5 and the thesis is rounded off in chapter 6 by presenting the conclusions of the work together with a number of recommendations for future work.
CHAPTER 2
LITERATURE SURVEY

2.1 Introduction

This chapter presents a review of literature in the field of ion implantation in GaAs. The importance of using ion implantation as a tool to fabricate integrated circuits and GaAs as a semiconductor material is stressed. A brief account of the influence of heat treatment on doped-semiconductors is also provided.

2.2 Ion Implantation

2.2.1 Introduction

Research and development on the use of ion implantation for integrated circuits is now entering a third phase. This follows the first phase in the early 1970's, when ion implantation of low doses was first successfully applied to the threshold voltage control in MOSFET's [16], and the second phase in the late 1970's, when high dose implantation was adopted in the production of MOS and bipolar transistors [17]. The third phase can be characterised by the trend towards wider applications and a higher degree of circuit complexity.
An important application is in compound semiconductor integrated circuits which opens a new avenue for very fast and low power ICs which may be difficult to achieve using the present silicon-based technology [18,56,66]. Recently, GaAs LSIs with more than 30,000 gates have been successfully fabricated by selective ion implantation directly into semi-insulating GaAs substrates. These circuits operate at a speed of 150 ps/gate which is two or three times faster than for silicon LSI circuits and with a power consumption much less than for silicon circuits [19]. Implantation is becoming the essential doping technique for these high speed compound semiconductor integrated circuits. With the advent of Molecular Beam Epitaxy (MBE) and Metal Organic Chemical Vapour Deposition (MOCVD) technology [28,93], the applications of ion implantation are also extending from GaAs MESFETs and JFETs [20] to hetero-structure devices such as High Electron Mobility Transistors (HEMT) [21] and Heterojunction Bipolar Transistors (HBT) [22] with the aim of developing even faster ICs. The future development and application will also depend on the applicability of the implantation technique on these materials.

The advantages of using ion implantation as a doping method are multifold. These include accurate control over depth profiles and sheet carrier concentration. In contrast to diffusion methods which require high temperature processing and also the concentration is
limited to the solid solubility of the species, ion implantation can be performed at any temperature and can introduce species with low diffusion coefficients, e.g. gaseous elements. Therefore very high doping concentrations can be achieved. Other advantages include uniformity across a wafer and reproducibility from wafer to wafer. In addition, the large volume capability of the process results in economy and high throughput. Lateral spread of dopant atoms is of vital importance as device geometry is decreased to submicrometer dimensions to allow for higher speed and packing density. Wilson [23] reported that the magnitude of the lateral spread that results from a 7 or 8 degrees tilt is about 1/8 of the projected range, this is significantly smaller than that in the case of diffusion. However, the drawbacks are non-abrupt profiles and the requirement of post-implantation annealing to restore crystallinity and activate dopant atoms.

2.2.2 Physics Of Ion Implantation

Ion implantation is a process that involves the direct impingement of positively charged energetic ions on the target. The ions are extracted from a source of plasma through an aperture which is held at a negative potential of a few kilovolts with respect to the source; the plasma is generated by means of a high frequency voltage source or a hot filament. The ion
beam is then focussed before undergoing acceleration and mass analysis. Mass analysis is based on the interactions between a moving charged particle of mass \( m \) in a magnetic field \( B \) and acceleration voltage \( V \), the relationship is:
\[
m = \frac{(e \cdot r \cdot B)^2}{2V} \]
where \( r \) is the radius of the circular path taken by the deflected ion.

The ion beam containing the selected ions is electrostatically scanned horizontally and vertically across the target substrate.

When an energetic ion enters a solid, it loses energy by interactions with the target nuclei and electrons and eventually comes to rest at a depth which is a function of ion energy and the mass and atomic number of both the ion and target atoms. Lindhard et al [24] have predicted a gaussian shape distribution of implanted impurities into an amorphous target. This gaussian distribution of implanted atoms can be described by the most probable range normal to the surface called the projected range \( R_p \) and a standard deviation, \( \Delta R_p \). Hence, the distribution of implanted atoms as a function of depth is given by:
\[
N(x) = \frac{N_0}{\sqrt{2\pi} \Delta R_p} \exp\left(\frac{(x-R_p)^2}{2(\Delta R_p)^2}\right)/\text{cm}^3
\]
where \( x \) is the depth into the substrate and \( N_0 \) is the ion dose. Many calculations and measurements for \( R_p \) and \( \Delta R_p \) have been made, these include LSS [24], Gibbons [25], Ziegler [26], and PRAL [27]. However, for
crystalline targets, radiation enhanced diffusion and/or channelling effects result in the development of a deep tail in the implant profile. Therefore profiles are often better described by mathematical functions containing higher moments of the gaussian distribution such as the joined half-gaussian with three adjustable parameters or the Pearson IV distribution with four adjustable parameters rather than the simple LSS gaussian distribution which has two adjustable parameters. The amount of disorder in a crystalline target as a result of ion implantation is dependent on the ion mass, energy, dose, dose rate and substrate temperature during implantation. Furthermore, the channelling effects can be a problem since the impurity distribution is calculated assuming an amorphous target. The effects of channelling can be minimised by tilting the target crystal by about 7 degrees from the vertical axis.

Post-implantation annealing is required to restore crystallinity and to activate impurity atoms. The problem of decomposition of GaAs at elevated temperatures has led to the development and use of suitable encapsulation methods. The topic of annealing of ion implanted GaAs will be presented in the following sections.
2.3 GaAs as a semiconductor material

2.3.1 Importance of GaAs

As far as semiconductor devices are concerned, GaAs has a number of desirable characteristics. One of its important properties that resulted in the early industrial interest arose from the transferred electron effect [29]. This effect is a result of the band structure of GaAs; it is not exhibited by silicon and has enabled relatively simple two terminal devices such as the Gunn oscillator to be fabricated which are used to generate r.f. power at frequencies up to 100GHz. A second important characteristic of GaAs is the very high electron mobility. The maximum electron mobility values are 1400 cm²/V.s and 8000 cm²/V.s for silicon and GaAs respectively at a doping density of about 10¹⁵/cm³. In the form of Metal Semiconductor Field Effect Transistor (MESFET) discrete transistors that operate up to at least 30GHz have been produced. At the present time, exciting developments are occurring in GaAs and its related compounds, these include devices such as the High Electron Mobility Transistor (HEMT) and the Heterojunction Bipolar Transistor (HBT). In the former technology, mobility values as high as 1.95x10⁵ cm²/V.s have been achieved at 77K [31]. Although the magnitude of the mobility is a limiting factor, the speed of operation of devices can be increased by reducing dimensions. However, a
continuous reduction in device dimensions, even if this were technologically possible, will not produce a corresponding increase in speed, since parasitics, such as the capacitance associated with metallic interconnections, will tend to dominate. As the gate length in a MESFET is reduced to below about 0.2 μm, the electrons in GaAs may reach velocities above the equilibrium maximum value of $2 \times 10^7$ cm/s. This phenomenon is known as velocity overshoot, calculations of overshoot in silicon suggest that no significant improvement should occur. On the other hand, there is experimental evidence that electron velocities up to $7 \times 10^7$ cm/s are attainable in GaAs [32]. A third important reason for interest in GaAs and its related compounds is a result of the material having a direct bandgap. Since the valence band maximum and conduction band minimum occur at the same momentum value, these materials are very efficient in opto-electronic applications such as LASERS and optical detectors [32].

The above desirable characteristics are accentuated by the property of a semi-insulating substrate ($>1 \times 10^8$ cm) that provides low parasitic capacitance and it is unnecessary to include many of the isolation structures common in silicon technology. Lastly, GaAs has an exceptional radiation hardness as a result of its larger bandgap. On these grounds, GaAs will also be preferable to silicon for applications where devices are required to operate at high temperatures [30]. This is a vital attribute in working environments such as
satellites and power control instrumentation. Zipperian et al [75] have demonstrated that GaAs/GaAlAs is a good material system for high temperature junction device applications. The full temperature range investigated was from 50°C—400°C; they observed significant improvements in the high temperature reverse junction leakage current compared to GaAs homojunction devices.

2.4 Doping of GaAs By Ion Implantation

2.4.1 Introduction

This section presents a review of literature in the field of ion implantation in GaAs. It is mainly divided into sections under acceptor, donor and co-implantation in GaAs. Much attention has been paid to the use of rapid thermal annealing of ion implanted layers. Also, a review of the topic of the influence of heat treatment on the electrical properties of doped-semiconductors is presented.

2.4.2 Acceptor implanted layers in GaAs

Beryllium, magnesium, zinc and cadmium ions are commonly implanted into GaAs to form p-type layers. Due to its limited range, cadmium has received less attention although Kular [33] has reported hole concentrations of up to $2.9 \times 10^{19}$ cm$^{-3}$ using silicon nitride as an encapsulant. On the contrary, beryllium,
magnesium and zinc have received much attention [3,9,12].

As beryllium is the lightest p-type dopant in GaAs, it has a large range and the lattice disorder produced by the implantation process is significantly less than for heavier ions. Consequently, electrical activation of the implanted beryllium atoms is obtained with anneal temperatures as low as 500°C [3]. However, in many integrated circuit applications such as the fabrication of p-i-n diodes and HBTs, it is important that high dopant activation efficiencies are achieved for both p- and n-type implants. This necessitates high temperature annealing which results in a loss of beryllium atoms by out-diffusion at the surface and a broadening of the atomic profile [6]. A solution to this problem is rapid thermal annealing [3]. Maezaua et al [8] have reported the effect of reverse annealing of beryllium implanted GaAs. The GaAs samples were implanted with $2.2 \times 10^{14}$ /cm$^2$ of beryllium ions at an energy of 50keV. The highest sheet hole concentration was obtained after an anneal at 700°C for zero seconds under a GaAs proximity cap with 80% electrical activity. The sheet hole concentration gradually decreases with increasing annealing temperatures above 700°C. Hutchby et al [35] reported that as the dose of beryllium is increased from $10^{13}$ /cm$^2$ to $5 \times 10^{15}$ /cm$^2$, the percentage activity is reduced from 100% to 7%; they concluded that the reduction in percentage activation for higher doses is
primarily caused by beryllium out-diffusion as part of its redistribution during high temperature annealing. The effect of hot implantation has been investigated by Sugata et al. [36] for $10^{15}$ /cm$^2$ beryllium ion dose implanted at 120keV and at substrate temperatures of 20°C, 300°C, 400°C and 500°C. Post-implantation annealing was performed using plasma CVD silicon dioxide films for 20 minutes in flowing nitrogen and hydrogen. Complete activation has been obtained by annealing at 650°C for an implantation temperature of 400°C. On the other hand, samples implanted at 500°C resulted in a lower electrical activation which the authors suggested was due to the result of diffusion of beryllium atoms towards the surface. It is worth noting that Helix et al. [37] have observed gallium out-diffusion into the SiO$_2$ encapsulation films during annealing and concluded that this process may account for high surface p-type activity.

Zinc has also received extensive attention as the alternative p-type dopant in GaAs. [9,38-39] Work on the diffusion of zinc in GaAs has shown that the process is not a simple one [40,41]. The diffusion of zinc atoms implanted into GaAs during annealing is further complicated by the presence of radiation damage [10]. In addition, Barrett et al. [9] have reported that the type of encapsulant or ambient in contact with the
GaAs surface has a significant effect on the diffusion of zinc atoms; higher electrical activity has been obtained by the use of silicon nitride rather than aluminium nitride and the authors suggested that the thermal stress at the encapsulant/GaAs interface can affect the activity significantly. Annealing in an arsine ambient limits the amount of in-diffusion of zinc atoms producing very sharp profiles [42], as do co-implantation of zinc and arsenic ions [43], electron beam annealing [44] and optical furnace annealing [45], all of which provide a means of limiting diffusion because of the short annealing times. Davies et al [47] have reported the use of incoherent light sources to anneal zinc implanted GaAs to temperatures of 1040°C and observed that the annealing time of 1s produced no significant diffusion of zinc atoms, whereas 10s anneals produced profiles which penetrate to about 1μm. This is illustrated in figure 2.1. Yuba et al [46] have reported a doping efficiency of up to 100% with doses up to $10^{15}$/cm² for both implantation at room temperature and 400°C; a saturation in sheet hole concentration for doses above $10^{15}$/cm² is observed. Also, the same authors reported that the saturation level for the samples implanted at 400°C is about twice as high as that for the room temperature implantation. Littlejohn et al [34] observed similar saturation effects and concluded that the saturation of hole concentration at high doses cannot be attributed to the solid solubility of zinc in GaAs, but rather to the
presence of radiation damage and compensating centres. Susuki et al [45] reported the characteristics of double peaks in the atomic and hole profiles after capless annealing at 800°C for zero hold time which the authors concluded were the result of gettering of zinc atoms at the implantation-induced damage regions.

![Fig. 2.1 Depth profiles of zinc implanted GaAs samples showing a pronounced redistribution after 10s and its prevention on annealing for only 1s (Ref. 47).](image)

Implantation of magnesium into GaAs has also been investigated extensively [5,12,13]. Patel et al [12] have reported a maximum hole concentration of about $10^{19}$/cm$^3$ for a dose of $10^{15}$/cm$^2$ implanted at 100keV and annealed at 900°C for 10s by incoherent light. The same authors observed that for doses greater than $10^{14}$/cm$^2$, the depth of penetration of the hole concentration profiles is dose dependent. Moreover, Yeo
et al [13] reported that out-diffusion of magnesium atoms during furnace annealing led to poor electrical activation efficiencies at doses greater than $10^{14}/\text{cm}^2$. Blunt et al [5] suggested that the reverse annealing effects observed at high annealing temperatures (>800°C) was due to the out-diffusion of magnesium atoms into the silicon nitride encapsulating layer. More recently, Daoud-Ketata et al [2] have demonstrated that through multiple implantation of magnesium and under appropriate annealing conditions, a doping level greater than $10^{19}/\text{cm}^3$ can be achieved over a depth of 0.5μm when a halogen lamp furnace is used to rapid thermal anneal magnesium implanted GaAs/GaAlAs heterostructures. In this work, high dose magnesium implantation is required to over-compensate the doping levels of the n-doped GaAlAs emitter and the n+ GaAs contact layers, thereby making the connection to the base region in a HBT.

2.4.3 Donor implanted layers in GaAs

N-type conducting layers in GaAs are commonly achieved by sulphur, silicon and selenium ion implantation [49-51], although tin and tellurium ions have also been investigated [52,53]. This is especially important in the formation of conducting n-channel and n+ regions for non-alloyed ohmic contacts in the MESFET technology. It has been observed by Kudman et al [54] that selenium is fully active electrically only at low
atomic concentrations; for atomic concentrations greater than about $4 \times 10^{18} / \text{cm}^3$, the carrier concentration rises at about the cube root of the total concentration. This is illustrated in figure 2.2 and similar trends have been observed for different ions implanted into GaAs as the sheet carrier concentration saturates when the dose is increased above a certain value.

![Graph](image)

**Fig. 2.2**

Electron concentration in the solid as a function of the selenium atomic concentration in the melt (Ref. 54).

- $\times$ electron concentration.
- $\circ$ selenium atomic concentration.
- $-$ theoretical electron concentration.

Furthermore, Williams [55] reported that the maximum doping concentration which can be reproducibly obtained in single crystal GaAs with selenium, tellurium or tin by either the Czochralski or Bridgeman method is about $5 \times 10^{18} / \text{cm}^3$. Through the development of a new
encapsulant consisting of a double layer of silicon nitride and aluminium nitride [82] and rapid thermal annealing, Bensalem et al [1] have demonstrated that electron concentrations of about $10^{19} / \text{cm}^3$ can be obtained with selenium implanted into semi-insulating GaAs using a dose of $10^{15} \text{Se } / \text{cm}^2$ at an energy of 300keV and at a substrate temperature of 200°C followed by rapid thermal annealing at 1050°C for 9s. In addition, Grange et al [51] have reported that for a certain dose, the electrical activity increases with implantation energy.

Due to its larger range, silicon ions are generally employed in industry to achieve n-type conducting layers in GaAs [50]. However, being a group IV element, silicon shows amphoteric behaviour in GaAs and type conversion occurs following implantation at high doses and annealing at high temperatures (>900°C) [56]. Sulphur implanted GaAs has also been subjected to extensive investigation [49,57]. However, conventional furnace annealing of sulphur implanted GaAs encapsulated with silicon nitride resulted in significant redistribution of the implanted sulphur atoms [57]. Banerjee et al [49] have reported the use of a graphite strip heater to rapid thermal anneal sulphur implanted GaAs and results show that the electrical activation and donor mobility values obtained are better than those using furnace anneals. In addition, there is less redistribution of the
implanted sulphur atoms and the background chromium atoms.

2.4.4 Co-implantation in GaAs

Ambridge et al [58] published a theoretical paper which suggested that an increase in electrical activity should be obtained if stoichiometry is maintained during implantation. Sealy et al [59] and Woodcock et al [60] have reported enhanced donor activation for selenium implanted GaAs by implanting an equal dose of gallium together with the selenium. Moreover, Davies et al [43] have reported that by co-implantation of zinc and arsenic ions and the use of rapid thermal annealing under a silicon dioxide encapsulant, abrupt electrical profiles with peak hole concentrations approaching $10^{20}$/cm$^3$ could be obtained. Various groups have reported to date on a large number of dual-implant combinations in GaAs such as zinc/arsenic [43,61], magnesium/arsenic [62,63] and magnesium/phosphorus [15]. From reference [15], the effect of co-implantation of phosphorus with magnesium on the shape of the electrical profile is given in figure 2.3 from which it can be observed that the resultant profile is gaussian in shape. Furthermore, Gwilliam et al [64] have reported the use of phosphorus implantation to create an amorphous target for the subsequent silicon implants, hence removing the problem of channelling so that atomic profiles are abrupt. More recently, Humer-Hager et al
[65] have demonstrated that oxygen co-implantation leads to carrier compensation in beryllium and magnesium implanted GaAs and that the influence of oxygen implantation on the shape of the carrier profile is more pronounced for the higher oxygen implant doses; the authors concluded that it is possible to achieve steeper carrier profiles and limit in-diffusion of dopant atoms by a suitable choice of oxygen implant dose and energy and that the compensation effect may be the result of the creation of deep oxygen donor complexes.

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**Fig. 2.3**

Depth profiles of hole concentration of Mg and Mg+P dual implanted GaAlAs samples (Ref. 15).

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2.4.5 Influence of heat treatment on the electrical properties of doped-semiconductors

Fuller et al. [67] have observed reversible
temperature-dependent changes in the electron concentration over the temperature range 650°C to 1100°C for GaAs doped with about $10^{19} \text{cm}^{-3}$ selenium or tellurium and suggested that a solubility equilibrium has been achieved by reversible precipitation and dissolution of the selenium and tellurium dopants in GaAs. Grinshstein et al [68] investigated the kinetics of precipitation of a supersaturated solid solution of tellurium in GaAs and observed that the decrease of electron concentration caused by heat treatment occurs in two stages with temperature. The same authors concluded that the fast "precipitation" during the first stage is due to the formation of complexes composed of tellurium atoms and gallium vacancies and the second stage may be due to the growth of precipitates. The activation energies of such processes are obtained by observing the temperature dependence of electron concentration during isochronal annealing using standard methods [69] and are calculated to be 0.2-0.4eV and 1.6eV for stage I and II respectively. Mil'vidski et al [70] have reported that during low temperature annealing of sulphur doped GaAs samples which had been quenched from 1100°C, a reduction of carrier concentration is observed. By the use of infra-red microscopy, precipitation of dopants at dislocations has been observed in the selenium and tellurium doped samples by the same authors and they concluded that the donor impurities being incorporated in GaAs exhibit a polytropy (existence of different
possible states) similar to that reported for elemental semiconductors. Furthermore, Lidow et al [71] have presented a physical model concerning the activation and diffusion of selenium atoms implanted into GaAs and speculated that only substitutional selenium is a shallow donor and that the species responsible for the redistribution of impurity profiles is the selenium-gallium vacancy complex. In addition, the authors speculated that precipitates and interstitial selenium appear to neither diffuse nor act like donors in GaAs. More recently, Numan et al [72] have studied the deactivation characteristics of rapid thermally annealed arsenic implanted silicon during subsequent furnace annealing. The same authors concluded that high concentrations of arsenic in silicon can exist in a metastable state after rapid thermal annealing, a decrease in carrier concentration is observed during subsequent heat treatment and they concluded that this deactivation process may initially involve the precipitation of inactive arsenic or cluster formation and dislocation loops are rapidly formed at higher temperatures. Kamgar et al [73] have reported similar results. By observing the temperature/time dependence of the sheet resistivity due to prolonged annealing, a value of 1.1eV has been calculated as the activation energy for the electrical deactivation process for arsenic atoms. This is observed to be the same as that obtained for the activation of arsenic clustering [74].
In conclusion, much attention has been paid to the characterisation of ion implanted layers in GaAs. Moreover, the problems associated with doping GaAs by ion implantation has generated a great deal of interest in developing reliable encapsulants and different methods for rapid thermal annealing. Many groups have demonstrated that rapid thermal annealing is a good way to activate implanted atoms with the advantages of limiting the redistribution of the dopants and less stringent requirement on the encapsulant and the substrate material, reduced possibility of cross contamination with excellent throughput. The major problem still remaining to be solved is the crystallographic slip introduced during rapid thermal annealing. However, by controlling the ramp rate of the heating cycle and the use of guard rings to control temperature gradients, this problem appears to have been solved.

As mentioned previously, the topic of the influence of heat treatment on rapid thermally annealed ion implanted GaAs has received little attention although results have been published on the influence of heat treatment of doped GaAs. This is an important research area as it may provide important insights and further existing knowledge on the various ways in which impurity atoms are incorporated into GaAs.
CHAPTER 3

EXPERIMENTAL TECHNIQUES AND ASSESSMENT METHODS

3.1 Introduction

This chapter presents the experimental techniques used during the course of the research. These include ion implantation and the corresponding procedures, encapsulation and annealing techniques. The assessment methods used to characterise ion implanted layers in GaAs are also discussed. These include Differential Hall measurements, Secondary Ion Mass Spectrometry, Auger Electron Spectroscopy and Rutherford Backscattering. The Differential Hall technique will be discussed in detail and only the principles of operation of the latter techniques are presented as these were not used substantially.

3.2 Ion implantation procedure

3.2.1 Material specification

The material used for this work was semi-insulating un-doped GaAs grown in the (100) direction by the Liquid Encapsulated Czochralski (LEC) method. The semi-insulating GaAs had an initial resistivity of the order $10^9$ $\Omega$cm.
3.2.2 Pre-implant qualification

The material used during the course of the research was supplied by GEC Hirst Research Centre. The GaAs boule used was pre-qualified by capless annealing at 850°C for 20 minutes under an arsine overpressure of $7 \times 10^{-3}$ atm. to check for surface conversion and that the material retained a sheet resistivity greater than $2 \times 10^8 \Omega$/cm. In addition, a 'standard' implant and anneal procedure was used for boule qualification; this involved implanting $4 \times 10^{12}$ Si/cm$^2$ at 200keV and annealing under the conditions given above to generate a peak carrier concentration of about $2 \times 10^{17}$/cm$^3$[51].

3.2.3 Ion implantation procedure

All samples were boiled in hot methanol prior to implantation in order to obtain clean surfaces. The samples were implanted using the 500keV accelerator of the University of Surrey. Ion implantation was carried out at room temperature with the pressure of the target chamber at typically $10^{-6}$ torr. This vacuum was achieved by a two-stage pumping system which consists of a rotary and a diffusion pump. The ion beam was aligned at 7 degrees to the (100) surface normal to minimise channelling effects. The ion beam was monitored electrically in two ways. Firstly, the ion beam emerging from the lens after acceleration was
intercepted by a vibrating wire detector. The signal was displayed on the oscilloscope and was used to monitor the focussing of the ion beam. The ion beam diameter and intensity can be monitored by observing the scanning pattern on the oscilloscope and the ion beam current meter reading as the dc bias was varied. Secondly, the ion beam current of typically 1 to 3 μA, was monitored by the current integrator in order to determine the ion dose. Once the total charge reached a predetermined limit corresponding to the dose required, the beam was automatically shut off from the sample by a pneumatically operated valve. The emission of secondary electrons from the sample as a result of excitation by the impinging ions, was limited by a suppressor plate which was maintained at -300V with respect to the sample and located between the sample and the aperture. The beam current was monitored throughout the radiation of the samples in order to ensure that the implantation conditions did not alter. The ion beam was scanned in a raster by the application of a triangular waveform to orthogonal electrostatic deflection plates. The potential applied to the plates was varied according to the implantation energy, and was sufficient to ensure that the ion beam overscanned the samples; the area of scan is greater than the area of the aperture in order to ensure uniformity across the sample.

Potential errors that may occur during ion implantation
arise from unstable power supplies to the magnet and the acceleration potential and the uncertainties are 0.01% and 4% respectively [76]. These problems are overcome by using a negative feedback control system. Furthermore, although an electromagnet is used to separate ions of different masses, there is the problem of distinguishing molecules of the same mass as the corresponding ion. For example, the molecules CO and N₂ have the same mass as Si²⁸. Hence, Si²⁹ is usually implanted to avoid such a problem although a lower beam current is used because of its lower isotopic abundance. The neutral components in the ion beam arising from charge exchange of the ions with residual gas molecules during beam transport through the accelerator will cause a further error. This error is minimised by using the dc bias to deflect the ion beam until it impinges on the edge of the aperture, then the magnet current is adjusted to re-centralise the ion beam. The variation of dose rate between runs can also affect the subsequent electrical and structural properties of the implanted samples and this is caused by a rise in the sample temperature which has been shown to be essentially equal to that of the plate on which it is mounted. Naden [76] has observed a temperature rise of the sample plate to about 50°C for a 1.5MeV He ion implantation at a beam current of 1.2µA after about 100 minutes of implant time. The same author suggested that by choosing implant time of typically 40 minutes, temperature variations of less
than 20°C were generally obtained. The variations in the effectiveness of the suppression voltage can also lead to an uncertainty in dose of between 5% to 10%. This variation is dependent on the beam current, implant energy, species and substrate material and also the size of the aperture used. Figure 3.1 is a schematic of the setup of the Surrey 500keV ion implanter.

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**Fig. 3.1** Schematic representation of the ion implantation facility.
Post-implantation annealing is necessary to remove the radiation-induced damage and to electrically activate the implanted species. Typical annealing temperatures of 800-900°C are considerably in excess of the congruent evaporation temperature of GaAs (~660°C). Consequently, steps must be taken to prevent the preferential evaporation of arsenic which can lead to degradation both chemically and electrically of the GaAs surface and possible loss of dopant atoms. Encapsulation of the GaAs surface with a suitable inert material during annealing is one method of preventing surface degradation and in addition may provide a masking or registration medium for selective area ion implantation. Several materials have been used for this purpose [77] but only Plasma Enhanced Chemical Vapour Deposited (PECVD) silicon nitride, pyrolytic silicon nitride and evaporated aluminium nitride will be discussed in the following sections, as these films were used during the course of this research.

3.3.1 Pyrolytic CVD Silicon Nitride

The CVD pyrolytic silicon nitride apparatus is similar to the one initially designed by Donnelly et al [78] for depositing CVD silicon nitride films. A schematic diagram of the system is given in figure 3.2. The fundamental process that governs the growth of silicon
nitride is determined by the decomposition and reaction of the silane and ammonia gases according to the following process:

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

the above reaction becomes significant for temperatures above 500°C. The typical thicknesses of silicon nitride used were in the range 300Å to 1500Å. The colour of the layer is an indication of the thickness, a table of the relationship between colour and thickness is given in Table 3.1.

GaAs samples were coated with the pyrolytic silicon nitride according to the following procedure. The sample was loaded on the graphite strip heater near its centre. The chamber was pumped down to about 10⁻⁴ torr and then flushed with nitrogen for about five minutes which minimises the oxygen contamination in the deposited silicon nitride films. Silane and ammonia were introduced into the chamber along with nitrogen. The flow rates of these gases together with the deposition temperature and time determined the thickness of the film. After a steady state condition was established, the sample was heated up to a growth temperature of 635°C for typically 35s to grow approximately 1000Å of silicon nitride.
3.3.2 PECVD silicon nitride

The reaction involved in the production of silicon nitride thin films in this case is essentially the same as that described for silicon nitride grown pyrolytically. The difference being for PECVD silicon nitride, the sample is held at a temperature of 300°C and the reaction is enhanced by the formation of a plasma, generated by a rf voltage source operated at 13.65MHz and at a constant power of 30W. The PECVD silicon nitride films were deposited at GEC Hirst Research Centre and the apparatus and method of deposition is well documented [77].

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Fig. 3.2 Pyrolytic silicon nitride apparatus.

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<table>
<thead>
<tr>
<th>ORDER</th>
<th>COLOUR</th>
<th>SILICON NITRIDE (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>0.093-0.10</td>
</tr>
<tr>
<td></td>
<td>VERY PALE BLUE</td>
<td>0.10-0.11</td>
</tr>
<tr>
<td></td>
<td>SILICON</td>
<td>0.11-0.12</td>
</tr>
<tr>
<td></td>
<td>LIGHT YELLOW</td>
<td>0.12-0.13</td>
</tr>
<tr>
<td></td>
<td>YELLOW</td>
<td>0.13-0.15</td>
</tr>
<tr>
<td></td>
<td>ORANGE-RED</td>
<td>0.15-0.18</td>
</tr>
<tr>
<td>FIRST</td>
<td>RED</td>
<td>0.18-0.19</td>
</tr>
<tr>
<td></td>
<td>DARK RED</td>
<td>0.19-0.21</td>
</tr>
<tr>
<td>SECOND</td>
<td>BLUE</td>
<td>0.21-0.23</td>
</tr>
<tr>
<td></td>
<td>BLUE-GREEN</td>
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</tr>
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<td></td>
<td>ORANGE-YELLOW</td>
<td>0.28-0.30</td>
</tr>
<tr>
<td>SECOND</td>
<td>RED</td>
<td>0.30-0.33</td>
</tr>
</tbody>
</table>

Table 3.1 Colour/thickness relationship of silicon nitride.

3.3.3 Evaporated aluminium nitride (AlN)

For annealing temperatures higher than 900°C, the expansive stress at the interface between the silicon nitride and the implanted material causes the encapsulant to crack or peel. As aluminium nitride has an expansion coefficient close to that of GaAs (6.6x10⁻⁶ /K and 6.9x10⁻⁶ /K respectively), the problem
of interfacial stress may be overcome by using AlN as an encapsulant. The experimental apparatus used for the deposition of AlN films is a simple metal evaporator with some modifications shown in figure 3.3. GaAs samples were coated with aluminium nitride according to the following procedure. Initially, ammonia gas was transported into the chamber and pure aluminium was melted and evaporated from a hot tungsten filament held at a pressure of about $10^{-2}$ torr. The flow rate of the ammonia was adjusted continuously to keep the pressure constant in the chamber which is continuously pumped. The evaporated aluminium reacted with the ammonia to deposit aluminium nitride on the substrate at room temperature, the reaction is given as follows:

$$2\text{Al} + 2\text{NH}_3 \rightarrow 2\text{AlN} + 3\text{H}_2.$$ 

This novel way of depositing AlN was first established by Bensalem et al and is well documented [82].

3.3.4 Double-Layer Encapsulant:

Silicon nitride/aluminium nitride

Poor quality aluminium nitride films (possibly aluminium rich) have been observed to react with the GaAs surface during annealing and were therefore difficult to remove [82]. The same authors [82] suggested that in order to avoid this reaction and thus improve reproducibility, a double layer encapsulant
consisting of approximately 300Å of pyrolytic silicon nitride and 700Å of aluminium nitride should be used which proved successful in annealing GaAs samples at temperatures up to 1150°C [52].

---

**Fig. 3.3** Schematic diagram of the evaporator used to deposit AlN: A, gauge; B, aqueous ammonia; C, flowmeter; D, tungsten filament; E, shutter; F, sample holder; G, gas inlet; V, valve; DP, diffusion pump; RP, rotary pump.
3.4 Annealing techniques

3.4.1 Introduction

A double graphite strip heater was used to perform rapid thermal annealing on the ion-implanted materials. The use of such a system was first reported by Gwilliam et al [78]. However, a conventional furnace was also used to perform long time anneals. Various other systems used for rapid thermal annealing have been reported, these include the use of incoherent light [12], electron beams [44] and also laser beams [79]. In the following sections, the conventional furnace arrangement and the double graphite strip heater are discussed.

3.4.2 Furnace annealing

The arrangement used for long time annealing is shown in figure 3.4. In order to maintain a constant atmosphere around the samples, nitrogen gas, pre-dried by flowing through silica gel, was passed through the furnace tube. This had the disadvantage, however, of producing temperature gradients in the tube of at least 4°C/cm. In addition, the samples in the silica boat were unlikely to be subjected to the same gas flow conditions as the more exposed thermocouple. As the gas has a cooling effect, there is therefore some
uncertainty regarding the sample temperature during annealing.

In order to improve the reproducibility of the annealing conditions, a modified annealing probe was designed as depicted in figure 3.5, on which the samples could be mounted between two thermocouples. The rise time of about five minutes after inserting the samples was necessary due to the thermal mass of the probe assembly. Finally, the sample could be removed to a cool part of the furnace so that it was possible to reduce the cooling period to below 100°C in about ten minutes. The annealing cycle is shown in figure 3.6.

---

**Fig. 3.4** Early annealing arrangement. Gas flow is from left to right.

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Fig. 3.5 Modified annealing probe. Gas flow is from right to left.

Fig. 3.6 A typical anneal temperature/time cycle.
--o-- TC1, --x-- TC2.
The annealing process involves passing a high current, typically 100A ac, through two thin graphite strips thereby generating a heating effect. A schematic diagram of the DGSH system is shown in figure 3.7. The dimensions of each graphite strip are 120mm by 40mm by 0.5mm. The strips are separated by a gap of about 1.5mm into which the implanted samples are placed. Temperature control and measurement are achieved by means of two thermocouples, T1 and T2; the former is embedded in the bottom graphite strip; T2 is placed in between the strips, thereby representing the sample temperature. In practice, the difference in T1 and T2 is small; typically less than \(+5\) degrees Celsius at the annealing temperature. A typical temperature/time cycle is given in figure 3.8.

The annealing procedure is as follows. After encapsulation with either silicon nitride or a combination of silicon nitride and aluminium nitride, the implanted samples were cleaved into squares of about 5mm by 5mm and were then placed in the middle region between the graphite strips. The chamber was then evacuated to about \(10^{-1}\) torr before being backfilled with nitrogen gas. Rapid thermal annealing was performed in a nitrogen atmosphere to reduce oxidation of the graphite. Following annealing, the
samples were allowed to cool to a temperature between 80-100°C before being removed. The power supply to the heater was from a 100A transformer at 10 Volts, the temperature being controlled via the feedback from the chromel-alumel thermocouple T1 embedded in the graphite. The thermocouple were calibrated against the melting point of silver.

Fig. 3.7 The double graphite strip heater system.
3.5 Preparation of samples for electrical measurement

3.5.1 Sample preparation

After the annealing process, the samples were cut into the shape of a clover leaf as depicted in figure 3.9 in order to satisfy the criterion for accurate Hall measurement by the van der Pauw technique [81]. The required shape was obtained by mounting a metal mask.
over the sample using melted wax. The unmasked portions of the sample were then cut away by means of a micro-blaster. The sample was separated from the mask and cleaned in boiling toluene for five minutes prior to removal of the encapsulant in 40% hydrofluoric acid.

3.5.2 Ohmic contact formation

Ohmic contacts to the ion-implanted GaAs samples were formed by alloying metallic dots (tin dots for n-type, indium for p-type) to the surface of the implanted layer. The samples were placed onto an electrical heater and the metallic dots were positioned on the four edges of each sample. A mixture of nitrogen and hydrogen (5% hydrogen in nitrogen) gas was allowed to flow over the samples for five minutes in order to purge the system of moisture and to produce a reducing atmosphere. Contact alloying was performed for a total time of three minutes at about 300°C during which the gas mixture was allowed to bubble through a solution of hydrochloric acid. This was performed to clean the surface of the sample and to enhance the wetting of the metallic dots to the GaAs. The linearity of the contacts was checked by means of a standard transistor curve tracer before undergoing Hall measurement.

3.6 Assessment methods

Several techniques have been developed to characterise
the properties of ion-implanted layers. The van der Pauw technique together with layer removal were performed to obtain the sheet and volume electrical properties of the implanted layers. The electrical characteristics of implanted layers can also be obtained by performing C/V measurements and resistivity measurements by using the 4-point probe. Secondary Ion Mass Spectrometry (SIMS) was used to obtain information about the atomic distribution of the implanted species and Channelling experiments using Rutherford Backscattering Spectrometry (RBS) were performed to assess the crystallinity of the implanted layers after annealing. Auger Electron Spectroscopy (AES) was also used to characterise the pyrolytic and PECVD silicon nitride encapsulant. However, the differential Hall measurement technique will be discussed in detail as this technique was used substantially. In contrast, the other techniques will be discussed only briefly.

3.6.1 Hall measurement for electrical characterisation

This technique is based on the Hall effect [80]: when a magnetic field is applied at right angles to the current flowing in a sample, an electric field is set up in a direction perpendicular to the magnetic field and the current. The parameters of interest are:-

a) sheet resistivity $P_s$,

b) Hall coefficient $R_H$, 
c) sheet carrier concentration $N_s$,
d) sheet mobility $\mu_s$.

The above sheet parameters are values per unit depth. The respective volume values are then obtained by the successive removal of layers.

Van de Pauw [81] showed that the above parameters can be obtained for an arbitrary shape if the following conditions are met,

i) the electrical contacts are positioned at the circumference of the sample and are as small as possible,

ii) the sample is homogeneous in thickness,

iii) the sample surface is free of any holes.

3.6.2 The Hall apparatus

A schematic of the Hall apparatus is presented in figure 3.10. The sample is first fixed onto a circuit board by using black wax and electrical connections are made using conductive silver paint. The Hall measurements are performed when the sample is placed in between the magnet pole-pieces; the magnetic field strength applied is 5 kGauss. The system performs a set of twelve separate measurements on the sample. Details of the measurements made during the computer-controlled switching sequence are presented in figure 3.11. The computer calculates the sheet values from these
measurements. Depth profiling is achieved by etching the sample in a solution of concentrated sulphuric acid, hydrogen peroxide and water in a volume ratio of 1:1:125. During this process, the solution is constantly stirred to provide uniform etching.

Fig. 3.9 The 'clover-leaf' shaped sample.

Fig. 3.10 Schematic layout of the Hall apparatus.

<table>
<thead>
<tr>
<th>Measurement Number</th>
<th>Current</th>
<th>Measured Voltage</th>
<th>Magnetic Field</th>
<th>Measurement Performed</th>
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<td>+I_{AB}</td>
<td>V_{CD}</td>
<td>0</td>
<td>Resistivity</td>
</tr>
<tr>
<td>2</td>
<td>+I_{BC}</td>
<td>V_{AD}</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>+I_{BD}</td>
<td>V_{AC}</td>
<td>0</td>
<td>&quot;</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>
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<td>7</td>
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</tr>
<tr>
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</tr>
<tr>
<td>10</td>
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<td>+B</td>
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<tr>
<td>11</td>
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<td>0</td>
<td>&quot;</td>
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<tr>
<td>12</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-B</td>
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</tr>
</tbody>
</table>

Fig. 3.11 Sequence of steps used in Hall measurements.
After etching for a certain time, say 30s, the sample is rinsed in de-ionised water to prevent any further etching and the next set of measurements are performed. This process is repeated until the voltage readings become too unstable to measure accurately.

The actual etch rate is determined by measuring the step height of the etched layer by means of the Rank-Taylor Hobson Talystep. The volume value of carrier concentration is calculated by using the corrected etch rate. The details of the mathematical acquisition of the sheet and volume values are given as follows:

a) sheet resistivity \( (P_s) \)

If the resistance between adjacent contacts is denoted by,

\[
R = \frac{V}{I} \quad \text{and} \quad R = \frac{V}{I} \quad \text{and} \quad R/R < 5, \quad 1 \quad C, D \quad A, B \quad 2 \quad A, D \quad B, C \quad 1 \quad 2
\]

then the sheet resistivity, \( P_s \), of the material can be expressed by,

\[
P_s = \pi \frac{(R + R)/2 \cdot F(R,R)}{\ln 2}
\]

where \( F \) is a function of the symmetry of the contacts and is given by,

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

therefore, for a symmetrical sample,

\[
R = R \quad \text{and} \quad F = 1.
\]
If the induced voltage developed as a result of the Hall effect, is expressed in terms of an equivalent resistance change between the contacts, $R_{B,D,A,C}$, then the sheet Hall coefficient, $RH_s$, may be expressed as,

$$RH_s = \frac{R_{B,D,A,C}}{B} \text{ (cm } / \text{Coulomb)}$$

where $B =$ applied magnetic field strength in Gauss.

$$\Delta R_{B,D,A,C} = \frac{\Delta V}{I_{B,D,A,C}} \quad \text{and} \quad B_{B,D,A,C} = B_{B,D,A,C}$$

**c) Sheet Hall mobility ($\mu_s$)**

This parameter can be derived from the equations for $P_s$ and $RH_s$:

$$\mu_s = \frac{R_{Hs}}{P_s} \text{ (cm } / \text{V.s)}$$

**d) Hall scattering factor ($r$)**

This is defined as the ratio of the sheet Hall mobility $\mu_s$ and the conductivity mobility, $\mu$,

$$r = \frac{\mu_s}{\mu}$$
The magnitude of \( r \) is a function of the magnetic field, the degeneracy and it also depends on the prevalent scattering mechanism in the material. However, by and large, the value of \( r \) is assumed to be unity although the assumption will introduce a maximum error of around 10 to 20 percent (Refs. 33, 87).

e) Sheet carrier concentration \((N_s)\)

This parameter can be obtained from the following relationship,

\[
N_s = \frac{r}{e R} \frac{1}{\text{Hs}} \text{ (/cm}^2\text{)}
\]

where \( e = \) electronic charge \((1.62 \times 10^{-19} \text{ C})\)

f) Carrier concentration \& mobility \((N_v \& \mu_v)\)

These parameters are obtained from the following relationship,

\[
N_v = \left( \frac{1}{(Ps)^n} - \frac{1}{(Ps)^{n+1}} \right) \frac{1}{ed} \mu \quad \text{(carriers/cm)}
\]

\[
\mu = \left[ \frac{(RHS)^n}{(Ps)^n} - \frac{(RHS)^{n+1}}{(Ps)^{n+1}} \right] \frac{1}{1} \frac{1}{1} \text{ (cm}^2/\text{V.s)}
\]

where \( n = \) nth layer

\& \quad d = \) the thickness of the layer removed.
3.6.3 Rutherford Backscattering Spectrometry (RBS)

This technique employs a highly collimated beam of helium ions which impinge on a target sample. Some of these helium ions are backscattered from the surface whilst others penetrate into the sample and suffer collisions with the host atoms causing them to be backscattered out of the surface. The scattering is due to the coulombic repulsion between the helium ions and the nuclei of the host atoms. This is an elastic scattering event when both the energy and momentum are conserved. The backscattered ions which recoil from the specimen penetrate a silicon surface barrier detector where they lose energy by creating ionization. The detector is a large area diode consisting of an extremely thin p-type layer on one side of a high purity n-type wafer. For every incident ion, the detector acts as a very rapid ionization chamber, producing a voltage pulse which is proportional to the energy of the backscattered ion. Since the energy of the backscattered particles is related to the mass of the struck atom and the number of collisions is proportional to the number of scattering centres, one may, by sorting the scattered particles into voltage groups, establish a backscattering spectrum directly related to the concentration profile. In addition to this feature, ion channelling enables lattice damage and atomic location of impurities to be studied. The
channelling technique using RBS is well documented [98,99].

---

Fig. 3.12 Schematic of the Rutherford Backscattering Spectrometry experimental set up.

Essentially, the system consists of a target chamber where the samples to be analysed are mounted on a 3-axis goniometer and are irradiated with monoenergetic light ions. The chamber is evacuated to typically $10^{-6}$ torr. Usually, helium ions are accelerated to energies in the range of 1 to 3 MeV. The helium beam is collimated to have a half angle of about 1/40 degrees in order to facilitate channelling experiments and also a cross-sectional area of about 1mm square as defined by the fixed aperture. A small proportion of the ions, typically $10^{-5}$, will be backscattered at a certain angle and detected by the surface barrier detector.
These signals are processed to enable the energy spectrum of the backscattered helium ions to be displayed. The channelling spectra yield information about the lattice damage and a parameter called $\chi_{\text{min}}$ which is the minimum ratio of backscattered yield of the sample at a random orientation and the yield at a channelling orientation. A block diagram of the RBS system is presented in figure 3.12.

3.6.4 Secondary Ion Mass Spectrometry (SIMS)

The basic principles of SIMS are as follows: an ion beam is used to irradiate the sample and the sample atoms are sputtered from the surface, some of these particles will be in an ionised state. A mass spectrometer is used to analyse these sputtered ions as a function of their mass/charge ratio. Static SIMS uses very low primary ion (argon) beam energies and current densities and is used to study surface composition in the monolayer regime. In dynamic SIMS, higher ion beam energies and current densities of the order of about 1keV to 20keV and $10^{-3}$ A/cm$^2$ respectively are required for high removal rate combined with good depth resolution. The primary beam can be focussed to micron sized spots and scanned over areas several hundred microns across. The primary ion species used for dynamic SIMS are oxygen and caesium as these species give increased secondary ion yields and oxygen bombardment produces less surface roughening in the
bombarded crater than does argon and hence the depth resolution is improved. The depth resolution is of the order of +10% and the technique is quantitative to +10% with standards for homogeneous dilute systems. A schematic diagram for the SIMS set up is presented in figure 3.13.

Fig. 3.13 Schematic of the Secondary Ion Mass Spectrometry experimental set up.

3.6.5 Auger Electron Spectroscopy (AES)

Auger electron spectroscopy is used to considerable advantage when combined with in situ ion etching to obtain composition-depth profiles. The basic principle of operation of AES is as follows. Auger electrons are produced by bombarding the specimen surface with low energy electrons (1-10keV). Some of the atoms within
the sample are ionised and figure 3.14 illustrates the kind of electron re-arrangement which can take place within the atom as a result. Thus, if, for example, an electron from the K energy level is ejected, an electron from the L2 level may fill the vacant site releasing an amount of energy $E_{K} - E_{L2}$. This energy may now be transferred to another electron possibly in the L3 level, which is then ejected from the solid. This latter electron is the Auger electron and its energy $E$ is given by

$$E = E_{K} - E_{L2} - E_{L3}$$

since $E_{K}$, $E_{L2}$ and $E_{L3}$ are all characteristics of the particular element concerned, it is possible by measuring the energies and the number of Auger electrons to determine the chemical composition of the sample surface. The Auger electron energies are low, typically in the range 20 to 2000eV. Thus, even though they may be generated from as far within the solid as the original electron beam penetrates, only those which are generated within the first two or three atomic layers (about 2nm) below the surface can escape with their original energies intact. Those Auger electrons which originate further within the solid lose energy in extra inelastic collisions and may no longer be identified as such. Thus, this technique has good surface sensitivity and as little as 0.1% of a monolayer of impurity in the surface can be detected [89]. Only hydrogen and helium cannot be detected since these elements possess insufficient energy levels for
the Auger transition to occur. As mentioned above, depth distribution of impurities can be obtained by performing sequential ion beam sputtering and surface analysis and this is used in the course of this research to detect the level of oxygen content in the encapsulant.

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Fig. 3.14 A schematic diagram illustrating a transition leading to the emission of a K-L₂-L₃ Auger electron. ---

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CHAPTER 4

EXPERIMENTAL RESULTS

4.1 Introduction

This chapter presents the experimental results obtained during the course of the research. The results are presented in a logical sequence rather than chronologically.

Results include firstly, the study of the electrical activation of zinc and beryllium implanted into GaAs. Secondly, the thermal stability and hence the deactivation characteristics of these rapid thermally annealed ion implanted layers are studied. The effects of co-implantation of phosphorus ions on the activation efficiency and thermal stability of these layers have also been investigated. In addition, the deactivation characteristics of selenium implants in GaAs have also been investigated in order to compare with the acceptors. The final section of this chapter presents a summary of the important results generated by the research and serves as an introduction to the discussion presented in chapter 5. Throughout the course of the research, undoped semi-insulating LEC grown GaAs of (100) orientation supplied by GEC Hirst Research Centre, was implanted with various ions in a non-channelling direction at room temperature.
4.2 Activation of Zn and Zn+P implanted GaAs

In this section, the results on the electrical activation characteristics of Zn and Zn+P implanted GaAs are presented. These results are divided into two sections: isochronal annealing results and the results on the electrical profiles.

4.2.1 Isochronal annealing results

Zinc ions were implanted at a dose and energy of $10^{15}$ /cm$^2$ and 260keV respectively. Some of these samples were further implanted with phosphorus ions at a dose and energy of $1.2 \times 10^{15}$ /cm$^2$ and 140keV respectively. The projected range $R_p$ is situated at around 1100Å as predicted by PRAL [27]. A peak atomic concentration of around $8 \times 10^{19}$/cm$^3$ is expected for both the zinc and phosphorus implants. Approximately 1000Å of PECVD silicon nitride was used as the encapsulant. Isochronal annealing in the temperature range of 600°C to 850°C was performed at 30s. The sheet carrier concentration and mobility values are plotted in fig.4.1 for both sets of samples. It can be observed that except at temperatures of 600°C and 850°C where the sheet carrier concentrations of $9 \times 10^{13}$/cm$^2$ and $9.8 \times 10^{14}$/cm$^2$ respectively are the same for both sets of samples, the electrical activation is higher for the dual-implanted samples at all temperatures. The sheet mobility values are lower.
for the dual-implanted samples for the range of temperatures investigated. For the dual-implanted samples, a maximum value of $60 \text{cm}^2/\text{V.s}$ is observed after annealing at 850°C for 30s as compared to $75 \text{cm}^2/\text{V.s}$ in the case of the zinc implanted sample after annealing at the same conditions.

Fig. 4.1. Sheet electrical properties as a function of annealing temperature. (t=30s)
4.2.2 Electrical profiles

It can be observed in fig. 4.2 that after annealing at 850°C for 30s, the electrical profile of the zinc implanted sample has broadened to a depth of about 5500Å with a peak of $2.5 \times 10^{19}/\text{cm}^3$ situated at around the projected range. On the other hand, the profile of the dual-implanted sample is abrupt and gaussian in shape with a peak carrier concentration of $6 \times 10^{19}/\text{cm}^3$ also situated at the projected range and the tail extending to a depth of around 3000Å.

---

**Fig. 4.2.** Electrical profiles of Zn and Zn+P implanted GaAs.
In addition, the electrical profile of the zinc implanted sample annealed at 800°C/30s has not broadened but has only extended to a depth of 3000Å with a peak hole concentration of $3 \times 10^{19}$/cm$^3$. This is presented in Fig. 4.3 together with the profile of the zinc implanted sample annealed at 850°C/30s.

Fig. 4.3. Electrical profiles of Zn implanted GaAs.

- a: 800°C/30s.
- b: 850°C/30s.

**Fig.4.3. Electrical profiles of Zn implanted GaAs.**
It is shown in the electrical profiles presented in fig. 4.4 that the electrical activation of the dual implanted samples is higher after annealing at 850°C/30s than at 800°C/30s. In contrast to the samples implanted with zinc alone, this increase in the activation is achieved with an increase in the peak hole concentration from about $4 \times 10^{19} / \text{cm}^3$ to $6 \times 10^{19} / \text{cm}^3$ without significant profile broadening.

![Graph showing electrical profiles of Zn+P implanted GaAs](image)

a: 800°C/30s.
b: 850°C/30s.

Fig. 4.4. Electrical profiles of Zn+P implanted GaAs.
4.3 Activation of Be and Be+P implanted GaAs

In this section, the results on the electrical activation characteristics of Be and Be+P implanted GaAs are presented. These results are divided into two sections: isochronal annealing results and the results on the electrical profiles.

4.3.1 Isochronal annealing results

Beryllium ions were implanted at a dose of $10^{14}$ cm$^{-2}$ at 25keV and some of these samples were further implanted with $8 \times 10^{13}$ cm$^{-2}$, 90keV of phosphorus ions. The projected range is situated at around 800Å as predicted by PRAL [27]. A peak atomic concentration of around $7 \times 10^{18}$ cm$^{-3}$ is expected for both the beryllium and phosphorus implants. Approximately 1000Å of PECVD silicon nitride was used as the encapsulant. Isochronal annealing was performed at temperatures from 550°C to 950°C for 10s. A plot of the sheet hole concentration and mobility against temperature is presented in fig. 4.5.

It can be observed from fig. 4.5 that for the beryllium implanted sample, the sheet hole concentration increases from $3 \times 10^{12}$ cm$^{-2}$ to $3.5 \times 10^{13}$ cm$^{-2}$ with an increase in temperature from 550°C to 750°C before
reverse annealing effects are observed.

Fig. 4.5. Sheet electrical properties as a function of annealing temperature. (t=10s)

The sheet hole concentration has decreased to $2 \times 10^{13}$/cm$^2$ after annealing at 950°C for 10s. For the dual-implanted samples annealed at temperatures below
800°C, the sheet hole concentration values are observed to be lower than those of the samples implanted with beryllium alone. However, the sheet carrier concentration continues to increase with temperature up to 950°C where the sheet hole concentration reaches 5\times10^{13}/\text{cm}^2. The average sheet mobility values for the dual-implanted samples are observed to be about 90 cm²/V.s which is about half that of the beryllium implanted samples over the range of temperatures investigated.

4.3.2 Electrical profiles

The electrical profiles for both sets of samples annealed at 750°C for 10s are presented in fig.4.6. An increase of carriers of the order of 3\times10^{18}/\text{cm}^3 near the surface is observed in the hole concentration profile for the beryllium implanted sample. Also, this profile extends to a depth of about 3000Å. Although it has not been presented here, similar profile shape and electrical activity have been observed for the beryllium implanted sample after capless annealing at the same conditions. On the other hand, the electrical profile for the dual-implanted sample after annealing at the same conditions is gaussian in shape. It can be observed in fig.4.6 that this profile has a peak concentration of about 2\times10^{18}/\text{cm}^3 situated at a depth of about 900Å which is close to the projected range of 800Å.
The electrical profiles of the dual-implanted samples which have been annealed at 750°C/10s and 950°C/10s respectively are presented in fig.4.7. It can be observed from fig.4.7 that there is no significant redistribution of the beryllium atoms after annealing at 950°C for 10s. Also, the hole concentration profile is gaussian in shape with a peak concentration of about $3 \times 10^{18} / \text{cm}^3$ situated at around the projected range. That is to say, the increase in the electrical

---

Fig.4.6. Electrical profiles of Be and Be+P implanted GaAs.
activation after annealing at 950°C/10s as compared to 750°C/10s, is achieved with an increase in the peak hole concentration from $2 \times 10^{18}$ /cm$^3$ to $3 \times 10^{18}$ /cm$^3$ without any significant profile broadening.

Fig. 4.7. Electrical profiles of Be+P implanted GaAs.

- **a**: 750°C/10s.
- **b**: 950°C/10s.
4.4 The influence of heat treatment on rapid thermally annealed ion implanted GaAs

In this section, the results on the thermal stability characteristics of various ions implanted into GaAs are presented. The section is therefore divided under the different ions being investigated.

4.4.1 Thermal stability of acceptor implanted layers in GaAs

The thermal stability characteristics of acceptor implanted layers in general are presented in this section. A more detail investigation of the zinc and beryllium implanted samples are presented in sections 4.4.4 and 4.4.5.

1) Isothermal annealing results

Beryllium, magnesium and zinc ions were implanted at doses of $5 \times 10^{14}$, $5 \times 10^{14}$, $2.5 \times 10^{14}$/ cm$^2$ and energies of 40, 100 and 260 keV respectively. The implant doses and energies were chosen to generate approximately the same projected range and peak atomic concentration as predicted by PRAL [27]. Approximately 1000Å of silicon nitride was deposited pyrolytically at 635°C for 35s as the encapsulating layer. A double graphite strip heater was used to rapid thermal anneal the samples at 800°C
for 15s. Both the 'as-capped' and the rapid thermal annealed (RTA) samples were subsequently annealed in the temperature range of 100-600°C for times up to 6 hours in nitrogen ambient in a furnace. Following annealing, sheet hole concentration and mobility were measured by the van der Pauw technique using indium contacts. The carrier and mobility profiles were obtained by the differential Hall effect technique. Table 4.1 is a summary of the sheet values.

<table>
<thead>
<tr>
<th>ANNEALING CONDITIONS</th>
<th>IONS</th>
<th>Be</th>
<th>Mg</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ENERGY (keV)</td>
<td>40</td>
<td>100</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>DOSE (/cm²)</td>
<td>5x10¹⁰</td>
<td>5x10¹⁰</td>
<td>2.5x10¹⁰</td>
</tr>
<tr>
<td>AS-CAPPED (RTA 635°C/35s)</td>
<td>Ns (10¹⁰/cm²)</td>
<td>2.3±0.1</td>
<td>1±0.1</td>
<td>1±0.1</td>
</tr>
<tr>
<td></td>
<td>μs (cm²/V.s)</td>
<td>115±10</td>
<td>90±5</td>
<td>40±4</td>
</tr>
<tr>
<td></td>
<td>Ps (Ω/□)</td>
<td>238±40</td>
<td>667±30</td>
<td>1574±80</td>
</tr>
<tr>
<td></td>
<td>%ACTIVITY</td>
<td>46±2</td>
<td>20±2</td>
<td>40±4</td>
</tr>
<tr>
<td>RTA at 800°C/15s</td>
<td>Ns (10¹⁰/cm²)</td>
<td>2.2±0.1</td>
<td>1.5±0.1</td>
<td>2.2±0.1</td>
</tr>
<tr>
<td></td>
<td>μs (cm²/V.s)</td>
<td>107±10</td>
<td>100±12</td>
<td>92±15</td>
</tr>
<tr>
<td></td>
<td>Ps (Ω/□)</td>
<td>275±40</td>
<td>400±20</td>
<td>320±35</td>
</tr>
<tr>
<td></td>
<td>%ACTIVITY</td>
<td>44±2</td>
<td>30±2</td>
<td>88±4</td>
</tr>
</tbody>
</table>

Table 4.1. Sheet values for various ions after rapid thermal annealing.

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(Sheet carrier concentration $N_s$, sheet mobility $\mu_s$ and sheet resistivity $\rho_s$) of samples following rapid thermal annealing. A value for the percentage activity can be obtained by expressing the sheet carrier concentration as a percentage fraction of the dose. Also, the sheet values are given as an average of three samples with plus and minus one standard deviation.

From the data given in table 4.1, it can be observed that a considerable amount of electrical activity is achieved for all three sets of implanted samples after a low temperature rapid thermal anneal at 635°C for 35s during the silicon nitride deposition process (as-capped). After RTA at 800°C for 15s, the beryllium implanted samples showed no significant change in the electrical activity of 46% when compared to the 'as-capped' samples. However, the electrical activity of the zinc and magnesium implanted samples increased from 40% and 20% to 88% and 30% respectively.

Figure 4.8 shows the isothermal annealing results of the 'as-capped' samples followed by annealing at 600°C for times of up to 6 hours. No changes in the $N_s$ values are observed for all three sets of implanted samples at temperatures below 600°C. The data for the magnesium implanted samples subsequently annealed at temperatures below 600°C are also shown on fig.4.8 for comparison. At 600°C, however, the $N_s$ values of both the beryllium and magnesium implanted samples decrease with time. In
contrast, the value for the zinc implanted samples increases with time. That is, the activities decreased from 46% to 32% for the beryllium implanted samples and from 20% to 7% for the magnesium implanted samples. The electrical activity of the zinc implanted samples, however, increased from 40% to 64%.

Fig. 4.8. Time dependence of the electrical activity at 600°C after silicon nitride deposition at 635°C/35s.

An increase in the mobility values as presented in fig
4.9 for all three sets of samples is observed over the 6 hour annealing period. In particular for the zinc implanted samples, the mobility value has increased by more than 50% from 40 cm$^2$/V.s to 65cm$^2$/V.s.

---

**Fig. 4.9.** Time dependence of the sheet mobility at 600°C after silicon nitride deposition at 635°C/35s.

For the RTA samples (800°C/15s), isothermal annealing at
600°C results in a decrease in the Ns values for all three sets of samples as shown in figure 4.10. The electrical activity of the zinc implanted samples has decreased from 90% to 60%. The electrical activities of the beryllium and magnesium implanted samples have decreased from 44% to 31% and 30% to 22% respectively.

Fig. 4.10. Time dependence of the electrical activity at 600°C after RTA at 800°C/15s.

The sheet mobility values again show a slight increase with the annealing time as presented in fig. 4.11.
Moreover, when the beryllium, magnesium and zinc implanted samples are annealed at 800°C/15s again, the electrical activities have changed from 31%, 22% and 60% to 30%, 21% and 90% respectively. That is to say, the electrical activity of the zinc implanted samples has recovered from 60% to 90%. But this recovery in the
electrical activity is not observed for the beryllium and magnesium implanted samples. This is illustrated in fig. 4.12.

---

Fig. 4.12. The electrical activity of zinc and beryllium implanted samples at various annealing conditions.

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ii) Electrical profiles

The electrical profiles for the beryllium implanted samples annealed at 635°C/35s (after silicon nitride deposition) and further annealed at 600°C for 6 hours are presented in fig.4.13.

---

![Graph showing electrical profiles of Be implanted GaAs]

a: as-capped, b: as-capped + 600°C/6hours.

Fig.4.13. Electrical profiles of Be implanted GaAs.

---

It can be observed from fig.4.13 that the hole concentration profile of the 'as-capped' sample is
gaussian in shape with a peak hole concentration of $10^{19} / \text{cm}^3$ situated at around the projected range. After annealing at 600°C for 6 hours, redistribution of the beryllium atoms occurs. There is an increase in the hole concentration to about $7 \times 10^{18} / \text{cm}^3$ near the surface of the profile. Also, the profile has extended about 500Å deeper into the bulk of the material to 3000Å. After further annealing at 635°C/35s, the shape of the profile is very similar to that described above for the ('as-capped' + 600°C/6hours) profile.

The electrical profiles of the zinc implanted samples which have been annealed at 800°C/15s, further annealed at 600°C/6 hours and again annealed at 800°C/15s are presented in fig. 4.14. For the sample that was annealed at 800°C for 15s, a double peak is observed in the hole concentration profile. The minimum hole concentration of about $4 \times 10^{18} / \text{cm}^3$ occurs near the projected range and also the peak concentrations of $10^{19} / \text{cm}^3$ and $6 \times 10^{18} / \text{cm}^3$ are situated on either side of the projected range. The tail of the profile extends to a depth of about 3000Å.

For the sample that underwent a subsequent heat treatment at 600°C for 6 hours, the profile is flat with an average carrier concentration of $5 \times 10^{18} / \text{cm}^3$. A further rapid thermal anneal at 800°C for 15s results in the profile being modified to become gaussian in shape with a peak carrier concentration of $10^{19} / \text{cm}^3$ at
around the projected range. No significant broadening of the profile is observed after the annealing processes.

![Graph showing electrical profiles of zinc implanted GaAs](image)

**Fig. 4.14.** Electrical profiles of zinc implanted GaAs.

- **a:** 800°C/15s. **b:** 800°C/15s + 600°C/6hours.
- **c:** 800°C/15s + 600°C/6hours + 800°C/15s.

The electrical profiles and the deactivation characteristics of the magnesium implanted samples have not been determined. However, the beryllium and zinc implanted samples are investigated in more detail.
4.4.2 Thermal stability of dual-implanted GaAs

i) Annealing results

The Zn+P and Be+P implanted samples described in section 4.2 and 4.3 were rapid thermally annealed at 850°C for 30s and 750°C for 10s respectively. Electrical activities of 100% and 25% were obtained. Further heat treatment at 600°C for 6 hours and 2 hours respectively has resulted in a decrease in the electrical activity to 70% and 20% respectively. For both sets of the dual-implanted samples, the decrease in the electrical activities is observed to have recovered to the original values after further annealing at the starting conditions. That is, at 850°C/30s and 750°C/10s for the Zn+P and Be+P implanted samples respectively.

ii) Electrical profiles

The hole concentration profiles of the Be+P and Zn+P implanted samples are presented in figs.4.15 and 4.16 respectively. It can be observed from fig.4.15 that the shape of the electrical profiles has not varied significantly after the various annealing stages for the Be+P implanted samples. As presented in fig.4.15, the hole concentration profile is gaussian in shape with a peak concentration of about $3 \times 10^{18}$/cm$^3$ situated at around the projected range. In addition, the hole...
concentration profile has not broadened after annealing at 600°C for 2 hours.

Fig. 4.15. Electrical profiles of Be+P implanted GaAs.

As for the Zn+P implanted samples, the profile remains gaussian in shape but there is a decrease in the peak hole concentration from $6 \times 10^{19} \text{ cm}^{-3}$ to $4 \times 10^{19} \text{ cm}^{-3}$ after annealing at 600°C for 6 hours. This is presented in fig. 4.16. Furthermore, no broadening of the hole
concentration profile is observed after further annealing.

\[ \text{C} \quad \text{O} \quad \text{E} \quad \text{2} \quad \text{0} \quad \text{I} \quad \text{1} \quad \text{0} \quad \text{i} \quad \text{Z} \quad \text{O} \quad \text{H} \quad \text{C} \quad \text{d} \quad \text{1} \quad \text{0} \quad \rightarrow \quad \text{Z} \quad \text{U} \quad \text{Z} \quad \text{o} \quad \text{u} \quad \text{1} \quad \text{8} \quad \text{1} \quad \text{0} \quad : \quad \text{C} \quad \text{d} \quad \text{L} \quad \text{U} \quad \text{C} \quad \text{d} \quad \text{C} \quad \text{d} \quad \text{<} \quad \text{1} \quad \text{7} \quad \text{V} \quad \text{1} \quad \text{0} \quad \quad \text{0} \quad \text{1} \quad \text{8} \quad \text{0} \quad \text{Z} \quad \text{n} \quad \text{c} \quad \text{m} \quad \text{2} \quad 260 \text{keV}, \]

\[ 1 \cdot 2 \times 10^{15} \text{P}^+/\text{cm}^2 \quad \text{140 keV}. \]

\( a: 850^\circ \text{C}/30\text{s}. \quad b: 850^\circ \text{C}/30\text{s} + 600^\circ \text{C}/6\text{hours}. \)

Fig. 4.16. Electrical profiles of Zn+P implanted GaAs.

4.4.3 Thermal stability of selenium implanted GaAs

1) Annealing results

Selenium ions were implanted at a dose and energy of
$10^{14}$/ cm² and 300keV respectively. The projected range is situated at a depth of about 1200Å as predicted by PRAL [27] and the peak atomic concentration is about $8 \times 10^{18}$/cm³. A double layer encapsulant consisting of 300Å of pyrolytic silicon nitride and 700Å of aluminium nitride was used since annealing temperatures higher than 900°C will be used. Thus, a single layer of silicon nitride is not adequate as discussed in section 3.3.4.

The implanted samples were annealed at 980°C for 20s using the double graphite strip heater and an electrical activity of 44% was obtained. Some of these samples were subsequently annealed at temperatures of 600°C to 850°C for times from 30 minutes up to 6 hours. Fig.4.17 is a plot of the time dependence of the electrical activity at different temperatures during subsequent heat treatment. It can be observed that in comparison to the acceptor implanted samples, the change in the electrical activity starts to occur at a higher annealing temperature of 700°C. After a subsequent anneal of 800°C for 6 hours, the electrical activity has decreased from 44% to 18%. Moreover, the electrical activity of about 26% obtained after a subsequent anneal of 850°C for 1 hour has not decreased as much as the sample annealed at 800°C for 1 hour where the electrical activity is measured to be about 22%. Also from fig 4.17, the electrical activity decreases towards a limiting value for each annealing temperature.
Fig. 4.17. Time dependence of the electrical activity as a function of annealing temperature.

As presented in Fig. 4.18, the sheet mobility values increase with the subsequent annealing times and temperatures. Due to the scattering of the data caused by the relatively small increase in the mobility values, only the data for temperatures of 600°C and 750°C
are shown.

\[ \text{SHEET MOBILITY (cm}^2/\text{V.s)} \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.18.png}
\caption{Time dependence of the sheet mobility at annealing temperatures of 600°C and 750°C.}
\end{figure}

Moreover, similar to the results of the zinc implanted samples presented in section 4.4.1, the electrical activity of the selenium implanted samples has recovered from 18% to 44% after further annealing at
ii) Electrical profiles

The electrical profiles of the selenium implanted samples which have been annealed at 980°C/20s, further annealed at 800°C/6 hours and again annealed at 980°C/20s are presented in fig.4.19.

![Graph showing electrical profiles of Se implanted GaAs]

- **a**: 980°C/20s.
- **b**: 980°C/20s + 800°C/6 hours.
- **c**: 980°C/20s + 800°C/6 hours + 980°C/20s.

**Fig.4.19. Electrical profiles of Se implanted GaAs.**
It can be observed that similar changes in the shapes of the electrical profiles are observed as in the case of the zinc implanted samples shown in section 4.4.1.

In this case, double peaks of electron concentration of $3 \times 10^{18}$ /cm$^3$ and $1.5 \times 10^{18}$ /cm$^3$ are observed after annealing at 980°C for 20s. The shape of this profile has been modified to become a flat profile with electron concentration of $10^{18}$ / cm$^3$ without significant profile broadening after subsequent heat treatment at 750°C for 6 hours. A further rapid thermal anneal at 980°C for 30s results in a gaussian shaped concentration profile with a peak of about $3 \times 10^{18}$ / cm$^3$.

4.4.4 Thermal stability of Zn implanted GaAs

In this section, the thermal stability of the samples implanted with zinc ions at a dose and energy of $10^{15}$/cm$^2$ and 260keV respectively are investigated in more detail. In contrast to the results already presented in section 4.4.1 which contains the thermal stability characteristics at 600°C only, a range of temperatures from 600°C to 750°C are investigated here. Approximately 1000Å of PECVD silicon nitride was used as the encapsulant. The electrical activation characteristics of this set of samples between annealing temperatures of 600°C to 850°C at t=30s have already been presented in section 4.2.
1) Annealing results

For the samples that were annealed at 850°C for 30s, further annealing was performed from 600°C to 750°C at times of 30 minutes to 6 hours. The time dependence of the electrical activity during subsequent heat treatment at different temperatures is presented in Fig. 4.20.

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RTA: 850°C/30s.

Fig. 4.20. Time dependence of the electrical activity as a function of annealing temperature.
It can be observed that the sheet hole concentration and hence the electrical activity decreases with time at a given temperature. Also, for sufficiently long times, the electrical activity reaches a limiting value for each temperature. These results are similar to those obtained for the selenium implanted samples as presented in section 4.4.3.

a: 850°C/30s. b: 850°C/30s + 600°C/6hours.

Fig.4.21. Electrical profiles of Zn implanted GaAs.

ii) Electrical profiles

It can be observed in fig.4.21 that the hole
concentration profile for the sample annealed at 850°C for 30s has a maximum hole concentration of 2.5\times 10^{19}/\text{cm}^3 situated at around Rp and the profile extends to a depth of 5500Å. The hole concentration profile corresponding to the sample which has been subsequently annealed at 600°C for 6 hours is also presented in fig.4.21. It can be observed that there is no profile broadening after further annealing at 600°C for 6 hours. However, a decrease in the hole concentration throughout the electrical profile is observed. Also, the peak hole concentration has decreased to about 1.5\times 10^{19}/\text{cm}^3.

4.4.5 Thermal stability of Be implanted GaAs

In this section, the thermal stability characteristics of the samples implanted with beryllium ions at a dose and energy of 10^{14}/\text{cm}^2 and 40\text{keV} respectively are presented. In contrast to the results already presented in section 4.4.1, a range of temperatures from 600°C to 750°C are investigated here. Approximately 1000Å of pyrolytic silicon nitride was deposited at 635°C for 35s as an encapsulating layer.

i) Annealing results

An electrical activity of 63% was obtained after the encapsulation process as presented in fig.4.22. These 'as-capped' samples were further annealed at
temperatures from 600°C to 750°C for times from 15 minutes up to 2 hours.

Fig. 4.22. Time dependence of the electrical activity as a function of annealing temperature.

The error bars are also given for the data obtained for the annealing temperature of 750°C. It is worth noting that the rise time needed to reach the pre-determined
temperature is included in the total anneal time and therefore the actual annealing time is less than that expected. This will contribute the largest error when the annealing time is less than 30 minutes but it can be neglected when the annealing time is longer than 30 minutes.

The time dependence of the electrical activity at different temperatures is presented in fig. 4.22. The electrical activity decreases with time for each temperature. The minimum electrical activity obtained is 22% after a subsequent anneal of 750°C for 2 hours. Also, an electrical activity of 20% is obtained after further annealing at 635°C/35s. That is to say, the electrical activity has not recovered to the original value. This result is similar to that reported earlier in section 4.4.1. In contrast to the results of the zinc and selenium implanted samples presented in sections 4.4.3 and 4.4.4, the electrical activity here does not tend to a constant value for each annealing temperature but continues to decrease with increasing time. Also, the magnitude of the decrease increases with increasing temperature.

ii) SIMS results

Secondary Ion Mass Spectrometry was performed to compare the atomic concentration of the 'as-implanted' and the 'as-capped' samples. As mentioned earlier in
section 4.4.1, the 'as-capped' samples have undergone a low temperature anneal at 635°C/35s during the process of silicon nitride deposition.

\[ 635°C/35s \]

Fig. 4.23. SIMS profiles of Be implanted GaAs.

It can be observed in fig. 4.23 that the atomic concentration of the 'as-capped' sample is about 70% of the 'as-implanted' value. This indicates that 70% of the implanted beryllium atoms remained in the sample.

a: as-implanted = \(1.1 \times 10^{14}\) Be atoms/cm².

b: as-capped = \(8 \times 10^{13}\) Be atoms/cm².
after silicon nitride deposition at 635°C for 35s and within experimental errors, all atoms are electrically active according to Hall effect measurements (see fig.4.22). Also, the atomic profile of the 'as-capped' sample has broadened compared to the 'as-implanted' sample. This indicates a diffusion of beryllium atoms both towards the surface and into the bulk of the material.

iii) RBS results

Channelling experiments were performed using Rutherford Backscattering Spectrometry to obtain information on the degree of crystallinity of the 'as-capped' sample prior to any subsequent heat treatment. The channel and random spectra of the 'as-capped' sample are presented in fig.4.24. A Xmin value of about 5%-7% is measured by expressing the minimum channel yield as a percentage fraction of the random yield.

iv) AES results

Auger Electron Spectroscopy was performed to obtain information on the quantity of oxygen and carbon which may have been incorporated in the silicon nitride film during the deposition process. Fig.4.25 demonstrates that oxygen and carbon are not present in the silicon nitride film.
RBS spectra of Be $1\times 10^{14}$, 40 keV

- Random
- As Implanted (channel)
- Pyrolytic Si$_3$N$_4$ at 635°C/35s/7s (channel)

Fig. 4.28. RBS spectra of Be implanted GaAs.
Fig. 4.25. AES profiles of pyrolytic and PECVD silicon nitride films.

4.5 Summary of results

The results presented in this chapter can be briefly summarised as follows:
1) High hole concentration and a reduction in both in- and out-diffusion of zinc and beryllium atoms has been achieved by the co-implantation of phosphorus.

2) The sheet carrier concentration of the rapid thermally annealed ion implanted samples remains unchanged during subsequent heat treatment at temperatures below 600°C. At 600°C, the sheet carrier concentration of the acceptor and dual implanted samples change significantly. For the selenium implanted samples, the change in the electron concentration occurs at a higher temperature of 700°C.

These changes in the sheet carrier concentration are observed to be reversible in the case of the zinc and selenium implanted samples but not for the beryllium and magnesium implanted samples. The shapes of the carrier profiles are also modified after the various subsequent annealing stages.

3) For the rapid thermally annealed selenium implanted samples, the sheet electron concentration decreases both towards a limiting value with time and with increasing annealing temperatures. Similar changes in the carrier concentration are observed for the zinc implanted samples. In contrast, the sheet hole
concentration of the beryllium implanted samples decreases with increasing subsequent annealing temperatures and times, but not towards a limiting value for each annealing temperature.
5.1 Introduction

The discussion of the experimental results is presented in this chapter.

The aims of this work have been to form electrically active layers in GaAs by ion implantation and to investigate the influence of heat treatment on the rapid thermally annealed, ion implanted layers. Thus the results on the activation characteristics of Be, Be+P, Zn and Zn+P implanted GaAs are discussed in section 5.2 in this chapter. Also in this section, the physical processes by which the implanted ions become electrically activated are studied by using a model which has been previously developed. The applicability and validity of interpreting the results obtained from this work by using such a model is also discussed.

The results of the influence of heat treatment on the electrical properties of ion implanted GaAs are discussed in section 5.3. A discussion of the reversibility of the electrical properties of Zn and Se implanted GaAs after heat treatments will also be presented in section 5.3. RBS, SIMS, AES and electrical data have led to the development of a model which explains the deactivation mechanisms of dopants in GaAs. Section 5.4 will discuss how these mechanisms are
related to the physical processes observed in the electrical activation. A review of the discussion is presented in section 5.5. This will serve as an introduction to the conclusions presented in chapter 6.

5.2 Activation of acceptor implanted GaAs

5.2.1 Be and Be+P implanted GaAs

1) Isochronal annealing results

The advantages of being the lightest acceptor species in GaAs are twofold. Firstly, the lattice disorder caused by implantation is less severe than the heavier ions. Secondly beryllium offers a larger range. The draw back of using beryllium as a doping species is that it has a relatively large longitudinal straggle. Hence, it is more difficult to produce abrupt junctions. Nevertheless, there is world-wide interest in the annealing of beryllium implanted GaAs [6,35,113]. Furthermore, Ambridge et al [58] have reported a theoretical paper on the importance of maintaining stoichiometry during ion implantation in order to achieve a high degree of electrical activation. Several groups [2,61,114] have reported that through the process of co-implantation of a dopant and a corresponding group III or group V element, abrupt electrical profiles with high peak carrier concentrations can be obtained.
From this work (see section 4.3.1), it has been shown that the problem of reverse annealing as a result of the out-diffusion of beryllium atoms can be overcome by co-implantation of phosphorus. This is of great significance because to date, there have not been any methods of effectively reducing the out-diffusion of beryllium atoms at high annealing temperatures. Therefore, through the use of rapid thermal annealing and co-implantation of phosphorus, an adequate way of activating beryllium implants as well as preventing out-diffusion has been achieved.

For the beryllium implanted samples, the phenomenon of reverse annealing (see section 4.3.1) is the result of firstly, the incorporation of the beryllium atoms during crystal regrowth at low annealing temperatures. Above a critical temperature, a decrease in the electrical activity is observed. This is the result of the completion of crystal regrowth within the implanted region. Hence the majority of the gallium vacancies in this region have been occupied by gallium and beryllium atoms. Consequently, there is a lower concentration of gallium vacancies remaining to trap the beryllium atoms and they can therefore diffuse more readily.

In addition, the diffusion length DL of beryllium at an annealing temperature of 850°C where reverse annealing has occurred, can be calculated by using a diffusion coefficient of $D = 10^{-12}$ cm²/s obtained by extrapolating the data of Poltoratskii et al [91].
Hence, for an annealing time of 10s, DL is calculated to be around 300Å since \( DL = \sqrt{(Dt)} \). This leads to a significant amount of out-diffusion of the beryllium atoms since the projected range is 800Å below the surface.

The effects of an additional phosphorus implantation are two-fold; firstly, stoichiometry will be restored as phosphorus is a group V element. It has the effect of building up the arsenic sub-lattice during crystal regrowth and effectively producing more gallium vacancies. Secondly, a higher concentration of vacancies is generated as a result of an additional implantation. The degree of crystal disorder after ion implantation has been predicted by SUSPRE (Surrey University Sputter Profile Resolution from Energy deposition) [97]. It showed that a surface disorder of about 5% is obtained as a result of the implantation of \( 10^{14} \) Be/ cm\(^2\) at 25keV (100% disorder implies that an amorphous material is formed and all of the host atoms have been displaced from lattice sites). On the other hand, after an additional implantation of \( 8 \times 10^{13} \) P/ cm\(^2\) at 90keV, the degree of disorder has increased by six times to 30%.

At annealing temperatures below 750°C, the sheet hole concentration values of the beryllium implanted samples are higher than the dual-implanted samples (see section 4.3.1). Also, the lower mobility values for the dual-implanted samples indicate a higher degree of...
crystal disorder after annealing at these temperatures. Hence the lower sheet hole concentration values for the dual-implanted samples may be related to residual defects caused by incomplete annealing. Above 750°C however, the mobility values are still lower for the dual-implanted samples than the samples implanted with beryllium alone. This is due to an increase in the amount of ionised impurity scattering, as the sheet hole concentration values are higher for the dual-implanted samples. The higher sheet hole concentration observed for annealing temperatures above 750°C is in turn, due to i) a reduction in the out-diffusion of beryllium atoms, ii) the annealing out of residual defects and iii) maintaining stoichiometry.

Moreover, similar reverse annealing effects have been reported for the magnesium and silicon implanted samples [5,100,101]. Blunt et al [5] have reported that the phenomenon of reverse annealing for the magnesium implanted samples is due to the out-diffusion of magnesium atoms at high annealing temperatures. On the other hand, it must be pointed out that the reverse annealing effects reported for the silicon implanted samples [101] is not due to the out-diffusion process as in the case of the beryllium and magnesium implanted samples. It is perhaps due entirely to the amphoteric nature of silicon in GaAs. Hence, a lowering in the sheet electron concentration above a critical annealing temperature is the result of self-compensation. This is
due to the fact that more of the implanted silicon atoms are promoted onto arsenic lattice sites at high annealing temperatures. This results in a net decrease in the n-type activity.

Although the out-diffusion behaviour of the beryllium atoms has been overcome by phosphorus co-implantation, this is achieved at the expense of the advantageous low annealing temperatures used to activate single beryllium implants. Anderson et al [102] have reported that beryllium is the only p-type dopant which can be activated at an annealing temperature as low as 475°C. Therefore, in view of the requirement of low temperature processing in for example, heterojunction devices [85], the co-implantation of beryllium and phosphorus may not be the ideal method to increase the electrical activation.

ii) Interpretation of the results using a thermodynamic model

By following the analysis first developed by Sealy et al [95] and Bensalem et al [84,96], a mathematical model concerning the electrical activation of implanted impurities in GaAs as a function of annealing time and temperature has been developed by Morris et al [83,115]:

\[ N(t) = N_d \exp(-E_a/kT) \{1 - \exp[-K'D \exp(-E_d/kT)]\} \],

where \( N_d \) = implant dose,
\[ k = \text{Boltzman's constant,} \]
\[ Ea = \text{activation energy,} \]
\[ Ed = \text{diffusion energy,} \]
\[ Do = \text{diffusion constant,} \]
\[ K' = \text{pre-exponential constant,} \]
\[ T = \text{annealing temperature,} \]
\[ t = \text{annealing time,} \]
\[ N_{\text{sat}} = N_d \exp(-E_a/kT). \]

This model shows that the electrical data of various ions implanted into GaAs can be divided into two regions. For each annealing temperature, there is at short times of say, 1 to 10s, a time-dependent region where the sheet carrier concentration increases linearly with time. After a detailed analysis of the thermodynamics, the data obtained from this region is thought to represent the rate dependent step of the electrical activation process and is modelled to be the diffusion of the host atoms/vacancies. Hence, a diffusion energy \( E_d \) is obtained. Secondly, there is a time-independent region which occurs at longer annealing times and the sheet hole concentration reaches a saturation and the saturation value increases with temperature. Also, with an increase in temperature, shorter times are required to reach saturation in the sheet carrier concentration. After a detailed analysis, the data obtained from this region is thought to represent the annihilation of an implanted atom by a host vacancy with an activation energy \( E_a \). These two regions are illustrated in the
examples given in figs. 5.1 and 5.2.

Fig. 5.1. Time dependence of the sheet hole concentration as a function of the annealing temperature. Be implanted GaAs. 40keV, $5 \times 10^{14}$/ cm$^2$. (Ref. 83)

As a result of this analysis, these energy values which characterise certain physical processes/mechanisms can be identified and compared with the published data. Hence, it is possible to gain an insight into the physical processes in the annealing of ion implanted
GaAs for electrical activation. It is hoped that a similar analysis can be performed on the data obtained from this work in order to investigate whether the energy values which characterise the activation processes are the same as those in the deactivation processes. Hence, it is possible to gain an insight into the physical nature of the reversible or in some cases irreversible electrical results as obtained in this work.

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**Fig. 5.2.** Time dependence of the sheet hole concentration as a function of temperature. Zn implanted GaAs. 150keV, $10^{15}$/ cm$^2$.

(Ref. 84)
Two main criteria must be satisfied if the electrical data are to be analysed using such a model. Firstly, if an energy of diffusion $E_d$ is to be obtained then the data must lie in a region where the sheet carrier concentration increases linearly with time.

The second criterion is that the defects which take part in the reactions are uniformly distributed within the implanted region. The gaussian shaped implant profile is thought to be adequate to satisfy this criterion provided that there is no profile broadening after annealing [95]. Furthermore, provided the sheet hole concentration values $N_s$ are in the saturation region, i.e. the time-independent region, it is possible to obtain the activation energy $E_a$ by plotting $\ln(N_s)$ against inverse temperature. It is predicted from fig. 5.1 that the sheet hole concentration of the beryllium implanted samples has reached a saturation at $t=10s$ for temperatures above 700°C. Hence, an activation energy $E_a$ can be measured by using the data obtained between temperatures of 750°C and 950°C of the dual-implanted samples from this work (see fig. 4.5).

The value of $E_a$ is measured to be $0.46 \pm 0.05 eV$ as
This value is very close to that reported by Morris et al [83,115] of 0.39±0.05eV for the beryllium implanted samples. These authors have assigned $E_a$ to be the activation energy for the annihilation of a beryllium interstitial by a gallium vacancy. These results suggest that the mechanism for the reaction between a
beryllium interstitial and a gallium vacancy is the same for both the Be and Be+P samples. This is due to the fact that the energy required for such a process to occur is the same in both cases. It can be observed from fig. 5.3 that the data of temperatures 600°C to 700°C do not lie in the line of $E_a$. This implies that the saturation in the sheet hole concentration has not occurred for these temperatures. These 'unsaturated' values can be used in principle, to calculate the diffusion energy $E_d$ by using the model. However, because of the small number of data points, the value of $E_d$ cannot be accurately determined. Therefore, the measurement of the $E_d$ value by using this model has not been attempted. The line of $E_a$ for the samples implanted with beryllium alone is also presented in fig. 5.3. Due to the reverse annealing effects (see fig. 4.5), only three data points between 650°C and 750°C are available for estimating $E_a$. Nevertheless, it is shown in fig. 5.3 that the magnitude of $E_a$ is close to both that measured for the dual-implanted samples and that reported by Morris et al [83,115].

It can be observed in fig. 5.3 that the rate of change of the sheet hole concentration with temperature in the time-dependent region is approximately the same for both the Be and Be+P implanted samples. Hence, the value of $E_d$ is expected also to be approximately the same. The inference here is that the mechanisms involved in the activation process are the same for both sets of samples. This process involves the
diffusion of gallium vacancies to annihilate the beryllium interstitials. Since the effects of a phosphorus co-implantation is essentially to produce more gallium vacancies, it should not affect the mechanism involved in the activation process and this is in good agreement with the model proposed by Morris et al [83,115]. Despite the fact that the rate of change of the sheet hole concentration in the time-dependent region is the same for both sets of samples, a lower sheet hole concentration value is observed for the dual-implanted samples. This is thought to be due to the higher degree of crystal disorder. As discussed in section 5.2.1, the degree of crystal disorder is approximately six times higher for the dual implanted samples than the samples implanted with beryllium alone. Hence, the amount of residual damage at a certain annealing temperature is higher for the dual-implanted samples.

The errors incurred in the experimental results arise mainly from the uncertainties in the measurement of the annealing temperatures and times. Also the effects of the rise and fall times are expected to produce a small contribution to the electrical activity. These uncertainties are used to calculate the error which may be incurred in the measurement of the $E_a$ values. As described in chapter 3, the double graphite strip heater has been shown to provide accurate and reproducible temperature measurements. The uncertainty in the sample temperature is estimated to be a maximum
of +5°C. The time taken to reach the pre-determined annealing temperature increased from 5s to 8s as the temperature was varied from 550°C to 950°C. The uncertainty in the dwell time was ±1s. The effects of the uncertainties in the measurements on the magnitude of the calculated activation energies is to produce an error of the order of 10% to 15% provided there are at least four data points for the straight line fit. Moreover, it is worth noting that it is more difficult to perform this type of analysis on data obtained from acceptor implanted samples than donors because of the short time required to reach saturation. Hence, there are relatively few data points in the time-dependent region for the measurement of the Ed values (see also fig.5.2).

iii) Electrical profiles

The electrical profile of the beryllium implanted sample annealed at 750°C for 10s shows that there is an increase in the hole concentration near the surface whereas a gaussian shaped profile results for the dual-implanted sample (see section 4.3.2). The increase in the carrier concentration near the surface may be the result of insufficient gallium vacancies being generated at around the projected range to prevent the beryllium atoms from diffusing towards the surface. An additional phosphorus implantation has the effect of creating i) vacancies and ii) a build-up of the arsenic sub-lattice. As a result, the diffusion of beryllium
atom has been reduced.

It has been shown in section 4.3.2 that the increase in carriers near the surface is not a result of the GaAs/encapsulant interfacial stress since similar profile shapes are obtained after capless annealing at the same conditions. Perhaps the effect is due entirely to the out-diffusion of beryllium atoms. If we assume that a hole concentration of about $5 \times 10^{18} \text{/cm}^3$ is required at the surface of the sample in order to build up a sufficiently high concentration gradient before any out-diffusion of beryllium atoms can take place, then this will cause a decrease in the carrier concentration throughout the profile due to the migration of beryllium atoms towards the surface. Therefore, it is suggested that the increase in the hole concentration near the surface is caused by the out-diffusion of beryllium atoms. The assumption that a hole concentration of about $5 \times 10^{18} \text{/cm}^3$ is required at the surface to build up a sufficiently high concentration gradient has also been reported by Hutchby et al [35]. In their work, such a hole concentration value is observed throughout the profile prior to the redistribution of the implanted atoms, they also concluded that this redistribution is primarily caused by the out-diffusion of the beryllium atoms. This is also in good agreement with various published data [6, 35] that the diffusion of beryllium is concentration dependent and occurs only for doses above $10^{14}/ \text{cm}^2$ where the peak atomic concentration is
around $5 \times 10^{18}$ cm$^{-3}$ or above.

5.2.2 Zn and Zn$+\!P$ implanted GaAs

i) Isochronal annealing results

Many research workers have reported anomalous diffusion behaviour during annealing of the zinc atoms implanted into GaAs [9,10,42,45]. It has been reported that the in-diffusion of zinc atoms is dependent on the relative magnitudes of the annealing time, temperature and implanted dose. The type of encapsulant used is also critical in determining the diffusion of zinc. Barrett et al [93 have reported that the thermal stress at the GaAs/encapsulant interface promotes the production of gallium vacancies and hence retards the diffusion of zinc atoms. However, they did not measure the oxygen content in the silicon nitride film which has been reported to have the effects of enhancing the out-diffusion of host atoms [82].

In addition to further degrading the quality of the encapsulant, the out-diffusion of host atoms can affect the electrical results in the following ways. The law of mass action can be written as,

$$[V_{Ga}] [V_{As}] = K_{GaAs\text{ Schottky}}$$

where $[V_{Ga}]$, $[V_{As}]$ represent the concentration of
gallium and arsenic vacancies and $K_{\text{Schottky}}$ is the Schottky constant. Hence, a loss of arsenic will cause a drop in the gallium vacancy concentration which will drive the following reaction to the right:

$$\begin{align*}
\text{Zn} + \text{hole} & \rightarrow \text{V} + \text{Zn} \\
\text{Ga} & \rightarrow \text{Ga}^{i}
\end{align*}$$

where $\text{Zn}_{\text{Ga}}$, $\text{Zn}^{i}$ and $\text{V}_{\text{Ga}}$ represent a zinc atom in a gallium site, a zinc atom in an interstitial site and a gallium vacancy respectively. Hence, a loss of arsenic atoms will also promote the deactivation of zinc atoms.

Secondly, a loss of arsenic atoms will render the substrate material p-type. This is due to the fact that the semi-insulating property of LEC grown GaAs material is achieved by growing the material in an arsenic-rich condition ($\text{Ga} : \text{As} = 0.48 : 0.52$) [104]. As a result of such a growth condition, a deep donor impurity level designated EL2 has been identified by various techniques [104]. The EL2 level is known to be due to a structural defect and is usually associated with the arsenic anti-site. This EL2 level acts to compensate any acceptor impurities which are unintentionally present. The acceptor impurity is normally carbon. Therefore, semi-insulating material is produced. However, a loss of arsenic atoms will reduce the EL2 concentration and render the substrate p-type.

From this work (see fig. 4.25), results obtained from performing Auger Electron Spectroscopy experiments have
shown that oxygen and carbon are not detected in the silicon nitride film. Therefore, it is assumed here that the activation characteristics and diffusion behaviour observed for the $10^{15}$/cm$^2$, 260keV zinc implants in GaAs (see section 4.2) is not affected by the out-diffusion of host atoms.

From the TEM results summarised by Stevens et al [18], removal of dense crystal defects in ion-implanted GaAs, such as stacking faults, occurs at an annealing temperature of about 600°C and results in some electrical activity. Therefore, the electrical activation which occurs is the result of the reordering of the crystal lattice accompanied by the incorporation of zinc atoms into the crystal lattice. This can be observed in the increase in the mobility values as the annealing temperature is increased (see section 4.2.1).

It has also been reported from this work that at an annealing temperature of 850°C, a broadening of the electrical profile indicates that in-diffusion of zinc atoms occurs (as presented in section 4.2.2). This is in agreement with the results reported by various other research workers [9,39,103]. The process of in-diffusion is the result of the completion of crystal regrowth within the implanted region. Hence the majority of gallium vacancies in this region have been occupied by gallium or zinc atoms. Consequently, there is a lower concentration of gallium vacancies to trap the zinc atoms. Therefore, there is a diffusion of zinc
atoms at high annealing temperatures.

Furthermore, it has been reported that the diffusion of zinc atoms implanted in GaAs is affected by radiation damage [10] and the type of encapsulant used during annealing [9]. Tuck et al [10] have reported an enhanced solubility of zinc atoms at regions which have been irradiated with protons. Furthermore, Barrett et al [9] have reported that the thermal stress at the GaAs/silicon nitride interface causes an increase in the concentration of gallium vacancies. Hence, a reduction in the diffusion of zinc atoms is observed. In essence, the increase in the solubility and the reduction in the diffusion of zinc atoms is the result of the generation of gallium vacancies.

From this work, co-implantation of zinc and phosphorus has been successful in producing abrupt electrical profiles with a peak hole concentration of around $6 \times 10^{19} \text{ /cm}^3$. The results of the dual implants of Zn+P and Be+P obtained from this work (sections 4.2 and 4.3) are original. It has been demonstrated for the first time that co-implantation of phosphorus can reduce the diffusion of zinc and beryllium atoms effectively.

Further to the many aspects discussed so far about the effects of the additional phosphorus implantation on the electrical activation, it is worth noting that Gwilliam et al [64] have reported results on the preamorphisation of GaAs by phosphorus implantation.
prior to silicon implantation. These authors concluded that the abruptness of the tail region of the electron concentration profile is dependent on the phosphorus dose. On the other hand, Patel et al [63] and Barrett et al [9] have reported that the sequence with which the dual implantation is performed does not affect the eventual electrical results. Hence, it is unclear whether the abruptness of the electrical profiles is a result of i) the preamorphisation of the crystal target before implantation of the dopants, ii) maintaining stoichiometry, iii) the result of a higher concentration of vacancies being generated by an additional implantation or iv) a combination of any or all of these effects.

As presented in section 4.2.1, the mobility values are consistently lower for the dual-implanted samples for the range of temperatures investigated (600C-850C). This is the result of the scattering caused primarily by the increase in the concentration of ionised impurities i.e. the charged acceptor atoms.

ii) Interpretation of the results using a thermodynamic model

Fig.5.4 is a plot of the ln(Ns) for the Zn and Zn+P data against inverse temperature where Ns represents the sheet hole concentration as obtained from section 4.2.1. It can be observed from fig 5.4 that for the zinc data, there are three regions for which a rate of
change in the sheet hole concentration with temperature can be measured. The three regions are between annealing temperatures of 600°C to 700°C, 700°C to 750°C and 750°C to 850°C respectively. Bensalem et al [84] have studied the time dependence of the sheet hole concentration as a function of annealing temperature for zinc implanted GaAs. These results are presented in fig.5.2. It can be observed from fig.5.2 that for an annealing time of 30s, saturation in the sheet hole concentration has occurred only for temperatures above 700°C.

![Graph showing sheet hole concentration against inverse temperature](image)

**Fig.5.4.** Sheet hole concentration against inverse temperature.
As a result, the data obtained here in the region between 600°C to 700°C are expected to be in the time-dependent region (see section 5.2.1 (ii)). Also, by plotting ln(Ns) against inverse temperature for temperatures above 700°C, a straight line of Ea should be obtained. However, it can be observed from fig. 5.4 that the data in the region for temperatures above 750°C do not lie in the line of Ea as expected. The inference here is that a different mechanism operates at annealing temperatures above 750°C which may well be the zinc atoms diffusing deeper into the material. This is certainly the case since a broadening of the electrical profile has been observed for annealing temperatures above 800°C (see fig. 5.5). Therefore, the data in this region should not be used in the determination of Ea. Therefore, there are only two data points for determining Ea and thus it cannot be accurately measured. Nevertheless, the Ea value indicated in fig. 5.4 for the zinc data is consistent with the value of 0.3±0.05eV measured for the dual-implanted samples (also presented in fig. 5.4).

In contrast to the samples implanted with zinc alone, the data obtained for the dual-implanted samples at annealing temperatures above 750°C can still be used in the determination of Ea since the diffusion of zinc atoms has been prevented (see fig. 5.6). The Ea value in this case is very close to the Ea value of 0.35±0.05eV measured for the samples implanted with zinc alone by
Morris et al [83] and Bensalem et al [84]. These results suggest that the mechanism for the annihilation of a zinc interstitial by a gallium vacancy is the same for both sets of samples since the energy required for such a process to occur is the same for both cases. As discussed in section 5.2.1, there is not enough data in the time-dependent region to permit a meaningful estimate of $E_d$.

---

Fig. 5.5. Electrical profiles of Zn implanted GaAs.
(as presented in section 4.2.2).

\[ 10^{15} \text{Zn/cm}^2, \text{260 keV} \]

\[ \text{CARRIER CONCENTRATION} (/\text{cm}^3) \]

\[ \text{MOBILITY} (\text{cm}^2/\text{V.s}) \]

\[ a: 800\text{C/30s.} \quad b: 850\text{C/30s.} \]
In contrast to the beryllium implanted samples, an amorphous layer is formed for both the zinc and dual-implanted samples (as predicted by SUSPRE [97]).

It can be observed in fig.5.4 that the sheet hole concentration values are very close for both sets of samples at annealing temperatures below 650°C. This is due to the fact that the amount of residual damage is the same for both sets of samples at a certain annealing temperature. Also, the rate of change of the sheet hole concentration with temperature in the time-dependent region is approximately the same for both sets of samples. Hence, the value of $E_d$ is expected also to be approximately the same. The inference here is that the mechanism involved in the activation process is the same for both sets of samples.

This process involves the diffusion of gallium vacancies to annihilate the zinc interstitials. Since the effects of a phosphorus co-implantation is essentially to produce more gallium vacancies, it should not affect the mechanism involved in the activation process. This is in good agreement with the model proposed by Morris et al. [83,115] and also in agreement with the interpretation of the results for Be and Be+P presented above (see section 5.2.1(ii)).
5.3 The influence of heat treatment on rapid thermally annealed ion implanted GaAs

In this section, the results on the thermal stability of the Be, Mg, Zn, Se and Be+P and Zn+P implanted samples will be discussed. The general results of acceptor implanted samples will be discussed in section
5.3.1. The results on the thermal stability of the selenium and zinc implants will be discussed in section 5.3.2. This is followed by the discussion in section 5.3.3 on the results of the thermal stability of the dual-implanted samples.

5.3.1 Acceptor implanted GaAs in general

The topic of heat treatment on rapid thermally annealed, ion implanted GaAs has received little attention. From this work, it has been shown that the electrical properties of acceptor implanted layers in GaAs do not change below an annealing temperature of 600°C (see section 4.4.1).

1) Zn implants

The electrical activity of the zinc implanted samples annealed at 635°C for 35s during silicon nitride deposition increases with time at 600°C with no significant profile broadening. This is accompanied by an increase in the mobility of up to 50% from 45 cm²/V.s to 65 cm²/V.s after annealing at 600°C for 6 hours. This suggests that the increase in the electrical activity is a result of crystal reordering within the implanted region. Therefore, more of the implanted zinc atoms are incorporated into the crystal lattice. For the samples which were annealed at 800°C for 15s, 90% of the implanted zinc atoms are active and this has decreased to 60% after further annealing at 600°C for 6 hours (see
Since the RTA cycle involves heating and quenching the samples in a matter of seconds, an excess number of zinc atoms may have been incorporated or dissolved into the crystal lattice as a result of the quenching process. During subsequent heat treatment at a lower temperature for a long time, for example at 600°C for 6 hours, an equilibrium has been achieved between zinc interstitials and substitutional zinc atoms. This is due to the fact that only a certain number of zinc atoms can be dissolved in the system at this temperature. The process described above can be represented by the following reaction:

\[
\begin{align*}
\text{Zn} + V_{i} \underset{600\,^\circ\text{C}/6\,\text{hours}}{\longrightarrow} & \text{Zn} + \text{hole} \\
& \text{Ga} \quad \text{Ga}
\end{align*}
\]

The RTA plus quenching cycle of 800°C for 15s will drive the reaction to the right. When energy is supplied to the system as a result of further annealing at 600°C for 6 hours, the reaction will be driven to the left until an equilibrium is achieved. It is worth noting that this reaction should be reversible if all the zinc atoms remain in the sample during the annealing processes. This has been observed for the zinc implanted samples (section 4.4.1) and it will be discussed in section 5.3.2.

Kamgar et al [74] have reported similar results for
arsenic implanted into silicon. The authors have shown that greater solubilities of the implanted arsenic atoms can be achieved with little or no diffusion through the use of rapid thermal annealing. Furthermore, the same authors have performed experiments on the low temperature long term anneal subsequent to a high temperature short time anneal. These authors have shown that the higher solubility achieved by rapid thermal annealing is a state of metastable activation. This state relaxes into clustering of dopants during subsequent prolonged lower temperature anneals and results in a decrease in the electrical activity.

ii) Be and Mg implants

In the case of the beryllium and magnesium implanted samples, a decrease in the electrical activity is observed after annealing at 600°C for 6 hours. The same reaction described above may have taken place. The reaction is represented by the following equation:-

\[
\begin{align*}
800°C/15s & \\
X + V & \rightarrow X + \text{hole} \\
1 \text{ Ga} & \leftarrow \text{Ga} \\
600°C/6\text{hours} & 
\end{align*}
\]

where \( X_i \) is a beryllium or a magnesium interstitial. \( X_{Ga} \) is a beryllium or a magnesium atom on a gallium site.

However, when these samples were again annealed at 800°C
for 15s, the electrical activity for both sets of samples did not recover to the original values. That is to say, the reaction is not reversible (see section 4.4.1). Hence, it is suggested that the decrease in the electrical activity during subsequent annealing processes is the result of the out-diffusion of beryllium and magnesium atoms. These atoms are lost into the encapsulant rendering the reaction irreversible. The process of the out-diffusion of beryllium atoms has been discussed in detail in section 5.2.1 (i).

The deactivation characteristics of the magnesium implanted samples have not been investigated further. However, it is speculated here that the characteristics would be similar to those obtained for the beryllium implanted samples since the electrical activation and diffusion behaviour of both species are reported to be similar [5,12,35,105]. These similar results include the reverse annealing effects (see section 5.2.1) and the concentration dependent diffusion behaviour [12,35]. Therefore, it is not unreasonable to speculate that the results on the thermal stability of the magnesium implanted samples will be similar to those of the beryllium implanted samples. However, it is thought that the inactive magnesium may be in the form of a complex defect with a neighbouring vacancy [83,115] rather than as an interstitial. This is very similar to the model used for explaining the inactivity of the implanted selenium atoms and this is presented in
5.3.2 Selenium and zinc implanted GaAs

i) Se implants

For the selenium implanted samples, the electrical activity obtained after annealing at 980°C for 20s remains unchanged at temperatures below 700°C. Between temperatures of 700°C and 800°C, the electrical activity decreases with increasing temperature and also decreases with time.

As discussed previously in section 5.3.1, an excess number of selenium atoms may have been incorporated or dissolved in the crystal lattice during the quenching of the samples after RTA. Subsequent heat treatments at lower temperatures will drive the following reaction to the left in order to achieve an equilibrium between the dissolution and 'precipitation' of the selenium atoms at that temperature:

\[
\begin{align*}
\text{980C/20s} & \quad (\text{Se—V}) + \text{Ga} \quad \rightarrow \quad \text{Se} + \text{Ga} + e^- \\
\text{As Ga} & \quad \text{1} \quad \leftarrow \quad \text{As Ga} \\
\text{750C/6hrs.}& \end{align*}
\]

where \((\text{Se}_{\text{As}}—V_{\text{Ga}})\) is a defect consisting of a selenium atom on an arsenic lattice site complexed with a gallium vacancy and is electrically neutral. However, it has been reported that the complex behaves as a deep acceptor [111]. Also, \(\text{Ga}_i\) and \(\text{Ga}_{\text{Ga}}\) represent a gallium
atom in an interstitial site and gallium lattice site respectively.

The above reaction can be driven to the left because of the long annealing time which allows an equilibrium to be achieved. The 'precipitation' of the selenium atoms in this case, implies that the selenium atoms are rendered inactive by forming some type of complex. These complexes may be in the form of interstitial selenium, selenium on an arsenic site complexed with a gallium vacancy or a conglomerate of selenium atoms precipitating at and around a dislocation loop.

A transmission electron microscopy study has shown that following an anneal at 500°C to 600°C, all of the implanted selenium is in the form of precipitates [106]. In addition, after annealing at 800°C to 900°C, only about 12% of the selenium was estimated to be in the form of precipitates [107]. These results suggest therefore that the active selenium atom is rendered inactive by either i) forming a complex with one or more gallium vacancies which is electrically neutral [71] or ii) by compensation with such a complex which acts as a deep acceptor [111].

Hence, it is likely that the 'precipitation' of the selenium atom in the reaction described above is a result of the formation of a complex between a selenium atom on an arsenic lattice site with a gallium vacancy.
This is reasonable since Ambridge et al [58] have published a theoretical paper concerning the importance of maintaining stoichiometry balance during ion implantation. These authors speculated that the implantation of a dopant such as selenium will only build up the arsenic sub-lattice and a 'compensating' defect may also be formed. Sealy et al [59] and Woodcock et al [60] have reported that co-implantation of gallium has the effect of reducing the concentration of such 'compensating' defects since a higher concentration of active selenium is obtained. This is further evidence that an electrically active selenium atom is complexed with one or more gallium vacancies and hence it is being compensated.

At annealing temperatures above 800°C, for example, 850°C for 2 hours, the electrical activity has not decreased as much as the sample annealed at 800°C for 2 hours (see section 4.4.3). That is to say, a maximum number of 'precipitated' selenium atoms relative to those dissolved exist in equilibrium at a temperature of 800°C. Below this temperature, more selenium atoms remain dissolved and act as donors. This is a result of insufficient thermal energy available at this temperature for diffusion to occur. It is pointed out here that the data for the samples subsequently annealed at temperatures greater than 850°C for times longer than 30 minutes are not available due to encapsulant failure. Provided that the encapsulant remains intact, higher electron concentrations can be
expected as the annealing temperature is increased above 850°C.

ii) Zn implants

For the samples implanted with $10^{15}$ Zn/cm² at 260keV, 100% electrical activity has been obtained after annealing at 850°C for 30s (see section 4.4.4). Also, it has been shown that further heat treatments on these annealed samples at lower temperatures for times up to 6 hours result in a decrease in the electrical activity. As in the case of the selenium implanted samples, the electrical activity decreases towards a limiting value for each temperature.

As discussed previously in section 5.3.1, an excess number of zinc atoms have been incorporated into the crystal lattice as a result of the RTA plus quenching process. Subsequently annealing at lower temperatures and long times will provide energy for diffusion to occur. The zinc atoms will be dissolved and 'precipitated' in order to achieve an equilibrium between substitutional zinc atoms and zinc interstitials for a certain temperature. A maximum number of zinc atoms are 'precipitated' after further annealing at 600°C for 6 hours (see section 4.4.4). Above this temperature, more zinc atoms are incorporated in the crystal lattice as a result of the more dominant process of dissolution over 'precipitation' at higher temperatures. The reaction is
represented by the same equation presented in section 5.3.1:

\[
\begin{align*}
850^\circ C/30s & \\
Zn + V & \rightarrow Zn + \text{hole} \\
i \quad Ga & \leftarrow Ga \\
600^\circ C/6\text{hours}
\end{align*}
\]

As the temperature is increased, the above reaction is driven to the right. The kinetics involved in the deactivation of beryllium, zinc and selenium implants will be discussed in section 5.4.

iii) Electrical profiles

As discussed so far, the dissolution and precipitation processes during heat treatments are reversible for the zinc and selenium implanted samples. Furthermore, the electrical profiles for both sets of samples are modified from a double peak characteristic to a flat profile to a gaussian shaped profile after rapid thermal annealing, followed by annealing at lower temperatures for a long time and a final rapid thermal annealing respectively (see section 4.4.1 and 4.4.3). The double peak characteristic in the carrier concentration profile has also been reported by Bensalem [94]. The author concluded that it is the result of incomplete crystal regrowth. Furthermore, Gibbons et al [92] have reported the predictions of the distribution of gallium and arsenic recoils and vacancies as a result of ion implantation.
A possible explanation for the double peak in the concentration profiles is that in the case of the samples implanted with $10^{14}$ Se/cm$^2$ at 400keV, there is an excess of host vacancies of about $8 \times 10^{18}$/cm$^3$ near the surface. Also, there is an excess concentration of host recoils of about $2 \times 10^{18}$/cm$^3$ at and around the projected range of the implanted atoms [92]. This is presented in Fig.5.7.

Fig. 5.7. Calculation of the stoichiometric distribution in GaAs (Ref. 92).
During annealing, these host recoils and the implanted atoms will be competing for vacancy sinks. This therefore causes a lack of electrical activity in this region and results in a minimum at the projected range in the carrier concentration profile. Near the surface however, the implanted atoms can find vacancies and
become activated since there is a high concentration in this region. If the annealing temperature and time is high and long enough to achieve a high degree of crystal regrowth, then the implanted atoms can be activated according to their distribution and not be affected by the distribution of defects such as host vacancies. Hence, a gaussian shaped profile will result (see fig.5.8). The predictions of the concentration and distribution of the host vacancies and recoils obtained from ref.92 are thought to be adequate for explaining the electrical results obtained from this work. These predictions are accurate to within 15% in both the concentration and depth resolution [112].

Furthermore, the type of encapsulant used during annealing can give rise to anomalous profile shapes. Davies et al [43] have reported an enhanced electrical activity of the zinc implanted samples after annealing under a silicon dioxide encapsulating layer. In this case, the enhanced electrical activity observed may be the result of gallium out-diffusion into the encapsulant. Hence, it is more probable that the zinc atoms will find gallium vacancies and become electrically active near the surface.

In addition, similar double peak characteristics in the hole concentration profiles after capless annealing have been reported by Kasahara et al [42] and Suzuki et al [45]. These authors have concluded that this characteristic is the result of the zinc atoms
diffusing both towards the surface and into the bulk of
the material, hence developing a 'shoulder' in the hole
concentration profile. Lidow et al [71] have suggested
that an inactive selenium atom may be caused by the
formation of a complex with one or more gallium
vacancies. The same authors suggested that the
annihilation of such a complex depends on the
availability of gallium atoms. Therefore, one may
expect that there will be a lack of electrical activity
near the surface since there are more gallium vacancies
for complex formation. It is suggested here that due to
the quenching process, an excess number of selenium
atoms have been quenched onto arsenic sites before the
formation of complexes can take place. This results in
a higher carrier concentration near the surface. As
mentioned earlier, this double peak characteristic is
not observed in all concentration profiles since it
depends on the degree of crystal disorder after
annealing. It also depends on the concentration and
distribution of the host vacancies and recoils.
Implantation conditions such as substrate temperature
and crystal orientation can also affect the shapes of
the electrical profiles.

After annealing at a lower temperature for a long time,
the concentration profile becomes flat for both the
zinc and selenium implanted samples (see fig.5.8). This
characteristic can be attributed to the diffusion and
annealing out of residual defects such as host recoils,
vacancies and also active implanted atoms. These
defects are now spread homogenously around the implanted region during this long time anneal. Thereby, for example in the case of the selenium implanted samples, a balance or an equilibrium between inactive complexes and active dopants has been achieved throughout the implanted region. Now that the residual defects are uniformly distributed around the implanted region, the implanted atoms can be activated in the last rapid thermal annealing cycle according to their distribution and not be affected by the distribution of defects such as the host vacancies. Hence a gaussian shaped profile is obtained.

5.3.3 Dual-implanted GaAs

The results on the Be+P and Zn+P dual-implanted samples have been presented in section 4.4.2. It has been shown that similar reversible reactions as in the selenium and zinc implanted samples also occur for the dual-implanted samples. In this case, the electrical activity of the Be+P implanted samples can be recovered from 20% to 25% after a long time anneal and a subsequent rapid thermal anneal respectively (section 4.4.2). This suggests that beryllium atoms have not out-diffused into the encapsulant in the case of the dual implant. SIMS measurements in the future will help to clarify this point by comparing the atomic concentration remaining in the samples after the annealing processes. These results suggest that the process of beryllium atoms deactivating followed by
out-diffusion during subsequent annealing has been overcome or is hindered by the effects resulting from the co-implantation of phosphorus.

For the Zn+P implanted samples, the dissolution/precipitation processes are observed to be reversible. The electrical activity varied from 100% to 72% to 100% after annealing at 850°C for 30s, further annealed at 600°C for 6 hours and further annealed at 850°C for 30s respectively. However, there is no profile broadening after the annealing processes. In this case, the 'precipitation' of zinc atoms occurs during the low temperature heat treatment but is not accompanied by any in-diffusion. That is, after the zinc atoms have become interstitials, the diffusion of these zinc interstitials is hindered by the effects caused by the co-implantation of phosphorus atoms. It is worth noting that similar effects for beryllium atoms are observed and have been discussed earlier.

The effects of a phosphorus co-implantation have been discussed in section 5.2 and 5.3. It has been pointed out that the abrupt electrical profiles results from i) maintaining stoichiometry, ii) preamorphisation iii) a higher degree of disorder due to the co-implantation generating a higher concentration of vacancies which has the effect of retarding diffusion and iv) a combination of any or all of these effects. Hence, the lack of diffusion observed here for the zinc and beryllium atoms during subsequent heat treatment is the
result of i) the presence of residual defects caused by incomplete annealing and ii) the effects of the phosphorus co-implantation which has the effect of building up the arsenic sub-lattice. Hence, a higher concentration of gallium vacancy sinks is created which reduces the diffusion of the implanted zinc and beryllium atoms.

5.4 Deactivation kinetics of ion implanted GaAs

In this section, an attempt has been made to investigate the deactivation kinetics of ions implanted into GaAs. The approach is based on thermodynamics.

5.4.1 Thermodynamic model

If a first order reaction is assumed, that is to say that the rate of change of the electrical activity \( N(t) \) at time \( t \) is proportional to \( N(t) \) then,

\[
\frac{d}{dt}[N(t)] = -K N(t).
\]

Thus,

\[
\frac{d}{dt}[N(t)] = K N(t) \quad (5.1)
\]

where \( K \) is the rate constant and is a function of the diffusion coefficient \( D \), since

\[
K = K'D
\]

and

\[
D = D_0 \exp\left(-\frac{E_d}{kT}\right).
\]
(The symbols used in the above equations are presented in section 5.2.1.(ii))

Therefore, \( K = K'Do\exp(-Ed/kT) \ldots (5.2) \).

By substituting equation (5.2) into equation (5.1), we obtain

\[
\frac{d}{dt}[N(t)] = K'DoN(t)\exp(-Ed/kT),
\]

therefore, \( \ln(|\frac{d}{dt}[N(t)]|) = \ln[K'DoN(t)] - Ed/kT. \)

Hence, by measuring the initial rate of change in the electrical activity i.e. at \( t=0s \), it is possible to estimate a value for \( Ed \) by plotting \( \ln(|\frac{d}{dt}[N(t)]|) \) against inverse temperature.

5.4.2 Interpretation of results

1) Be implants

Despite the relatively small number of data points, it has been possible to fit them to the thermodynamic model. This model is in contrast with that suggested so far for the selenium and zinc implanted samples (section 5.3.2). It describes that the RTA plus quenching cycle has resulted in the incorporation of an excess amount of dopants into the crystal lattice. Also, subsequent heat treatments at lower temperatures
for long times will cause a relaxation effect as the impurity atoms are deactivated. Furthermore, more of the impurity atoms are then dissolved as the subsequent annealing temperatures are increased and there is a saturation limit for each temperature.

In the case of the beryllium implanted samples, it has been reported by many research workers [35,36] and also from this work (sections 4.3.1 and 4.4.5) that, provided the annealing temperature is high enough and/or the annealing time is long enough, the beryllium atoms will diffuse towards the surface and will be lost into the encapsulant. Consequently, the beryllium atoms will not be dissolved in the crystal lattice. Hence, as the subsequent annealing temperature is increased, more beryllium atoms will become deactivated or 'precipitated' and out-diffusion will occur. Therefore, there is not a saturation limit for each temperature. It is not unexpected that the out-diffusion of beryllium atoms occurs at an annealing temperature of 600°C as approximately 30% of the implanted beryllium atoms have out-diffused during the silicon nitride encapsulation process which takes place at 635°C for 35s (see section 4.4.5 (ii)).

The graph showing the initial rate of change in the electrical activity of these samples is presented in fig.5.9. As presented in fig. 5.10, by plotting ln{|d/dt[P(t)]|} against inverse temperature, an activation energy of 0.9±0.1eV is obtained.
Poltoratskii et al [91] have reported the diffusion energy of beryllium atoms in crystalline GaAs to be 1.1eV which is close to the value of 0.9eV measured here. Therefore, it is suggested that the beryllium atoms have out-diffused into the encapsulant during subsequent heat treatment. This is the main reason for the decrease in the activation shown in fig.5.9. The value of 0.9eV therefore corresponds to the energy of diffusion of beryllium in ion implanted GaAs.

\[
\frac{14}{10} \text{Be}^+ / \text{cm}^2, 40 \text{keV}
\]

\[
\begin{array}{c}
- \frac{60}{600^\circ} \\
- \frac{30}{650^\circ} \\
- \frac{30}{700^\circ} \\
- \frac{30}{750^\circ} \\
\end{array}
\]

RTA: 635°C/35s.

Fig.5.9. Time dependence of the electrical activity as a function of the annealing temperature. (Also showing the initial rate of change in the electrical activity).
Fig. 5.10. Initial rate of change of the electrical activity against inverse temperature.

Further experiments indicate that the electrical activity after a long time anneal of 750°C for 2 hours (22%) cannot be recovered to the original value of 63% by a further rapid thermal anneal at 635°C for 35s where an activity of 20% is obtained (section 4.4.5 (i)). This is further evidence that beryllium atoms have
out-diffused and can no longer be incorporated into the crystal lattice. Plumton et al [93] have observed a similar decrease in the electrical activity for the beryllium implanted samples after a two-step rapid thermal anneal. However, they did not conclude whether this is caused by the 'precipitation' of beryllium atoms followed by out-diffusion.

In addition, the results obtained from channelling experiments using RBS show that the Xmin value of the 'as-capped' samples is about 5%–7% which indicates that reasonably crystalline material has been obtained after silicon nitride deposition at 635°C for 35s (see section 4.4.5 (iii)). This suggests that the diffusion of beryllium atoms which occurred at long annealing times took place in a crystalline material. Hence, the diffusion energy obtained here can justifiably be compared with that obtained by Poltoratskii et al [91] as they obtained an Ed value of 1.1eV by diffusing beryllium atoms into crystalline GaAs.

Furthermore, since the SIMS results show that there is a loss of beryllium atoms during the encapsulation process (section 4.4.5 (iii)), this may have degraded the quality of the encapsulant and have allowed the preferential out-diffusion of host atoms. This will in turn affect the rate of beryllium deactivation by for example, loss of arsenic atoms. By the law of mass action,
As explained in section 5.2.2(1), a loss of arsenic will cause a drop in the gallium vacancy concentration which will drive the following reaction to the right (see section 5.3.1(ii)):

$$\text{Ga}^0 + \text{hole} \rightarrow \text{V}^0 + \text{Be}$$

Hence, a loss of arsenic atoms will also promote the deactivation of beryllium atoms. This analysis has of course, not taken into account the effects on the electrical properties as a result of the loss of arsenic atoms.

Moreover, results obtained from AES have shown that oxygen and carbon contamination is not detected in the silicon nitride film (section 4.4.5 (iv)). Therefore, the quality of the encapsulating layer may not have been degraded by the loss of beryllium atoms and may not have affected the electrical results observed here.

ii) Se and Zn implants

It is found by performing the thermodynamic analysis that for the selenium and zinc implanted samples, the value of $E_d$ lies in the range between 1.5-2.5eV. The data are not presented here since only a rough estimate is obtained because of insufficient data points (as presented in sections 4.4.3 and 4.4.4, only three
temperatures are studied). A more detailed analysis for the beryllium implanted samples has been presented in section 5.4.2 (i).

It is suggested here that the value $E_d$ of 1.5-2.5eV represents the rate dependent step in the two reactions described earlier (section 5.3.2) concerning the activation and deactivation of the selenium and zinc atoms. These two reactions are:

\[
a) \quad 980°C/20s
\begin{align*}
(Se-V) + Ga & \rightarrow Se + Ga + e^- \\
As Ga & \leftarrow As Ga
\end{align*}
750°C/6hrs.
\]

\[
b) \quad 850°C/30s
\begin{align*}
Zn + hole & \rightarrow V + Zn \\
Ga & \leftarrow Ga
\end{align*}
600°C/6hours
\]

In addition, it has been proposed by Morris et al [83,115] that the host atoms/vacancies rather than the implanted atoms are the dominant diffusing species during the annealing of ion implanted GaAs. A diffusion energy in the range of 2-2.5eV is measured which corresponds to the diffusion energy of a gallium vacancy or atom. Therefore, it is suggested here that the rate dependent step for the reactions described above involves the diffusion of gallium atoms and/or vacancies since the measured $E_d$ values are close to that measured by Morris et al [83].
For example, in the case of the selenium implanted samples (equ.(a) above), the rate dependent process for the reaction to be driven to the left is the diffusion of a gallium vacancy to form the complex. In order for the reaction to be driven to the right, the rate dependent step for the reaction is the diffusion of a gallium atom to annihilate the $\text{Se}_\text{As}-\text{V}_\text{Ga}$ complex and/or the diffusion of a gallium vacancy away from the complex which is essentially the same process in reverse.

Furthermore, as in the case of the activation of beryllium and zinc discussed in section 5.2, it is possible to obtain an activation energy $Ea$ by plotting $\ln(Ns)$ against inverse temperature if the values of $Ns$ are in the time-independent region and $Ns$ is the sheet carrier concentration. Hence, a value in the range of 0.6-0.9eV and 0.2-0.4eV is obtained from the deactivation characteristics for the selenium and zinc implanted samples respectively. Despite the large errors involved in the estimation due to the small number of data points, these values are close to that measured for the energy required for the annihilation of a $\text{Se}_\text{As}-\text{V}_\text{Ga}$ complex which is about 1.2eV [83,115]. Also, the $Ea$ value in the range of 0.2-0.4eV agrees well with that measured for the annihilation of a zinc interstitial by a gallium vacancy which is about 0.3eV [83,84]. The inference here is that the processes involved in the deactivation and activation of selenium
and zinc atoms implanted into GaAs is reversible. Also, the mechanisms for such reversible reactions are the same since from this work (see earlier in this section), it has been found that the energy characterising such 'two-way' processes are the same. However, a more detailed study of the deactivation characteristics of selenium and zinc implanted samples in the future will enable a more accurate determination of $E_d$ and $E_a$ to be made.

5.5 Review

In this section, a review of the work done and the discussion that followed is presented.

The research area of co-implantation in GaAs is not new. However, the combinations of beryllium plus phosphorus and zinc plus phosphorus have not previously been investigated. From this work (sections 4.2 and 4.3), it has been shown that the diffusion of zinc and beryllium have been overcome by the co-implantation of phosphorus. It is of particular significance in the case of beryllium because to date, there have not been any methods of effectively reducing the out-diffusion of beryllium atoms at high annealing temperatures. Therefore, through the use of rapid thermal annealing and co-implantation of phosphorus, an adequate way of activating beryllium implants as well as preventing out-diffusion has been achieved.
The results on the thermal stability and thus the deactivation characteristics of various implants is of great significance as far as both industrial applications and the understanding of the physics behind the incorporation of dopants in GaAs are concerned. Prior to this work, there has not been any information on the effects of subsequent anneals on the electrical characteristics of ion implanted layers in GaAs. It is found from this work that the temperature at which the electrical properties start changing occurs at 600°C for beryllium, magnesium and zinc implanted samples and at 700°C for the selenium implants.

The results on the influence of heat treatment on the electrical characteristics of ion implanted GaAs may have numerous applications. For example, in the processing of Heterojunction Bipolar Transistor (HBT). For this device, beryllium or zinc ions may be implanted at the base contact region in order to reduce the resistance and improve the frequency response. Oxygen ions are also implanted for the formation of isolation regions between adjacent transistors \[85,110\]. As a result of this work, it is found that the electrical characteristics of the zinc or beryllium implanted layers after rapid thermal annealing could be affected by the subsequent anneal for the oxygen implants. This can in turn degrade the performance of the circuits.
To conclude, a number of interesting results have been generated. These results include the discovery of the reversible electrical behaviour of zinc and selenium implants in GaAs. Also, the effects of subsequent annealing on the shapes of the electrical profiles of these samples have been investigated. Furthermore, it has been found that the co-implantation of phosphorus has the effects of producing abrupt profiles with high hole concentrations. Also, the mechanisms involved in the activation of both the single and dual implanted samples are the same. Lastly, it is discovered that the activation and deactivation mechanisms are the same for the zinc and selenium implanted samples whereas the process of out-diffusion of the beryllium atoms occurs during subsequent heat treatment which rendered the reaction irreversible.
CHAPTER 6

CONCLUSIONS & RECOMMENDATIONS FOR FUTURE WORK

This chapter presents the conclusions of the work. The chapter is divided into two sections; the first part presents a summary of the important experimental results and the main conclusions. The second part of this chapter presents some recommendations for future work.

6.1 Conclusions

A number of interesting results have been obtained from this work. It has been demonstrated for the first time that the in- and out-diffusion of zinc and beryllium implanted GaAs respectively have been overcome by the co-implantation of phosphorus. Hence, abrupt electrical profiles with high hole concentrations have been produced. It is of particular significance in the case of the beryllium implanted samples because to date, there have not been any methods of reducing the out-diffusion of beryllium atoms at high annealing temperatures. It is therefore concluded that through the use of rapid thermal annealing and the co-implantation of phosphorus, an effective way of activating beryllium implants as well as preventing the out-diffusion has been achieved.
Prior to this work, there is no information on the effects of subsequent anneals on the electrical characteristics of ion implanted layers in GaAs. It has been shown for the first time that the electrical characteristics of rapid thermally annealed, ion implanted layers can vary significantly during further annealing. It is found that the temperature at which the electrical properties start changing occurs at 600°C for beryllium, magnesium and zinc implanted samples and at 700°C for the selenium implants. It is concluded that these results on the deactivation characteristics of various implants is of great significance as far as both industrial applications and the understanding of the physics behind the incorporation of dopants in GaAs are concerned.

Further to the important results/conclusions presented so far, it has been found that the mechanisms involved in the activation of both the single and dual implanted samples are the same. In addition, it has been shown for the first time that the activation and deactivation processes of the zinc and selenium implants are reversible. It is concluded here that the rate dependent step for such reversible processes is thought to be the diffusion of gallium vacancies/atoms. In contrast, the out-diffusion of beryllium atoms occurs during subsequent heat treatment which rendered the reaction for the beryllium implants irreversible.
To conclude, some very interesting results have been obtained from this work. These results are original and is of great significance as far as both industrial applications and the understanding of the physics are concerned.

6.2 Recommendations for future work

The work which has been recommended to further this research work is divided into two areas.

a) Work that is required to further and/or confirm some of the present results:–

   i) investigation into the deactivation characteristics of the magnesium implanted samples in order to compare with the results of the beryllium implants.

   ii) a detail study of the deactivation characteristics of the zinc, selenium and dual implanted samples in order to determine the energy for the rate dependent step for the reversible reactions.

   iii) Secondary Ion Mass Spectrometry (SIMS)
should be performed on the Be and Be+P implanted samples to determine and confirm the atomic distribution of the beryllium atoms.

b) New areas of interest:

i) the activation and the thermal stability of silicon implanted GaAs should be investigated in detail. Also, the effects of phosphorus co-implantation on the activation efficiency should be investigated. These results will lead to the determination of the activation and diffusion energy values. Hence, a model similar to that discussed here for the beryllium and zinc implants may be developed to interpret the results. In particular, the reverse annealing results reported for silicon implants [101] should be investigated by co-implanting phosphorus at different energies and doses.
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