A COMPARATIVE STUDY OF LASER AND THERMAL

ANNEALING OF ZINC ION IMPLANTED

GALLIUM ARSENIDE

by

S. S. KULAR

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University of Surrey

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ABSTRACT

A comparative study of laser and thermal annealing of Zn and Cd ion implanted GaAs is presented in this thesis. The techniques used were Rutherford backscattering, transmission electron microscopy, Hall effect and sheet resistivity measurements. The variation in the properties of the implanted GaAs with implantation temperature, ion dose, ion energy and annealing temperature were investigated. For laser annealing they were studied as a function of laser pulse length, laser energy density and multiple irradiations.

For the thermal annealing process, the results indicated that an annealing temperature of 900°C was needed for perfect recrystallization and maximum electrical (∼86%) activation. In the temperature range 650 to 800°C the sheet hole concentration increased with increasing dose up to a dose of about $1 \times 10^{14}$ Zn/cm$^2$ and above this dose it saturated between $(1-2) \times 10^{14}$ holes/cm$^2$ when implanted at room temperature. Results were similar for implant energies of 60 to 450 keV. For samples implanted at 200°C, the sheet hole concentration increased with increasing dose and the maximum value observed was in the range $(1-2) \times 10^{19}$ holes/cm$^3$.

Irradiation with a freely generated ruby laser produced electrical activities from about 27% to 50% and peak concentrations from about $1 \times 10^{19}$ to $7 \times 10^{19}$ holes/cm$^3$. RBS measurements showed that residual damage still remained in these samples. In contrast a Q-switched ruby laser pulse produced complete recrystallization ($X_{\text{min}} = 4\%$) with electrical activities up to 100%. The highest peak hole concentration was measured to be about $1 \times 10^{20}$ holes/cm$^3$.

Profiles of the implanted ions are shown to depend on most of the parameters mentioned above. The possible explanations for the diffusion of Zn and Cd in thermal annealing and laser annealing samples are discussed.
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1.1. **Introduction**

In the light of recent developments in microwave devices, solar cell technology, integrated optics and a variety of devices the compound semiconductor GaAs has gained tremendous technological importance. Vapour phase epitaxial growth techniques for GaAs and for compound semiconductors have been meliorated over the years, greatly improving the quality of the commercially available crystals. However compound semiconductor technology has not been able to attain the level of sophistication that state of art silicon technology has achieved. The essential handicap in the case of compound semiconductors such as GaAs, stems from the lack of an oxide technology and the susceptibility of the GaAs material to decompose during heat treatment processes that are essential for device fabrication.

Ion implantation is now well established and an accepted method for controlled doping of semiconductors. However, this technique causes lattice disorder, which must be removed by a subsequent heat treatment in order to activate electrically the implanted dopant ions. When GaAs is annealed below $660^\circ$C, congruent evaporation of gallium and arsenic occurs\(^{(1)}\). The GaAs surface must therefore be protected during annealing at temperatures above $660^\circ$C. Although various encapsulating films\(^{(2-10)}\) ($SiO_2$, $Al$, $AlN$, $Si_3N_4$, $Si_3N_4 + SiO_2$) have been used, $Si_3N_4$ layers appear to
be the best for annealing both n-type and p-type implants in GaAs. However, the protection of GaAs during annealing is still a major problem since perfect encapsulation is difficult to achieve, and thus changes in the electrical properties of the substrate material can occur, as well as variations in the properties of the implanted surface layers. Therefore the development of an alternative annealing process would be useful.

A new and potentially powerful annealing process, laser annealing, may overcome the problems associated with thermal annealing. It has been reported\(^{11}\) that pulse annealing of implanted layers by high power laser radiation leads to greatly increased electrical activities compared to the results obtained using the conventional annealing processes. Furthermore, the parameters of the laser pulse, e.g. wavelength, pulse energy density and pulse duration can be chosen such that the region of annealing is limited to the implanted layer and the substrate remains unaffected.

Another new annealing process reported recently made use of an electron beam\(^{12-14}\). The penetration depth of the electron is much deeper than the photons which may be a disadvantage when very thin surface layers are to be annealed. However, the penetration depth of the incident electron can be reduced by using a low angle of incidence.

Annealing processes may also alter the distribution of the implanted ions in the substrate. Early work\(^{15}\) on zinc implanted into GaAs indicated that during the post
implantation anneal, there was a rapid diffusion of zinc. The implantation thus served as a predeposition step and the junction depth was determined by the subsequent diffusion process i.e. the annealing temperature. This creates many serious problems. The significant redistribution of the implanted atoms defeats one of the main advantages of ion implantation doping, which is the control over the doping level and the distribution with depth of the implanted impurity. Furthermore, this diffusion is particularly undesirable if devices of small geometry are to be fabricated by ion implantation.

Of all the p-type dopants used for GaAs, the behaviour of the ion implanted Be is probably the best understood. Early work (15-17) on zinc implanted GaAs, reported 100% electrical activity but no information of the carrier concentration profiles were reported. For the fabrication of devices the electrically active impurity profile is of great importance.

In an attempt to resolve some of these problems we have chosen to study zinc implanted GaAs.

1.2. Aims of the Project

The aims of the project are to investigate the effects of several annealing processes (i, ii, iii) on the electrical and physical properties of GaAs implanted with zinc ions:
(i) Conventional Annealing

The electrical properties of zinc implanted GaAs have been studied as a function of:--

(a) The annealing temperature
(b) The implant temperature
(c) The ion dose
(d) The ion energy

(ii) Thermal Pulse Annealing

The effect of a short thermal pulse on the properties of ion implanted GaAs and a comparison of results with those obtained by conventional thermal annealing has been studied.

(iii) Laser Annealing

The effects of laser annealing on properties of ion implanted GaAs have been studied and results are compared with those of conventional (i) and thermal pulse annealing (ii).

Our aim has been to assess the effects of laser pulse irradiations using both Q-switched and freely generated modes of operation of a ruby laser. The effects of laser energy density and irradiation with multiple pulses were investigated. Laser annealing of both hot and cold implants as well as capped and uncapped GaAs was also carried out.
Differential Hall effect and sheet resistivity measurements have been used to obtain the electrically active impurity profile following annealing. Rutherford backscattering (RBS) measurements and transmission electron microscopy (TEM) were used to study the structure of the implanted layers before and after annealing. A correlation between electrical, RBS and TEM results was established.

1.3. Ion Implantation

Ion implantation is a process whereby a controlled amount of impurity can be introduced into the near surface region of a material. Some of the principal advantages of this technique over the diffusion and epitaxial processes are:

(i) The total implanted dose can be precisely controlled and monitored. This is not so in the case of diffusion in which surface phenomena, crystal strains etc., can affect the amount which diffuses into the host material.

(ii) The shape of the implanted profile and the concentration of impurities as a function of depth can be controlled accurately by means of ion dose and ion energy.

In the case of diffusion, the shape of the profile is determined by the kinetics of diffusion.

(iii) Implantation and subsequent annealing are comparatively low temperature processes and therefore diffusion of unwanted materials from the surface is minimised.
Diffusion processes involve high temperature (1000 to 1300°C) which means that extremes of cleanliness have to be maintained to avoid contamination since many materials vaporise at these temperatures and will diffuse into the host material together with the desired dopant.

(iv) Ion implantation is a non-equilibrium process, so that the solubility limits can be exceeded and it is possible to implant species which cannot be introduced by diffusion, due to their low diffusion coefficients.

(v) Highly uniform layers can be achieved by implantation which is not the case in diffusion.

(vi) Using implantation, high lateral definition of doped regions can be achieved using conventional photolithographic masking techniques, whereas a diffusion takes place in all three dimensions.

(vii) Dual implants can be performed easily.

(viii) Ion implantation processing can be, in principle, easily made automatic since the basic parameters of doping (depth, concentration, profile) may be controlled by the ion beam current and the accelerating voltage.

The main disadvantage of the ion implantation process is that the energy absorption by the target as the ions slow down creates damage. However, this can be removed by a thermal anneal following implantation.
Ion implantation is now an established technique applied to the manufacture of devices based on silicon\(^{18-19}\). In GaAs it is being applied increasingly to fabricate devices. In 1974 Barnoski et al\(^{20}\) demonstrated for the first time that ion implantation could be used to fabricate p-n junction laser diodes in GaAs. Berenz et al\(^{21}\) produced Read-type GaAs IMPATT diodes by S\(^+\) ion implantation into n on n\(^+\) epitaxial material followed by a subsequent annealing process. Similar implants were also used by Hunsperger et al\(^{22}\) and Higgins et al\(^{23}\) to fabricate microwave field effect transistors.

Another application of ion implantation has been to produce high resistivity layers, using proton and oxygen bombardment, for device isolation. In GaAs proton isolation was used by Speight et al\(^{24}\) to produce good IMPATT diodes and these diodes were reported to be superior to mesa etched diodes.

1.4 Laser Processing

1.4.1 Introduction

Intensity and spatial coherence are properties of the laser which give a source of radiant energy that can be concentrated to achieve extremely high power densities. When absorbed by matter, this energy can be sufficient to overcome the binding forces associated with the atomic and molecular structure of materials, so that high temperature
phase changes are easily effected. This has been utilized widely in the processing of metals and recently to the annealing of semiconductors following ion implantation. Fig. 1.1 illustrates the operating regimes for annealing together with other laser material processing.

The applications of lasers cover a wide range from medicine to civil engineering, from chemical analysis to laser communications, from cutting and welding of steel to fabrication of microelectronic circuits and components. Several books\(^{25-28}\) have been written on lasers and their applications. The basic principles, the construction of different types of lasers and the effects of various types of lasers also have been fully covered. Therefore only those aspects which are relevant to the present work are discussed here.

1.4.2. The Choice of a Laser for Annealing GaAs

Pulsed and continuous wave output from lasers have found a wide variety of applications in the processing of materials commonly used in industry. However, many materials would appear to be unsuitable for laser processing because of their high reflectivity at certain laser wavelengths. Fig. 1.2 shows the absorption coefficient as a function of laser wave-length for several semiconductor materials. At 10.6 µm, the carbon dioxide laser wavelength, most of the semiconductors are transparent and most of the incident beam energy is transmitted through the material. On this basis
the CO₂ laser does not appear to be a very good laser for processing semiconductors. The argon laser with \( \lambda = 0.488 \, \mu m \) has excellent absorption into metals and semiconductors, it seems to be potentially attractive for processing materials. For Si, CdS and GaAs, (Fig. 1.2) the highest absorption occurs when the photon energy \( h\nu > E_g \) (band gap energy) of the semiconductor.

The solid state lasers, ruby (\( \lambda = 0.694 \)) and Nd:YAG or Nd:glass (\( \lambda = 1.06 \)) produce the highest energy and peak power output. However, GaAs is transparent at 1.06 \( \mu m \), whereas at 0.694 \( \mu m \), the absorption coefficient of GaAs is approximately \( 10^4 \, \text{cm}^{-1} \). Therefore we selected the ruby laser for annealing ion implanted GaAs. The determining factors were laser energy, peak power output and the absorption coefficient of GaAs at this wavelength.

1.4.3 Laser Operation

The solid state lasers, such as the ruby laser, used in producing high power effects are generally used in pulsed operation. The relationship between power output, energy in the pulse and pulse duration is given by:

\[
\text{Power output (watts)} = \frac{\text{Pulse energy (Joules)}}{\text{Pulse duration (seconds)}}
\]

Therefore by reducing the pulse duration the laser power output can be greatly increased. This is done by a process known as Q-switching.
Fig. 1.1 The operational regimes for laser materials processing techniques. (From ref. 74).

Fig. 1.2 Absorption coefficient for several semiconductors at room temperature and at 77 K (dashed lines). (From ref. 74)
The difference between a freely generated mode and a Q-switched mode is in the power output.

In the case of a ruby laser operating in a freely generated mode, the pulse energy is typically ten joules delivered in one millisecond. However, Q-switching reduces the pulse duration to about ten nanoseconds and so increased the power output from ten kilowatts to one gigawatt ($10^9$ watts).

A simplified diagram of a ruby laser is shown in Fig. 1.3. The operation of a ruby laser in a freely generated mode and Q-switched mode is briefly described below.

(i) Freely Generated Mode

The operation of a laser in the freely generated mode is illustrated in Fig. 1.4 and 1.5. The exciting lamp pulse increases the stored energy in the laser rod until there is sufficient fluorescent radiation bouncing back and forth between the two mirrors for laser oscillations to take place as shown in Fig. 1.5. Laser oscillation rapidly reduces the stored energy in the rod and after one short pulse of approximately one microsecond duration there is a short delay before the stored energy again reaches the threshold condition for oscillation. Thus the stored energy is effectively clamped at this level and the laser output consists of a series of pulses or spikes which continue until the pump light can no longer maintain the stored
The essential components of the ruby laser

Fig. 1.3. The ruby laser (From ref. 27)
energy at this threshold level. The output envelope profile of the pulses follows a form similar to the pumping light pulse, although the duration is always somewhat less. For high gain laser materials and high power pumping rates, spikes can be superimposed on top of a quasi continuous wave output as shown in Fig. 1.5d, and if the laser is well mode controlled this can take the form shown in Fig. 1.5e. With this type of operation pulse width in the range 100 to 10 000 µ seconds are typical.

(ii) Q-switched Operation

In Q-switched operation a high speed shutter is inserted into the optical resonator between the laser rod and the 100% reflecting mirror as shown in Fig. 1.6. The shutter is initially closed thereby preventing laser action, so that the stored energy in the laser rod builds up according to solid curve in Fig. 1.7c. Before this energy is allowed to die away by normal fluorescence according to the dotted line of Fig. 1.7c, the shutter is rapidly opened i.e. the Q of the resonator is switched from a low to a high value. This results in a single pulse with a duration of typically 5 to 50 nano-seconds which contains most of the energy stored in the rod at the time of switching (Fig. 1.7d). The power output in this case is much higher than the freely generated mode operation.
Fig. 1.4

100% mirror

Laser rod in pumping chamber

Partially reflecting mirror

Pig. 1.5

The operation of freely generated mode ruby laser.

Fig. 1.5
Fig. 1.6

100% mirror

High speed shutter

Laser output

Fig. 1.7

Ruby laser
Q-switched mode operation
The effect of a high speed shutter can be obtained by rotating the laser mirrors or by inserting an absorbing element between the laser rod and the 100% reflecting mirror. The most practical form of shutter used comprises an electro-optic device called a Pockel's cell and an associated polarizer. These have the advantage of being extremely fast and electronically controllable.

1.4.4 Laser Annealing

Laser annealing consists of simply exposing the surface of the sample to the beam. The electromagnetic energy may be deposited on to the sample surface in a variety of pulsed or continuous modes. Up to date the following techniques have been used to anneal ion implanted semiconductors:

(i) Continuous wave output (CW)
(ii) Scanning continuous wave output
(iii) Millisecond pulses
(iv) Q-switched (nanosecond) pulses
(v) Scanning Q-switched pulses

Lasers that have been used successfully to anneal semiconductors are:

(a) Ruby laser, both in the freely generated mode and the Q-switched mode.
(b) Nd:YAG, Nd:glass, Q-switched mode, scanning mode and also frequency doubled operation.

(c) Continuous wave argon laser in the scanning mode.

(d) Continuous wave krypton laser in the scanning mode.

(e) Continuous wave or Q-switched carbon dioxide (CO₂) laser.

(f) Dye laser operating at a wavelength of 0.6 μm.

The scanning of the focused laser beam produces nearly the same action as the single pulses except that much larger areas can be annealed in the former case which may be of great advantage when fabricating large scale integrated circuits. However, scanning equipments are expensive and scanning large areas can take a rather long time.

The two regimes of laser annealing are:

(i) In the pulsed or high-power laser mode, ruby and Nd:YAG or Nd:glass, where the semiconductor (Si or GaAs) melts and regrowth occurs from a liquid-solid interface via liquid phase epitaxy.

(ii) In the continuous or low-power mode, scanning Ar and Kr lasers, in this case annealing occurs without melting (Si) and regrowth occurs in the solid phase.
Some of the principal advantages of laser annealing over the conventional thermal annealing process are:

(1) A very thin surface layer can be annealed without appreciable heating of the sample. This can be carried out by selecting the laser parameters which control the absorption coefficient.

(2) Local annealing can be carried out using a focused laser beam. For example, neighbouring areas of a circuit can be annealed differently which is not possible in the case of thermal annealing.

(3) A much higher percentage, up to 100% of the implanted atoms can be incorporated on lattice sites and made electrically active as compared with only a few percent achieved by thermal annealing.

(4) Perfect recrystallization can be achieved with laser processing compared to thermal annealing.

(5) Under certain conditions, such as the solid-phase epitaxy regime, the diffusion of the implanted impurity can be reduced during laser annealing because this is an extremely fast process. Furthermore the diffusion of the unwanted impurities from the surface into the crystal can be avoided, again because heating times are brief (∼ 1ms) compared to the times associated with conventional annealing and diffusion (30 mins).

(6) For laser annealing, solid solubility limits of the impurity concentrations can be exceeded in some cases, such as liquid-phase epitaxy, by more than an order of magnitude.
because of melting, rapid regrowth and very fast quench rates.

(7) Lasers can be used to anneal highly doped diffusion layers as a means of achieving higher electrical activation and dissolving precipitates formed during the diffusion process.

(8) Deposited amorphous layers on semiconductors (Si on Si) can be recrystallized and metal layers on semiconductors (Si and GaAs) can be alloyed, for contacts, using laser irradiations.

The main disadvantage of laser annealing is that, at present it is very difficult to obtain a laser with a highly uniform laser beam intensity over a large area.

1.5 Conclusion

Laser annealing is an important new technique in material science. It is complementary to ion implantation because the surface heating occurs over about the same depth as the ion implantation range and with such rapidity that many of the conventional advantages of ion implantation are retained. The continuous research in ion implantation and the fast progress in laser annealing indicates that these two techniques combined together will play an important role if not dominate the fabrication of semiconductor devices and therefore will have an enormous impact on the semiconductor industry.
2. LITERATURE SURVEY

This chapter will give a review of the literature dealing with the physical properties of ion implanted acceptors in GaAs and laser irradiation of semiconductors.

2.1 ACCEPTORS IN GALLIUM ARSENIDE

2.1.1 Introduction

In GaAs, Group VI elements (S, Se and Te) act as n-type dopants, Group II elements (Be, Mg, Zn and Cd) are p-type dopants and Group IV elements (C, Si, Ge and Sn) are thought to be amphoteric.

The effects of most of these impurities in GaAs have been studied to varying extents. Early work on the implantation of p-type dopants in GaAs was encouraging since doping efficiencies as high as 100% were reported for samples implanted at room temperature and annealed at 800°C. However, for the implantation of n-type dopants, it was much more difficult to achieve high doping efficiencies compared with p-type dopants. The implant temperature, the encapsulation and the annealing temperature were found to be more critical for donor ion implanted material than for acceptor ion implanted material.

2.1.2 Electrical Properties of Be Implanted GaAs

Beryllium is the lightest known p-type impurity in GaAs, but it is difficult to introduce by standard diffusion methods because of its small diffusion coefficient. However, it can be conveniently introduced into GaAs by ion implantation.
Many groups (29-35) have investigated the electrical properties of Be implanted into GaAs. In general it has been found that for Be implanted at an energy in the range 40 to 350 keV at room temperature and annealed at 800°C or at 900°C, the sheet hole concentration increased as the dose increased (Fig. 2.1). Nearly 100% electrical activation was measured (sheet carrier concentration/implanted dose) up to a dose of $1.10^{14}$ ions/cm$^2$. Above this dose the percentage electrical activity decreased as the dose increased.

Original work on Be implanted GaAs by Hunsperger et al (29) and later studies by Zölch et al (30) indicated that the maximum electrical activation occurred at annealing temperatures of 600°C to 700°C. Above this temperature the electrical activity decreased with increasing annealing temperature. This reduction in electrical activation above 700°C, they believed (29, 30, 34) was due to outdiffusion of Be into the encapsulant during annealing. Fig. 2.2 shows the sheet electrical properties as a function of annealing temperature together with electrical profiles of Be implanted GaAs obtained by Zölch et al (30). They have observed very similar electrical activation from samples encapsulated with SiO$_2$ or Si$_3$N$_4$ layers. However, Chatterjee et al (31) reported that annealing with Si$_3$N$_4$ leads to a more efficient luminescence, better electrical properties and more perfect lattice than does annealing with SiO$_2$ encapsulants.

In general it has been found that diffusion of Be increases with increasing annealing temperature for doses above $1.10^{14}$ ions/cm$^2$ (30, 34, 36). This is best illustrated by Fig. 2.2, which shows the profiles for samples implanted...
with $1.10^{15}$ Be ions/cm$^2$ and annealed in the temperature range 650°C to 850°C$^{(30)}$. Significant diffusion of Be is observed after 800°C and 850°C anneals. However, samples annealed at 650°C show very good correspondence to the theoretical LSS profile. The diffusion coefficient calculated from these profiles is$^{(30)} D = 1.46 \times 10^{-4} \exp (-1.84/kT)$ cm$^2$/s.

The concentration dependent diffusion behaviour of the implanted Be was investigated by McLevige et al$^{(32)}$. For concentrations less than approximately $10^{18}$ cm$^{-3}$ no significant diffusion occurred during annealing up to 900°C. However, for concentrations greater than $5 \times 10^{18}$ cm$^{-3}$ extremely rapid diffusion was observed at temperatures near and above 800°C. (see for example Fig. 2.3$^{(32)}$). The gaussian profiles tended to be flattened and diffused as the dose increased from $1.10^{13}$ to $1.10^{15}$ ions/cm$^2$.

Comas et al$^{(36)}$ using electrical and SIMS measurements for samples implanted to a dose less than $1.10^{14}$ ions/cm$^2$ and annealed up to 900°C, have shown that there was no change in the Be distribution in GaAs. For doses greater than $6.10^{14}$ ions/cm$^2$ significant redistribution occurred after annealing at 900°C. SIMS measurements indicated a considerable build up of Be at the GaAs surface which was not electrically active.

Donnelly et al$^{(37)}$ have used multiple energy (100 to 400 keV) Be ion-implantation in GaAs to obtain uniform carrier concentrations ($\sim 2.10^{18}$ cm$^{-3}$) of
approximately 1.5 µm thick. They reported that there was no difference in the observed values of sheet concentration and mobility after annealing at 900°C of the samples implanted at either room temperature or at 200°C.

Many researchers\(^{(32,34,36,38)}\) have investigated the photoluminescent properties of Be implanted GaAs and GaAs\(_{(1-x)}\)\(_{P_x}\). McLevige\(^{(32)}\) suggests that an annealing temperature of 900°C is necessary for maximum optical activation for Be implanted GaAs.

Be implantation into GaAs and GaAs\(_{(1-x)}\)\(_{P_x}\) has been used successfully to fabricate devices such as light emitting diodes\(^{(39)}\), \(p^+n^-n^+\) GaAs diodes\(^{(37)}\), low loss \(p^+n^-n^+\) optical striplines, channel-stop strip guides\(^{(40)}\) and double heterostructure (Al, Ga)As diodes\(^{(34)}\).

2.1.3 Electrical Measurements of Mg Implanted GaAs

Original work on magnesium implanted GaAs\(^{(29)}\) reported 100% electrical activity for doses less than \(1.1 \times 10^{14}\) ions/cm\(^2\) after annealing at 800°C. For doses greater than \(1.1 \times 10^{14}\) ions/cm\(^2\) the hole concentration saturated in the range \((1 - 2) \times 10^{14}\) holes/cm\(^2\). However these results do not agree with the more recent findings of Zolch et al\(^{(30)}\) and Kular et al\(^{(41)}\). They found that after annealing at 800°C the sheet hole concentration increased with increasing dose up to \(1.1 \times 10^{15}\) ions/cm\(^2\) and above this dose tended to saturate at about \((2 - 3) \times 10^{14}\) holes/cm\(^2\) (Fig. 2.4).
Fig. 2.1. Hole concentration as a function of ion dose for Be implanted GaAs. (From ref. 29-35).
Annealing behaviour of Be implanted at 150 keV in GaAs. Hole concentration and mobility as a function of annealing temperature.

Diffusion profiles of Be implanted GaAs. E = 150 keV, N_d = 10^{15} cm^{-2}. Hole concentration profiles as a function of annealing temperature. From Zölch et al (30).

Fig. 2.2.
Fig. 2.3 Net acceptor concentration profiles obtained from differential Hall-effect measurements on GaAs implanted with Be to the doses shown and annealed for $\frac{1}{2}$ h at 900°C.

From McLevige et al. (32)
Very similar electrical activities have been reported\(^{(41)}\) after annealing at 700\(^\circ\)C and at 800\(^\circ\)C using either aluminium or Si\(_3\)N\(_4\) as the encapsulant. However, Zölch et al\(^{(30)}\) have observed slightly higher electrical activities with Si\(_3\)N\(_4\) than with SiO\(_2\) layers.

Several groups\(^{(29,30)}\) found that the percentage electrical activity decreased after annealing at 750\(^\circ\)C and 800\(^\circ\)C respectively and they thought this was due to the formation of complex defects and out-diffusion of magnesium into the SiO\(_2\) or Si\(_3\)N\(_4\) encapsulants. Electrical profiles\(^{(41)}\) suggested a build up of Mg at the GaAs-Al interface. The diffusion coefficient of Mg was found to be\(^{(30)}\)
\[ D = 4.4 \times 10^{-4} \exp(-1.87/kT) \text{ cm}^2/\text{s} \] which is very close to the value reported for Be by the same group.

The photoluminescent properties of Mg implanted GaAs and GaP have been reported by some groups\(^{(42-44)}\). From these measurements it was found\(^{(44)}\) that for low doses, annealing temperatures 750 to 900\(^\circ\)C were sufficient for recovering the lattice damage. However, for doses greater than 5.10\(^{13}\) Mg\(^+\)/cm\(^2\) the implantation damage still remained after annealing at 750\(^\circ\)C to 900\(^\circ\)C.

2.1.4 Electrical Characteristics of Zn Implanted GaAs

Several investigations have been reported on the electrical\(^{(16,17,30,45-47)}\) properties of zinc implanted GaAs (see Fig. 2.5). In general for samples implanted at room temperature or at 400\(^\circ\)C in the energy range from 20 keV to 150 keV, the sheet hole concentration increased with
Fig. 2.4 Hole concentration as a function of ion dose for Mg implanted GaAs.

(From references 29, 30 and 41).
increasing dose. Electrical activities were found to lie in the range from 10% to 100% after annealing at 800°C.

Up to a dose of $1 \times 10^{14}$ ions/cm² good agreement between the reported results exists and the electrical activities of up to 100% have been observed\(^{(17,30,45-47)}\). However, above this dose the published results\(^{(17,30,46,47)}\) do not agree with each other. Above a dose of $1 \times 10^{14}$ ions/cm² Littlejohn et al\(^{(47)}\) reported an electrical activity of 10% whilst Yuba et al\(^{(17)}\) and Zölch et al\(^{(30)}\) have measured electrical activities of 100% for doses up to $1 \times 10^{15}$ ions/cm², after annealing at 800°C or 900°C.

For an ion energy of 60 keV, Yuba et al\(^{(17)}\) have observed 100% electrical activities for samples implanted at either room temperature or at 400°C, with doses up to $1 \times 10^{15}$ ions/cm². This is in conflict with the findings of Fujimoto et al\(^{(46)}\) who have observed 10% and 40% activation for a dose of $1 \times 10^{15}$ ions/cm², for implants carried out at room temperature and for 400°C respectively.

SiO₂ has often been employed as a cap for Zn implanted GaAs\(^{(16,17,30,45-47)}\). Zölch et al\(^{(30)}\) used SiO₂ and Si₃N₄ during his investigation and found lower electrical activation and a smaller diffusion coefficient of Zn in GaAs when Si₃N₄ was used.

Apart from Zölch et al\(^{(30)}\), none of the other publications show electrical profiles of the zinc implanted layers. Fig. 2.6 shows the profiles reported following annealing in the temperature range 850°C to 950°C of samples implanted with 150 keV $1 \times 10^{15}$ Zn⁺/cm² at room temperature\(^{(30)}\).
The results show hole concentrations greater than $10^{19}$ holes/cm$^3$ and an increased diffusion of zinc into GaAs with increasing annealing temperature.

All the above groups$^{(17,45-47)}$ have reported that an annealing stage for mobility existed between an annealing temperature of 600$^\circ$C and 700$^\circ$C and generally the sheet mobility observed was around 100 cm$^2$/V.s. Also these workers$^{(17,45-47)}$ stated that the saturation of the sheet hole concentration with increasing dose resulted from reaching the solubility limit of Zn in GaAs, which is $1.7 \times 10^{20}$/cm$^3$ at 800$^\circ$C$^{(17)}$.

Hunsperger and Marsh$^{(45)}$ have shown that for doses greater than $1.1 \times 10^{16}$ cm$^{-2}$, of 20 keV Zn ions, considerable damage still remained even after annealing at 600$^\circ$C, while most of the damage annealed below 600$^\circ$C for lower doses. From measurements of the depth of the p-n junction, using the technique of angle lapping and staining they reported$^{(16)}$ that appreciable diffusion of Zn occurred above annealing temperatures of 700$^\circ$C.

Itoh and Oana$^{(48)}$ investigated the effects of the substrate temperature during implantation, on the electrical properties of zinc implanted GaAs$_{(1-x)}$P$_x$. By using the staining technique they found the p-n junction depth decreased from 10.1 µm to 1.6 µm as the implant temperature was increased from room temperature to 450$^\circ$C. In contrast Okabayashi$^{(49)}$ reported very similar electrical properties from GaAs samples implanted at room temperature and at 400$^\circ$C.
with zinc ions. Similarly Zelevinskaya et al\(^{(50)}\) found no difference in the sheet resistivity measurements carried out on GaAs samples implanted with zinc ions at room temperature, at 300°\(\text{C}\) and at 500°\(\text{C}\) respectively. However, the conductivity profiles indicated that the conducting region increased considerably both with increasing implant dose and annealing temperature.

Zn ion implantation into GaAs and GaAs\(_{(1-x)}\)P\(_x\) has been used successfully to fabricate devices. For example both abrupt and graded junction p-n diodes have been formed by implanting 20 to 80 keV \(1,10^{15}\) Zn\(^+\)/cm\(^2\) at room temperature\(^{(15,51)}\).

Solar cells have been fabricated by implanting Zn and Cd into GaAs\(^{(52)}\) at room temperature followed by annealing at 600 to 800°\(\text{C}\). These devices were found to have characteristics similar to those produced by diffusion but higher efficiencies of the order of 9.0 to 9.5%. Barnoski et al\(^{(20)}\) have made an injection laser by implanting 20 keV \(1,10^{16}\) zinc ions/cm\(^2\) into GaAs at room temperature and followed by annealing at 900°\(\text{C}\) for three hours which acts as a drive-in diffusion process. Boissy and Diguet\(^{(53)}\) have fabricated light emitting diodes by implanting a high dose of Zn as a predeposition process prior to annealing at 800 to 900°\(\text{C}\). They found that the light emitting power was 1.5 times greater for an implanted diode than for the diffused diode. The high efficiency of the implanted device was thought to be due to better minority carrier injection from the gradual shape of the zinc concentration profile.
Yuichi Ono et al. investigated the properties of GaAs\(^{1-x} \rightleftharpoons x\) light-emitting diodes produced by Zn ion implantation. They found that ion implanted LED's had greatly improved luminescent efficiencies compared with LED's made by thermal diffusion. The light intensity of the implanted diodes depended upon the ion dose and peaks at around 4 to 8\(x10^{15}\) cm\(^{-2}\) and maximum light intensity exceeded twice that of the diffused diode. High luminescence efficiency in the case of ion implanted diodes was due to a wider luminescent region as compared with a thin region in the case of a diffused diode.

2.1.5 Rutherford Backscattering Studies of Zn Implanted GaAs

Gamo et al. have used Rutherford backscattering to investigate the reordering of the amorphous layers in GaAs produced by implanting 100 keV, 3.10\(^{13}\) zinc ions/cm\(^2\) at room temperature. Their findings indicated that the reordering of the amorphous layer occurred over a broad temperature range and the recovery of this layer had no significant orientation dependence. They also stated that amorphous GaAs layers recrystallised in an epitaxial manner.

Photoluminescence measurements on zinc implanted GaAs have been performed to investigate the recovery of the radiation induced damage. Increased recrystallization was achieved with increased annealing temperature and after annealing at 600\(^\circ\)C for 20 minutes the radiation damage was reported to be almost reformed.
Fig. 2.5 Sheet hole concentrations as a function of ion dose for Zn implanted GaAs.
(From ref. 17, 30, 46 and 47).
Fig. 2.6 Hole concentration profiles as a function of annealing temperature.
From Zöllch et al(30).
Electrical Properties of Cd Implanted GaAs

Fig. 2.7 summarizes the electrical properties of cadmium implanted GaAs reported by various investigators \( (30, 45, 59) \). The early studies of Hunsperger et al.\(^{(45)}\) and later findings of Shin et al.\(^{(59)}\) reported 100% electrical activity for doses less than or equal to \( 1.10^{14} \) ions/cm\(^2\). For doses greater than \( 1.10^{14} \) ions/cm\(^2\) sheet hole concentration saturated at about \( 2.10^{14} \) holes/cm\(^2\) and they believed this was due to the solubility limit of cadmium in GaAs, which is \( 2.10^{19} \) cm\(^{-3}\) at 900°C. However, Zölch et al.\(^{(30)}\) found that the sheet hole concentration increased with increasing ion dose and after annealing at 800°C the electrical activities observed were 90%, 40% and 5%, for doses of \( 1.10^{14}, 1.10^{15} \) and \( 1.10^{16} \) ions/cm\(^2\) respectively. Also they measured lower activation from samples encapsulated with Si\(_3\)N\(_4\) than for those encapsulated with SiO\(_2\).

Published sheet mobilities\(^{(45, 59)}\) (\( \sim 100 \) cm\(^2\)/V.s) were believed to be good, but Zölch et al.\(^{(30)}\) found that the mobility in the implanted layer was poor after annealing at 800°C or at 900°C.

Electrical profiles for Cd implanted GaAs indicated that a considerable diffusion of cadmium occurred during annealing in the temperature range 650°C to 850°C\(^{(30, 59)}\). Profiles showed a peak hole concentration greater than \( 1.10^{19} \) holes/cm\(^3\) and the profiles tended to flatten with increasing annealing temperature. The diffusion coefficient
calculated from these profiles was \( (30) \)
\[ D = 4.33 \times 10^{-4} \exp (-2.3/kT) \text{ cm}^2/\text{s}. \]

Aoki et al \(^{(60)}\) reported the photoluminescence properties of Cd implanted GaAs. From the depth distribution of the Cd acceptor emission, after annealing at 800°C, they found less diffusion for implants carried out at 300°C than for samples implanted at room temperature. Furthermore the emission intensity for the cadmium acceptor was more intense for 300°C implantation.

### 2.1.7 Rutherford Backscattering Analysis of Cd Implanted GaAs

Grob et al \(^{(61)}\) have used Rutherford backscattering to study the lattice disorder produced by implanting 20 to 60 keV cadmium ions into GaAs. Their findings indicated that implantation induced disorder in GaAs increased linearly with Cd doses between \( 1 \times 10^{13} \) to \( 1 \times 10^{14} \) ions/cm\(^2\) and above these doses reached a saturation level, for example, the samples became amorphous. The disorder caused by low doses (\( \leq 10^{14} \) ions/cm\(^2\)) showed a maximum amount of annealing at about 400°C, whereas a high annealing temperature (approximately 700°C) for reordering was required for high doses.

Takai et al \(^{(62)}\) have shown that 70 keV cadmium ions implanted into GaAs at room temperature to a dose of \( 3 \times 10^{15} \) ions/cm\(^2\), the implantation induced disorder decreased gradually with increasing annealing temperature in the range 100 to 800°C. Some disorder was still present after
Fig. 2.7 Hole concentration as a function of ion dose for cadmium implanted GaAs.
(From ref. 30, 45 and 59).
annealing at 800°C. The fraction of Cd occupying lattice sites increased with increasing annealing temperature. After annealing at 700°C to 800°C most of the cadmium was found to lie on sites displaced 0.3 to 0.8 Å from lattice sites.

Implanting Cd into GaAs at substrate temperature between room temperature and 600°C has also been carried out\(^{(62,63)}\). It was found that low residual damage, high activity and high substitutionality of cadmium to about 70 to 100% are best achieved by implanting at 150°C to 350°C. Above an implant temperature of 400°C the percentage of Cd on lattice sites decreased with increasing implant temperature which may be due to evaporation of As atoms from the GaAs surface and/or formation of As vacancies during implantation\(^{(62)}\).

2.1.8 Transmission Electron Microscopy Studies

The Structural defects before and after annealing of the GaAs samples implanted with 60 keV \(1.10^{15}\) ions/cm\(^2\) of Be, Mg, Zn and Cd ions was studied by Benson et al\(^{(64)}\) using transmission electron microscopy. Electron diffraction analysis indicated that for as-implanted samples there was an amorphous region in the samples implanted with Zn and Cd, while those implanted with Be and Mg were completely crystalline. Following annealing at 800°C for thirty minutes, small defects of about 200 Å diameter were observed in samples implanted with Be, Mg and Cd, while zinc implanted samples contained ZnGa\(_2\)O\(_4\) precipitates.
They believe these defects can have a significant effect on the electrical properties of the implanted layers.

In an earlier publication the same author\(^{(8)}\), reported the existence of second phase structures of \(\text{Zn_3As}_2\) and \(\text{ZnGa}_2\text{O}_4\) which formed in Zn implanted GaAs after annealing at 600\(^{\circ}\)C and 800\(^{\circ}\)C respectively. They thought that the observed effect was due to out-diffusion of As or Ga and in-diffusion of oxygen from the \(\text{SiO}_2\) encapsulant.

2.1.9 Diffusion of Zinc in GaAs

Most workers now agree that zinc diffuses into GaAs by a substitutional-interstitial mechanism. This mechanism was first suggested by Frank and Turnbull\(^{(65)}\) to account for the anomalous diffusion behaviour of copper in germanium. It has since been generalised by Sturge\(^{(66)}\) and adopted by Chang and Pearson\(^{(67)}\) to explain their results for Zinc diffusion in GaAs. They assume that while the great majority of zinc atoms exist substitutionally on gallium sites in concentration \(C_g\), a very small proportion, \(C_i\), occurs interstitially. The diffusion coefficient for the interstitials, \(D_i\), is very much greater than that for substitutionals, \(D_g\), and the interstitial atoms therefore dominate the diffusion process. The diffusion may be described as follows. The zinc atom joins the lattice at the surface, goes interstitial and diffuses through the lattice very quickly. It eventually joins up with a gallium vacancy and becomes substitutional.
again. The crystal has now lost a vacancy, which can be replaced either by one diffusing from the surface or by one obtained from a defect in the bulk material, such as a dislocation loop or complex.

The interstitial and substitutional concentrations are related by an equation involving gallium vacancies\(^{68}\).

\[ \text{Zn}_{i}^{+} + V \rightleftharpoons \text{Zn}_{s}^{-} + 2e^{+} \]

Where it is assumed that the interstitial species exists as a singly ionised charges.

\[ \text{Zn}_{i}^{+} \text{ zinc interstitials, singly ionised.} \]

\[ \text{Zn}_{s}^{-} \text{ zinc substitutionals, un-ionised.} \]

\[ V \text{ gallium vacancies.} \]

After making a number of assumptions, Tuck\(^{69}\) has derived an approximate expression for the diffusion coefficient of zinc in GaAs:-

\[ D \sim \left( \frac{3AD_{i}}{C_{v}} \right) C_{s}^{2} \]

where \( A \) is an equilibrium constant dependent on temperature. 
\( C_{v} \) is the gallium vacancy concentration. 
\( D_{i} \) diffusion coefficient for interstitial species 
\( C_{s} \) substitutional concentration.
In the case of ion implantation the diffusion of the implanted impurities will generally be more complex than for non-implanted materials. When ions are implanted into crystalline substrate, they create many vacancies and interstitials. Some of these vacancies may recombine with interstitials while others may produce complex defects. The post bombardment heat treatment of the disordered layers release a large number of vacancies which may substantially alter the diffusion coefficient of the implanted atoms.

Work on ion implantation of zinc in GaAs indicated that zinc diffused in GaAs during annealing. Zelevinskaya et al. reported an increased diffusion of Zn and Cd with increasing annealing temperature and ion dose. The presence of a large number of vacancies increased the solubility of zinc in GaAs and slowed down its diffusion out of the doped layer.

Gavrilov et al., investigated the diffusion of Zn and Cd in gallium-arsenide irradiated with arsenic ions. Their findings indicated that the additional implantation of As ions slowed down the diffusion of Zn and Cd, which they believed was due to the formation of excess gallium vacancies during annealing. These vacancies absorbed the fast interstitial diffusing atoms. Similarly Kachurin et al. showed that the presence of gallium vacancies in ion implanted GaAs led to the enhanced diffusion of Sn and retarded diffusion of Zn and Cd.
They thought that the diffusion retardation was on the basis of trapping of the fast interstitial impurity atoms by the vacancies.

For zinc implantation in GaAs$_{0.6}$P$_{0.4}$, Stoneham and Gibbons(73), have shown that the addition of As and P prior to annealing, inhibits the diffusion of Zn during annealing whereas the addition of Ga has negligible effect.

2.1.10 Conclusion

In general the published results indicate that for ion implanted acceptors (Be, Mg, Zn and Cd) in GaAs, doping efficiencies up to 100% can be achieved after annealing in the temperature range 700°C to 900°C. Diffusion of the implanted ions occurs for doses greater than 10$^{14}$ ions/cm$^2$ and this is dependent upon the annealing temperature. An excess of gallium vacancies inhibits the diffusion of Zn and Cd during annealing.

2.2. Laser Irradiation of Semiconductors

2.2.1. Introduction

Since the pioneering Russian work on laser annealing, there has been a strong interest in the laser treatment of semiconductor materials. Most of the work so far reported has been on silicon and has involved either crystallization of amorphous Si films or the annealing of ion implanted silicon. Far less has been published on laser
recrystallization of GaAs or laser annealing of ion implanted gallium arsenide. However some work has been reported on laser processing of ohmic contacts on GaAs devices.

This section will give a brief review of the literature dealing with laser annealing of Si and GaAs. Review on laser processing of silicon is presented because there has been a large number of papers published over the past year, as well as the two conferences(74,75) held during 1978, which were mostly devoted to this topic. Furthermore, much of the progress made in understanding the processes by which a laser pulse can anneal the damage produced near the surface region of the semiconductor during ion implantation, has been in Si. Therefore it is important to include the related literature on silicon in this survey. This may also be helpful in explaining the results in gallium arsenide.

2.2.2. Laser Annealing of Ion Implanted Silicon

(a) Ruby and Nd:YAG Lasers

(i) Introduction

Laser annealing of ion implanted Si using both ruby and Nd:YAG lasers was first demonstrated by several Soviet groups(76-78). This stimulated a large number of research groups and as a result a large number of publications have occurred since(79-136).
The effect of laser annealing on implanted Si has been studied extensively by measurements of electrical, physical and optical properties, such as transmission electron microscopy, high energy electron diffraction, ion channelling, secondary ion spectroscopy, X-ray diffraction, Raman scattering and ellipsometry. Ions which have been studied include B⁺, As⁺, P⁺, O⁺, Ar⁺, Ga⁺, Sn⁺, Pb⁺, Si⁺, Sb⁺, Pt⁺, Cu⁺ and Fe⁺, implanted into silicon in the energy range 10 to 400 keV and a dose range from $6 \times 10^{13}$ ions/cm² to $6 \times 10^{16}$ ions/cm². Laser irradiation has been carried out either with ruby or Nd:YAG lasers and the energy density used was up to 10 J/cm². The pulse duration corresponds to the freely generated mode of operation, approximately milliseconds ($\sim$ ms) or to the Q-switched mode of operation, approximately nanoseconds ($\sim$ ns).

In general, laser annealing of ion implanted silicon was found to lead to complete recovery of the crystallinity (76,79,81) and high electrical activity in the implanted region. Transmission electron microscopy (81-83) showed that following laser irradiations the implanted layers were perfect with no defects, e.g. dislocation loops or stacking faults. Rutherford backscattering (84-88) and electrical measurements (76,83), indicated that a very high percentage of atoms occupied lattice sites (80 to 90%) and the percentage electrical activity was also equally high. Peak carrier concentrations of dopants observed were as high as $5 \times 10^{20}$ cm⁻³, which is well above the solubility limit of most impurities in silicon.
(ii) **Dose Dependence**

Laser annealing of Si implanted with various ion doses indicated\(^{78,81,83-84,89}\) that for lower doses, less than \(5 \times 10^{14}\) ions/cm\(^2\), the effect was not as good as the conventional thermal annealing process. At a dose of \(5 \times 10^{14}\) ions/cm\(^2\) similar results were obtained for both techniques and for higher doses laser annealing was found to give better electrical activation\(^{78,81,89}\).

The above results indicate that for high dose implants, laser irradiation is an excellent technique and produces superior results to the conventional annealing process. Unfortunately, at present, problems exist in obtaining high annealing efficiencies in the case of low dose implants. However, these can be overcome using CW Ar or Kr ion lasers (see section 2.2.2.b).

(iii) **Energy Threshold**

For ion implanted silicon, the results indicated that the transition from amorphous to single crystal Si requires a threshold energy density\(^{90-92}\) \(E_{th}\) which depends upon:-

1. The amorphous layer thickness (for example see fig. 2.8)
2. The type of laser employed for annealing.

For annealing an amorphous layer of 1000 Å to 4000 Å thick, the threshold energy density in the case of Q-switched ruby\(^{81-85,90-93}\) and Nd:YAG\(^{86,94-96}\) lasers was found to be in the range 1-3 J/cm\(^2\) and 2 to 10 J/cm\(^2\).
Residual disorder, as measured by channeling, for amorphous silicon of different thicknesses, after pulsing laser irradiation. The threshold mechanism of the transition to single crystal is clearly evidenced by the step decrease of the data points. (Silicon implanted into Si followed by laser irradiation with Q-switched ruby laser, $\lambda = 0.6943 \, \mu m$ pulse lengths 50 nsecs). Measurement technique RBS. After G. Foti(93)
respectively. The higher energy density for Nd:YAG laser (factor of two to three times that of a ruby laser) was due to the lower absorption coefficient at this wavelength (see section 1.4.2).

Further difference in the energy density threshold was reported\((95-96)\) to be dependent upon the dopants (As, Sb, Sn or Ga) when Nd:YAG laser was used and it was independent of these parameters when ruby laser was used.

Above a threshold energy density, single crystal material was obtained\((78,91-92)\), while below it the amorphous layers became polycrystalline\((92)\) or remained amorphous\((91)\). An excellent example of this was reported by Foti\((93)\) (see fig. 2.9), using ion channelling and transmission electron microscopy. Increased grain size with increasing laser energy density was also observed \((92,93,97)\) (fig. 2.10).

The threshold energy density was also found to be dependent on the analysis techniques\((88,94)\). For example, for an amorphous layer of 1800 Å thick, irradiating with Q-switched ruby laser, threshold energy density of 1.5 J/cm\(^2\) and 2.5 J/cm\(^2\) was reported\((88)\) using RBS and TEM measurements respectively. Similarly for 150 keV, \(1\times10^{16}\) As\(^+\)/cm\(^2\) implanted into silicon and irradiated with Nd:YAG laser, Nakamura et al\((94)\) reported the threshold energy density of 2 J/cm\(^2\) and 3 J/cm\(^2\) as obtained by ellipsometry and RED techniques.
Fig. 2.9 Structure of amorphous Si layers of different thicknesses after pulsing laser annealing. Open, full and partially full symbols indicate good single crystal, polycrystal and single crystal with high residual disorder respectively. The full line represents the threshold energy density versus the amorphous thickness. \( R = 0.6 \); \( \alpha = 5 \times 10^4 \) cm\(^{-1}\) for amorphous and \( \alpha = 4 \times 10^3 \) cm\(^{-1}\) for single crystal. (Silicon implanted into Si and laser annealed with Q-switched ruby laser, 50 nsecs. pulse length). Measurement techniques RBS and RHEED. After Foti and co-workers (91 and 93).
Fig. 2.10 The average grain size of poly-Si obtained by irradiation of 4000 Å amorphous self-implanted thick layers with ruby laser single pulse. Pulse length 20 or 50 nsec. From Foti (93)
In summary, most results indicate that the energy threshold for annealing ion implanted Si depends upon the thickness of the amorphous layer as well as on the type of laser used and the measurements technique employed for characterisation. A strong disagreement exists between the energy threshold values reported by various research groups (Italian group, Oak Ridge and Bell Labs); however the energy threshold difference may be related to the non-uniformities in the laser beam and perhaps to the method used for measuring the energy.

(iv) Profile Broadening

It has been found that the implanted dopant profile was changed by the laser annealing process, indicating that diffusion had occurred\(^{(76-77,79,81,84,86,98-101,104-108)}\). It was believed that the laser pulse melted the silicon\(^{(93,107,109-113)}\) and the implanted impurity diffused in the liquid state\(^{(81,87,99-101,103)}\). The diffusion coefficient of As and B in Si estimated by a number of groups was reported to be about \(10^{-4}\) cm\(^2\)/s, which is consistent with the diffusion in liquid silicon. This is best illustrated by Fig. 2.11 showing the measured and the calculated redistribution of B and As in Si after laser irradiation\(^{(105)}\).

The segregation of Cu and Fe to the front surface of the silicon was observed by White et al\(^{(105)}\) and Cullis et al\(^{(106)}\) and they thought this occurred due to Si becoming molten.
Fig. 2.11 Profiles of B and As in silicon after laser annealing with Q-switched ruby laser, pulse length 20 to 60 nsecs. From ref. 105.
It was concluded that liquid phase epitaxy is the most probable process for recrystallization\(^{(85,101,103,111,114)}\). Later Auston et al\(^{(115)}\) carried out time resolved reflectivity measurements on ion implanted silicon during laser annealing which confirmed that single crystal growth occurred from a melted surface layer (see Fig. 2.12). The reflectivity of Si increases from 0.17 to 0.47 when silicon melts and remains at this value for about 300 ns and finally drops to the value for a single crystal material indicating annealing has completed.

By using RBS, TEM, SEM and interference optical microscopy techniques, Poate et al\(^{(87)}\) concluded that for As implanted silicon, irradiated with a Nd:YAG laser the annealing occurred via liquid phase regrowth from the underlying solid liquid interface. The regrowth layer is free of extended defects and dopant profiles are consistent with diffusion in liquid Si.

(v) **Surface Topography**

Ripples have been observed on the surface of the laser annealed silicon\(^{(116-118)}\). Leamy et al\(^{(116)}\) believed that the geometry of the ripple pattern is determined by the interference effect of the primary laser beam with wave scattered from the surface disturbance. However Von Allmen\(^{(117)}\) suggested that the ripple pattern was due to anisotropic melting of the silicon during laser irradiation.
Fig. 2.12 Shown as a function of time are, $I_0$, the incident laser intensity at 1.06 $\mu$m (a), $I_t$, the transmitted laser intensity (in arbitrary units) (b) and $R$ (c) the absolute value of reflectivity at 0.63 $\mu$m. Incident energy 5.2 J/cm$^2$, Si implanted with $10^{15}$ As/cm$^2$ at 50 keV. Laser irradiation with Q-switched Nd: glass laser, pulse duration 50 nsecs.

After Auston et al.(115).
Marcus et al. \cite{118} observed that ripples both linear and circular are related to the presence of several different frequencies in the laser beam spaced by multiples of axial mode intervals. The ripples arise from the interaction between simultaneously oscillating axial modes of the laser. However, the conclusion is that ripples originate from the surface of the silicon when the melting threshold is exceeded.

(b) **Scanning Argon Ion Laser**

Laser annealing of ion implanted silicon using a continuous wave argon laser was first reported by Klimenko et al. \cite{119} and Kachurin et al. \cite{120}. They observed good electrical activation and lattice reordering in ion implanted Si. These results were later confirmed by Gat et al. \cite{121,122} who measured 100% electrical activation after laser annealing of Si samples implanted with $5 \times 10^{14}$ As$^+$/cm$^2$. Furthermore, SIMS measurements showed that the impurity concentration profile was identical to the as implanted profile indicating that no diffusion took place.

Using Rutherford backscattering, channelling, optical microscopy and in situ optical reflectivity, Auston et al. \cite{123} concluded that recrystallization in this case is in an accelerated solid phase epitaxial regrowth process similar to thermal annealing. Williams et al. \cite{124} and Poate et al. \cite{87} demonstrated that the regrowth process is one of
solid state epitaxial recrystallization from the amorphous
to single crystal and no dopant redistribution occurred.
However, the same authors\(^{(125)}\) recently reported that the
crystal regrowth of As implanted silicon is strongly
dependent on implant dose, substrate orientation and
laser irradiation parameters (power and dwell times).
Furthermore the diffusion of the dopant in Si occurred
when the solid solubility of As in silicon was exceeded
\((50\ \text{keV},\ 3\times 10^{16}\text{As}^+/\text{cm}^2\text{ into Si})\).

Gat et al\(^{(126,127)}\) have further demonstrated that
a continuous wave Kr laser can also be used in a similar way
to the Ar laser to obtain high electrical activation and
essentially perfect recrystallization with no significant
diffusion of the implanted species in silicon.

(c) Other Applications of Laser Processing in Si

Finally some of the other applications of laser
processing in silicon reported includes the following:

(i) The epitaxial regrowth of deposited amorphous thin
films \((\sim 3000\text{ to }4000\ \AA)\) on single crystal Si
substrate, using Nd:YAG\(^{(128)}\), Q-switched ruby\(^{(129)}\)
and CW Ar ion laser\(^{(130)}\) has been carried out.

(ii) Laser induced diffusion has been used to fabricate
p-n junction diodes in silicon\(^{(131-133)}\).

(iii) Diffusion induced imperfections, such as precipitates\(^{(134)}\)
and misfit dislocations\(^{(135-136)}\) produced by high dose
implants of \(P^+\), \(As^+\) and \(Sb^+\) in silicon have been
removed using laser irradiation.
The results on these topics (i), (ii) and (iii) are consistent with melting of the silicon during laser irradiation.

2.2.3 Laser Processing of Gallium Arsenide

(a) Laser Annealing of Ion Implanted GaAs

Pulsed annealing of ion implanted GaAs was first reported by Kachurin et al.\(^{(137-138)}\), Bogatyrev et al.\(^{(139)}\) and Bolotov et al.\(^{(140)}\). Following irradiation with a ruby laser, high electrical activation was measured from capped gallium arsenide samples implanted with 35 keV, \(1 \times 10^{15}\) and \(1 \times 10^{16}\) ions/cm\(^2\) of Zn and Te ions respectively.\(^{(137-138)}\)

The mobility was about 1000 cm\(^2\)/V.s for the Te doped material which indicated that the implanted layer had recrystallized.\(^{(137)}\).

Uncapped GaAs implanted with \((1-7) \times 10^{15}\) Te\(^+\)/cm\(^2\) in the energy range 50 to 400 keV has been studied.\(^{(93, 141-143)}\) Using RBS Golovchenko et al.\(^{(141)}\) observed up to approximately \(10^{21}\) atoms/cm\(^3\) on lattice sites after irradiating with 0.25 J/cm\(^2\) from a Q-switched ruby laser. This value far exceeds the solubility limit of Te in gallium arsenide.

Campisano et al.\(^{(143)}\) reported that a single pulse of energy density 1.2 J/cm\(^2\) from a ruby laser, incorporated 90% Te on substitutional lattice sites and there were no signs of tellurium diffusion into GaAs.
Transition of the implanted amorphous gallium arsenide layers to polycrystal or single crystal structure requires an energy threshold (93, 142-143) which depends upon the thickness of the amorphous layer. For an amorphous layer of 2300 Å, RBS measurements indicated that the energy threshold ($E_{th}$) was between 1.2 J/cm$^2$ to 1.4 J/cm$^2$ (142-143). Laser irradiation with an energy density of 0.4 J/cm$^2$ ($< E_{th}$) no annealing took place (143). However when the laser energy density of 1.4 J/cm$^2$ ($> E_{th}$) was used, a $X_{\text{min}}$ value of 4% was measured (143) indicating that the implanted amorphous layer had become a single crystal.

Foti (93) and Campisano et al (143) found that the threshold energy for the amorphous GaAs layer was lower than for the amorphous silicon layer of the same thickness. The difference in the energy density being about 50%. Fig. 2.13 illustrates the amorphous to single crystal transition measured for Ge, GaAs and Si using RBS (93).

Electrical measurements of laser annealed ion implanted gallium arsenide have been reported recently (144-149). For high doses ($\geq 10^{15}$ ions/cm$^2$) of Se, Te, Ge, Sn and Si better electrical properties can be achieved with laser annealing compared with the conventional thermal annealing process. For example a dose of $1 \times 10^{15}$ Se$^+$/cm$^2$, implanted at room temperature or at 200°C, produces electrical activities in the range 10 to 40% for capped and uncapped GaAs after irradiating with a single pulse from a ruby laser of energy density around 1 J/cm$^2$ (144-148). Electron concentrations greater than $10^{19}$ cm$^{-3}$ have been measured (144-148).
Residual disorder as measured by channeling for Ge, GaAs and Si single crystals with amorphous implanted layers of different thickness after ruby laser single pulse irradiation (Q-switched ruby laser) pulse length 50 nsecs). Measurement technique RBS.

After Foti(93).

Fig. 2.13 Residual disorder as measured by channeling for Ge, GaAs and Si single crystals with amorphous implanted layers of different thickness after ruby laser single pulse irradiation (Q-switched ruby laser) pulse length 50 nsecs). Measurement technique RBS.

After Foti(93).
This is an order of magnitude higher than the values measured following conventional thermal annealing at 900°C. The mobilities\(^{144-148}\) lie in the range from 300 to 800 cm\(^2\)/V.s which are lower than the values expected from gallium arsenide layers (Sze and Irvin\(^{160}\)) with the same carrier concentrations.

Electrical profiles were broader than the theoretical profiles indicating that diffusion of the dopants occurred during laser annealing\(^{144,146-148}\). This is in agreement with the change in atomic profiles of tellurium measured by Golovchenko et al\(^{141}\) and Sealy et al\(^{146}\). The diffusion coefficient of Te in GaAs estimated by Gamo et al\(^{149}\) was reported to be approximately \(10^{-6}\) cm\(^2\)/s and from this it was suggested that annealing took place via liquid phase epitaxy.

Laser annealing of gallium arsenide implanted with various ion doses\(^{148}\) of Se, indicated that low dose implants, doses less than \(10^{14}\) ions/cm\(^2\), do not anneal as well as high dose implants when irradiated with similar energy densities. The conclusion is that amorphous layers anneal better than crystalline or partially crystalline layers\(^{148}\). This is in disagreement with the findings of Woodcock et al\(^{145}\) and Sealy\(^{146}\), who were able to anneal GaAs samples which were partially crystalline or crystalline.

Transmission electron microscopy and Rutherford backscattering measurements carried out by Sealy et al\(^{146}\) suggested that gallium arsenide samples irradiated without Si\(_3\)N\(_4\) coatings do not recrystallize perfectly. At an energy
density of about 1.3 J/cm$^2$ samples were almost defect free, however at lower energy densities there were large numbers of defects present. Gamo et al (149) using RBS, C-V and DLTS reported that during laser irradiation with 0.64 J/cm$^2$ of the uncapped GaAs samples, a very small amount (several monolayers) of arsenic and gallium evaporated from the surface. However the effect of the GaAs surface decomposition was found to be insignificant.

Kim et al (150) carried out ellipsometry and Hall measurements on laser annealed gallium arsenide samples implanted with $1 \times 10^{15}$ ions/cm$^2$ of C, Te, Ge and Mg ions. After irradiating with a Q-switched ruby laser they reported that the energy density threshold was 0.2 J/cm$^2$ and 0.3 J/cm$^2$ when estimated by ellipsometry and sheet resistivity measurements respectively.

Annealing of ion implanted gallium arsenide using a Nd:YAG laser in the energy density range from 0.2 to 2.5 J/cm$^2$ was investigated by Liu et al (151). For silicon implanted into GaAs in the dose range $3 \times 10^{14}$ to $3 \times 10^{15}$ ion/cm$^2$, the sheet concentration was 2 to 5 times higher than that obtained by thermal annealing. However electron mobility was low and samples implanted with low doses (less than $10^{14}$ ions/cm$^2$) were either partially active or not active at all. SIMS profiling indicated that no appreciable broadening of the impurity profile occurred as a result of laser annealing up to an energy density of 1 J/cm$^2$. 
Kachurin et al\textsuperscript{(120)} and Fan et al\textsuperscript{(152)} used scanning Ar and Nd:YAG lasers respectively to anneal ion implanted gallium arsenide. They found that the laser scan-rate and the temperature of the substrate during laser irradiation were very important. For a dose of 1x10\textsuperscript{14} Se\textsuperscript{+}/cm\textsuperscript{2} implanted at 400 keV, the best results obtained at a scan-rate of 0.53 mm/s and the substrate temperature of 580\textdegree C\textsuperscript{(152)}. Electrical activity of 59\% and sheet mobility of 1300 cm\textsuperscript{2}/V.s was reported\textsuperscript{(152)}.

Tsu et al\textsuperscript{(153)} investigated laser induced damage of tellurium implanted gallium arsenide by using a frequency doubled Nd:YAG laser. RBS measurements showed that perfect recrystallization of the amorphous GaAs and slight diffusion of Te into gallium arsenide occurred following irradiation with overlapping pulses of 0.2 J/cm\textsuperscript{2}. Above this energy density additional humps in the RBS spectrum appeared, which they thought were due to laser induced damage and also to the loss of arsenic near the gallium arsenide surface.

Raman scattering measurements suggested\textsuperscript{(153)} that the best energy density for good crystal regrowth lies between 0.18 J/cm\textsuperscript{2} and 0.26 J/cm\textsuperscript{2}. Below this energy density there exists a mixture of polycrystalline and disordered GaAs, while above the threshold density, disorder seems to increase. The conclusion was that decomposition of the GaAs occurs during laser irradiation\textsuperscript{(153)}. 
Frequency doubled Nd:glass laser was employed by Venkatesen et al.\(^{(154)}\), in studies of surface crystallinity and stoichometry of Te implanted gallium arsenide. Using time resolved reflectivity and channelling measurements they showed that loss of arsenic occurs during laser annealing. However by optimising the duration of the liquid melt it is possible to laser anneal the implanted layers in uncapped GaAs with good surface crystallinity and minimum loss of As due to surface decomposition\(^{(154)}\).

In conclusion the published results indicate that the threshold energy density for annealing gallium arsenide is much lower than that required for annealing silicon of the same amorphous layer thickness \(E_{\text{th}} \text{GaAs} = \frac{1}{2} E_{\text{th}} \text{Si}\).

Both capped and uncapped GaAs implanted with Se, Te, Ge, Si and Sn can be recrystallized perfectly and up to 90% of the implanted atoms can be incorporated on lattice sites, using Q-switched ruby and Nd:YAG laser irradiation. Good electrical activation (up to 40% for a dose of \(1 \times 10^{15}\) ions/cm\(^2\)) and high peak concentrations (\(\sim 10^{19}\) cm\(^{-3}\)) were reported. However the measured mobilities were found to be low (approximately 300 to 800 cm\(^2/V.s\)).

The diffusion of ion implanted tellurium in GaAs was observed and the estimated diffusion coefficient was reported to be consistent with molten GaAs.

Finally we at Surrey\(^{(102)}\) have shown that the decomposition of both Si\(_4\)N\(_4\) capped and uncapped GaAs occurred during laser annealing (this will be discussed further in section 5.3).
(b) Laser Fabrication of Ohmic Contacts on GaAs

(i) Introduction

The performance of almost all GaAs devices (for example lasers, solar cells, IMPATT diodes and FETs) is critically dependent on the quality of their contacts. The conventional technique for formation of such contacts consists of evaporation of say Ni-Au-Ge layers and subsequent thermal alloying at temperatures of 100 to 500°C. Some of the problems associated with this conventional technique are the formation of high contact resistance, poor edge definition and surface roughness. Also, during metallization the whole of the sample or device is subjected to the alloying temperature and this may seriously degrade the properties of the device. However some of these problems can be alleviated using pulsed laser irradiations as a processing technique.

(ii) Ohmic Contacts

Formation of ohmic contacts on \( \text{III} - \text{V} \) compound semiconductors using a focused laser beam was initially reported by Pounds et al\(^{155}\). Since then a number of groups\(^{156-159}\) have fabricated ohmic contacts on gallium arsenide layers and on GaAs devices, using pulsed or continuous wave lasers.

Barnes et al\(^{156}\) produced ohmic contacts by implanting 50 keV, \(1 \times 10^{16} \text{ Te}^+ / \text{cm}^2\) into n-type GaAs followed by laser annealing using a Q-switched Nd:YAG laser.
Margalit et al (157) and Gold et al (158) fabricated ohmic contacts by evaporating a thin layer of Au-Ge on to n-type gallium arsenide, followed by laser alloying using a ruby laser in the Q-switched mode and in the freely generated mode respectively.

Eckhardt et al (159) produced ohmic contacts on GaAs layers and on FETs by using several different evaporated metal combinations such as AuGe, AuGe-Au, AuGe-Ni-Au, prior to laser alloying. Lasers used included Q-switched ruby both in the single mode and the multimode, multimode Nd:YAG, CW CO\textsubscript{2} and CW scanning Ar laser. The continuous wave laser seemed to produce the best results.

In general the above mentioned investigations reported that the laser processed ohmic contacts on gallium arsenide can have excellent surface morphology, superior dimensional control and excellent contact properties. The specific contact resistance obtained by laser processing are summarised in table 2.1. The best contact resistance of 2x10\textsuperscript{-6} ohms-cm\textsuperscript{2} was obtained by Gold et al (158), which is an order of magnitude lower than the best value of 5x10\textsuperscript{-5} ohms-cm\textsuperscript{2} obtained using the conventional process.

2.2.4 Summary

In general the published results have shown that, ion implanted silicon and gallium arsenide, and deposited layers on Si, can be recrystallized using pulsed ruby, Nd:YAG and continuous wave Ar and Kr lasers.
TABLE 2.1

The best results on ohmic contact formation reported by several groups (155-159):

<table>
<thead>
<tr>
<th>Reference No.</th>
<th>GaAs Substrate Parameters</th>
<th>Specific Contact Resistance ($\Omega \cdot \text{cm}^2$)</th>
<th>Laser Energy Density J/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>155</td>
<td>Te 4.6.10$^{17}$ Zn 1.5.10$^{19}$</td>
<td>5 x 10$^{-4}$</td>
<td>0.05-20</td>
</tr>
<tr>
<td>156</td>
<td>Si 3 x 10$^{18}$</td>
<td>2 x 10$^{-5}$</td>
<td>2.5</td>
</tr>
<tr>
<td>157</td>
<td>Sn 3 x 10$^{16}$</td>
<td>7 x 10$^{-5}$</td>
<td>1.02</td>
</tr>
<tr>
<td>158</td>
<td>Si 7 x 10$^{16}$ Sn 1 x 10$^{17}$</td>
<td>2 x 10$^{-6}$</td>
<td>15</td>
</tr>
<tr>
<td>159</td>
<td>Si 2 x 10$^{17}$</td>
<td></td>
<td>0.2-3.0</td>
</tr>
<tr>
<td>159</td>
<td>Sn 7 x 10$^{16}$ Te 10$^{17}$-10$^{18}$</td>
<td>1 x 10$^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>

* Conventional alloying process.
For silicon it has been established that in the case of ruby and Nd:YAG lasers, regrowth occurs in the liquid phase. The regrown layer is free of defects, dopant profiles are consistent with diffusion in the liquid and equilibrium solid solubilities can be exceeded.

In the case of CW Ar and Kr laser irradiations, solid phase regrowth occurs from the amorphous-single crystal interface and no dopant redistribution takes place during this process if the solid solubility is not exceeded.

Up to 100% of the ion implanted impurity atoms in silicon and gallium arsenide can be incorporated on substitutional lattice sites and made electrically active using laser irradiation.

In GaAs, laser irradiation was shown to be a very useful and efficient technique for producing ohmic contacts, either from deposited layers or from high dose implants. Furthermore results have established that gallium arsenide can be annealed without a capping layer, however there is evidence of surface decomposition.
3. EXPERIMENTAL TECHNIQUES

3.1 Material Preparation

In most of the experimental work the material used was bulk n-type or SI gallium arsenide with a \(<100>\) orientation. A small amount of epitaxial material was also used for some comparative experiments. The properties of the materials used are shown in table 3.1.

The bulk grown GaAs material was in the form of ingots which were sawn into wafers approximately 1.5 mm thick using a slow speed circular saw. The slices were cleaned in warm trichloroethylene and methanol and then mounted on quartz discs. Polishing was done on a Hyprocel Pellon Pan-W pad with a 4\% bromine-methanol solution, for approximately twenty minutes. Following this step the slices were transferred to a rotating beaker assembly and free etched in 1\% bromine-methanol solution for about 5 to 10 minutes, to remove residual surface damage. These polished slices were diced into 4x8 mm\(^2\) samples using a diamond-impregnated wire saw and subsequently degreased in warm trichloroethylene. Finally the samples were dipped in boiling methanol in order to obtain residue free surfaces.

3.2 Ion Implantation

All implants were carried out on the 90 degree beam line of the Department's 600 keV heavy ion accelerator\(^{(161)}\).
<table>
<thead>
<tr>
<th>INGOT NUMBER</th>
<th>SUPPLIER</th>
<th>ORIENTATION</th>
<th>TYPE</th>
<th>CARRIER CONCENTRATION ((\text{cm}^{-3}))</th>
<th>MOBILITY ((\text{cm}^2/\text{V}\cdot\text{s}))</th>
<th>RESISTIVITY ((\Omega\cdot\text{cm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>X156</td>
<td>MCP</td>
<td>100</td>
<td>Bulk n-type</td>
<td>1.1 \times 10^{-6}</td>
<td>3500</td>
<td>-</td>
</tr>
<tr>
<td>X152/1</td>
<td>MCP</td>
<td>100</td>
<td>n-type</td>
<td>1.1 \times 10^{-6}</td>
<td>3500</td>
<td>-</td>
</tr>
<tr>
<td>X158/2</td>
<td>MCP</td>
<td>100</td>
<td>n-type</td>
<td>8.5 \times 10^{-7}</td>
<td>3500</td>
<td>-</td>
</tr>
<tr>
<td>X124.12/1</td>
<td>MCP</td>
<td>100</td>
<td>n-type</td>
<td>1.3 \times 10^{-7}</td>
<td>3500</td>
<td>-</td>
</tr>
<tr>
<td>X2054</td>
<td>MCP</td>
<td>100</td>
<td>Bulk SI</td>
<td>10 \times 10^{-8}</td>
<td>3600</td>
<td>-</td>
</tr>
<tr>
<td>MR</td>
<td>MR</td>
<td>100</td>
<td>Bulk SI</td>
<td>10 \times 10^{-8}</td>
<td>3600</td>
<td>-</td>
</tr>
<tr>
<td>PIESSEY</td>
<td>100</td>
<td>Epi. n-type</td>
<td>Epi. n-type</td>
<td>7.1 \times 10^{-6}</td>
<td>108 \times 10^{-8}</td>
<td>-</td>
</tr>
</tbody>
</table>

This table lists the material used in this work.

SI: Semi-insulating
Epi: Epitaxially grown
Prior to implantation the samples were rinsed first in hydrochloric acid and then in methanol in order to remove any surface films that may have formed, since the presence of these could result in an inhomogeneous implanted region.

Implantation of zinc and cadmium was carried out at room temperature and at 200°C, in a direction at 8° to the \( \langle 100 \rangle \) surface normal to minimise channelling effects. The implant energies were 150 keV for Cd, 60 keV, 150 keV and 450 keV for Zn. The implant doses were \( 1 \times 10^{15} \) ion/cm\(^2\) and \( 1 \times 10^{13} \) to \( 1 \times 10^{15} \) ions/cm\(^2\) for cadmium and zinc respectively. The majority of samples were implanted at a dose rate in the range 0.2-0.4 \( \mu A/cm^2 \) and the pressure in the target chamber during implantation was about \( 1-2 \times 10^{-6} \) torr.

3.3. **Encapsulation**

After implantation, most of the samples were encapsulated to prevent out-diffusion of the dopant atoms and decomposition of the gallium arsenide. The two main encapsulants used were evaporated aluminium (Al) and silicon nitride (Si\(_3\)N\(_4\)).

3.3.1. **Aluminium (Al)**

Aluminium encapsulation layers were deposited by evaporating Al from a tungsten filament. The samples were held at room temperature and the evaporation was carried out in vacuum of \( 1-5 \times 10^{-6} \) torr. Following evaporation the
thickness of the encapsulant, measured using a Rank Taylor
Hobson talystep, was found to vary from run to run from
0.9 μm to 3 μm.

After annealing, the aluminium layer was dissolved
by soaking in hot concentrated HF acid for about one minute,
followed by rinsing in distilled water and then in methanol.

3.3.2 Silicon Nitride (Si₃N₄)

The nitride deposition system was very similar to
the one described by Donnelly(162) (shown in Fig. 3.1).
The deposition procedure employed was as follows:

The GaAs sample was loaded on to the carbon heater
strip, the chamber was pumped down to 0.1 torr and then
flushed with nitrogen. The sample was baked for five
minutes at 200°C in flowing nitrogen before the introduction
of the silane, since silane can react at room temperature
with trace amounts of oxygen in the system. The ammonia
and silane flow rates were then established. These flow-
rates, along with the deposition temperature determined the
deposition rate. The flowrates used were 200 Scc/min,
400 Scc/min and 1000 Scc/min of SiH₄, NH₃ and N₂
respectively. After a steady state condition was established
the sample was heated from 200°C to the growth temperature
(700 or 750°C) for fifteen seconds. The time to reach the
growth temperature was about seven seconds, after which the
growth continued for a further period of eight seconds.
Fig. 3.1

The $Si_3N_4$ Apparatus. From Donnelly (162).
The sample was cooled and thickness typically about 1000 Å of the Si$_3$N$_4$ film was assessed from the colour of the film.

Some of the earlier Si$_3$N$_4$ grown films were found to contain a large amount of oxygen which was due to a small air leak in the system. However the later films were oxygen free and the ratio of about 3:4 of silicon to nitrogen was measured using Rutherford backscattering technique.

After annealing, the Si$_3$N$_4$ film was dissolved by soaking in a concentrated HF acid, followed by a rinse in distilled water and then in methanol.

3.4 **Annealing**

Three different annealing techniques were employed:

(a) Conventional Thermal Annealing.

(b) Thermal Pulse Annealing.

(c) Laser Annealing.

3.4.1 **Conventional Thermal Annealing**

Conventional annealing of the samples was performed in a flowing nitrogen atmosphere in a resistivity heated furnace. The annealing temperature was in the range from 300 to 800°C and the annealing time was either five minutes or fifteen minutes. Isothermal annealing was performed at 700°C for a period from 5 to 60 minutes.
The annealing procedure employed was as follows:

After setting the required temperature and the nitrogen flowrate, the furnace reached equilibrium in about one hour. The sample was placed on a quartz boat and pushed into the hot zone of the furnace. The temperature was monitored with two thermocouples attached to the quartz boat. After the required annealing period the sample was removed from the hot zone and allowed to cool.

The measured temperature was accurate to ± 5°C. The annealing times refer to the time the samples spent in the hot zone of the furnace, and include a period of about two minutes to reach the annealing temperature.

3.4.2 Thermal Pulse Annealing

Thermal pulse annealing was carried out in the Si$_3$N$_4$ deposition apparatus shown in Fig. 3.1. Following the Si$_3$N$_4$ deposition the sample was heated from 200°C to 900°C for thirty seconds in flowing nitrogen. The time to reach 900°C was about twelve seconds after which the annealing continued for a further period of about 18 seconds. The annealing temperature quoted is accurate to ± 1.5%, this includes an overshoot in the temperature of about 10°C.

3.4.3 Laser Annealing

Laser annealing of samples coated with Si$_3$N$_4$ and with no Si$_3$N$_4$ coating was carried out using both a freely generated mode and a Q-switched mode ruby laser.
(i) **Freely Generated Mode**

All the laser irradiations with a freely generated mode ruby laser were carried out at NPL, Teddington. The wavelength was $0.6943 \, \mu m$ and the pulse duration 0.8 milliseconds. Energy densities were in the range from $0.2 \, J/cm^2$ to $12 \, J/cm^2$ and the energy of each pulse was measured using an energy monitor.

The multimode beam was converted (suppressed) to a single mode ($TEM_{00}$) beam by inserting a 2 mm diameter aperture into the resonator. The 2 mm diameter beam was magnified to 4 mm diameter using lenses. The values of the beam diameter quoted corresponds to the measured burnt spot on the photographic film following exposure of this film to the laser pulse. The laser energy values quoted are the average energy values per pulse, however, the peak energy per pulse may be two or three times the measured value. This is due to the gaussian cross-section of the laser beam and pulse and the superimposed spikes on the pulse.

(ii) **Q-switched Mode**

Initial annealing using a Q-switched ruby laser was carried out in the Electrical Engineering Department at the City University, London, but the final experiments were performed using our own laser (see Fig. 3.2).
Fig. 3.2 The Surrey University Laser.
Laser energy densities used were in the range from 0.2 J/cm$^2$ to 2.6 J/cm$^2$ per pulse and the pulse duration was 15 or 25 nanoseconds. The laser was always operated at the maximum output and this was attenuated either using a beam splitter or with a set of filters. Each filter transmits 60% of the input and so it was possible to obtain energy densities as low as 0.2 J/cm$^2$. The beam spot used was either 4 mm, 5 mm or 8 mm in diameter and it was measured as described earlier. The result of exposing a photographic film to the laser beam indicated that the beam from the laser at City University was approximately elliptical in shape. In contrast the beam from the Surrey laser was circular and a set of apertures ranging from 1 mm to 8 mm were used to define the beam diameter.

For all the experiments carried out using Surrey's laser, the energy of each pulse was measured using an energy monitor. The energy monitor comprises a head unit which is fitted to the laser and a separate display unit. The head consists of a 45° quartz beam splitter, an aluminium diffusing reflector, a photodiode and a filter assembly. The beam splitter picks off approximately 10% of the laser output and sets up a photocurrent in the photodiode. The system operates by integrating the photocurrent generated in the photodiode on a capacitor and displays the peak voltage achieved with each laser pulse. The relationship between the voltage and the laser pulse energy is made linear by operating with a reversed biassed voltage on the
photodiode and therefore the display unit indicates the measured energy directly in joules. The energy values quoted are accurate to about ± 10%.

3.5 Ohmic Contacts

For Hall effect measurements ohmic contacts to the implanted layers were required and the following systems were investigated:

(a) Indium-zinc alloy (99:1% in wt.).
(b) Cadmium
(c) Gold
(d) Gold-zinc alloy (90:10% in wt.)
(e) Indium
(f) Gallium-indium alloy (75:25% in wt.)

Out of all these, evaporated gold was found to give the best results. Therefore gold was used for ohmic contacts during the course of this work. The procedure used is described below:

Initially the central region of the clover leaf shape sample was covered with a small 2 mm diameter steel mask. Gold was evaporated under vacuum of about 2x10^-6 torr on to the front surface of the sample held at room temperature. However it was found that with this method, a thin gold layer was also formed on the side faces of the sample as well as on the front surface. Subsequently
small steel masks of clover leaf shape were made with a 1 mm hole in each corner of the clover leaf and these were used to define the contact areas. No subsequent alloying cycle was used or was needed in this system. After evaporation, ohmic contacts were checked with a curve tracer.

Prior to deposition of ohmic contacts each sample was boiled in toluene and then in methanol to ensure that the sample surface was clean and free of dirt.

3.6 Measurement Techniques

3.6.1 The Four-Point Probe

The four-point probe technique is one of the most useful methods of measuring resistivity as it is quick to use and requires minimum sample preparation.

The four-point probe (Fig. 3.3) comprised four equally spaced metal probes which were pressed onto the semiconductor surface. The current was passed through the two outer electrodes and floating potential measured across the inner pair. Fig. 3.3b shows the experimental circuit schematically.

The sheet resistivity of an infinite thin layer in which the current flows parallel to the surface is 

\[ \rho_{\text{sheet}} = \frac{1}{\rho_{\text{bulk}}} \] 

\[ \frac{1}{\rho_{\text{sheet}}} = \frac{1}{\rho_{\text{bulk}}} \] 

(Smits)\textsuperscript{(163)}:  

\[ \rho_s = \frac{n \cdot V}{\log_e 2 \cdot I} \quad (3.1) \]

Where: \( I \) is the current flowing between the outer probes.

: \( V \) is the voltage measured across the inner probes.

Equation 3.1 becomes:

\[ \rho_s = 4.53 \frac{V}{I} \quad (3.2) \]

For a rectangular shape sample (shown in Fig. 3a) with dimensions \( a \) and \( d \) and with symmetrical probe arrangements with spacings, \( s \), between the probes, the sheet resistivity is (Smits):\(^{163}\):

\[ \rho_s = \frac{V}{I} \cdot C \left( \frac{a}{d} ; \frac{d}{s} \right) \quad (3.3) \]

This becomes:

\[ \rho_s = \frac{V}{I} \cdot C \quad \ldots \ldots \ldots \ldots \quad (3.4) \]

Where \( C \) is the correction factor obtained from tables (Smits).\(^{163}\).

The current source used was a Keithley Instrument Model 225, which enabled the desired current to be digitally selected in the range from 7 nA to 70 mA. The floating voltage was measured using a Solatron A 200 DVM. Sheet resistivity values measured are accurate to about \( \pm 50\% \).
(a) model used for four-point probe resistivity measurements

(b) Circuit used for sheet resistivity measurements

Fig. 3.3. Four-point probe.
3.6.2 Hall Measurement Technique

3.6.2.1 Introduction

The Hall effect and sheet resistivity were measured in order to determine the carrier concentration and mobility profiles.

3.6.2.2 Theory

Hall (164) discovered that when a magnetic field is applied at right angles to the current flow an electric field is set up in a direction perpendicular to both the direction of the magnetic field and the current flow (Fig. 3.4).

(a)
Relative direction of current and magnetic field.

(b)
Conducting material in x-y plane

Fig. 3.4.
If in an extended medium the current density is $J_x$, the magnetic field $B_z$ and Hall electrical field $E_y$, then the Hall coefficient is defined by the equation:

$$E_y = R_H J_x B_z$$

Where $R_H$ is the Hall coefficient.

In 1958 Van der Pauw(165) showed that the specific resistivity and Hall effect of a flat sample of arbitrary shape could be measured without knowing the current pattern if the following conditions are fulfilled:

(a) The contacts are at the circumference of the sample.
(b) The contacts are sufficiently small.
(c) The sample is homogeneous in thickness.
(d) The surface of the sample is singly connected, i.e. the sample does not have isolated holes.
Sheet Resistivity

Consider a sample which fulfils the above conditions and has four contacts A, B, C and D (Fig. 3.5), then the resistivity is given by (165):

\[ \rho = \frac{\pi d}{\ln 2} \cdot \frac{R_{AB,CD} + R_{BC,DA}}{2} \cdot f \quad \ldots \quad (3.6) \]

where \( d \) = specimen thickness.

The resistance \( R_{AB,CD} \) is defined as the potential difference between contacts C and D for unit current through A and B.

i.e. \( R_{AB,CD} = \frac{V_{CD}}{I_{AB}} \)

and similarly \( R_{BC,DA} = \frac{V_{DA}}{I_{BC}} \)

and \( f \) is a function of the ratio \( \frac{R_{AB,CD}}{R_{BC,DA}} \) only and satisfies the relation (165):

\[ \frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} = f \ \text{arc sinh} \ \frac{\exp(\ln \frac{2}{f})}{2} \quad \ldots \quad (3.7) \]

In an ideal situation \( R_{AB,CD} = R_{BC,DA} \) and \( f = 1 \).
Generally sheet resistivity is measured. So:

\[ \rho_s = \frac{\rho}{d} = \frac{\pi}{2n^2} \cdot \frac{R_{AB,CD} + R_{BC,DA}}{2} \cdot f \]

instead of bulk resistivity.

\[ \therefore \quad \rho_s = \frac{\pi}{2n^2} \cdot \frac{R_{AB,CD} + R_{BC,DA}}{2} \cdot f \quad \ldots \quad (3.8) \]

**Hall Coefficient**

The Hall coefficient can be obtained by measuring the change in \( R_{BD,AC} \) caused by applying a magnetic field normal to the surface and is given by:

\[ R_H = \frac{d \cdot \Delta R_{BD,AC}}{B} \]

Here again sheet Hall coefficient is usually measured.

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

\[ \therefore \quad R_{HS} = \frac{\Delta R_{BD,AC}}{B} \quad \ldots \quad (3.9) \]

**Hall Mobility**

Having obtained \( \rho_s \) and \( R_{HS} \), the Hall mobility \( \mu_H \) can be calculated using:

\[ \mu_H = \frac{R_H}{\rho} = \frac{R_{HS}}{\rho_s} = \mu_s \quad \ldots \quad (3.10) \]
This Hall mobility must be distinguished from the conductivity mobility:

\[ \mu = \frac{1}{ne\rho} \quad \ldots \quad (3.11) \]

These two mobilities are related by the Hall scattering factor

\[ r = \frac{\mu_H}{\mu} \quad \ldots \quad (3.12) \]

**Carrier Concentration**

Having obtained \( R_H \) or \( R_{HS} \), the carrier concentration can be calculated as follows:

\[ n = \frac{r}{e R_H} \quad \text{or} \quad \frac{r}{e R_{HS}} \quad \text{or} \quad p_s \quad \ldots \quad (3.13) \]

The theoretical value of \( r \) depends upon the scattering mechanism and impurity concentration (167-169). It is generally assumed that the conductivity and Hall mobilities are equal in implanted layers. Use of this assumption might lead to a 15% error in \( n_s \) (170).

**Layer Removal Measurements**

In an ion implanted sample the carrier concentration and carrier mobility are depth dependent and both the sheet carrier concentration and sheet mobility are weighted averages.
In 1958 Petritz\(^{(171)}\) showed that where there is a depth dependence in the concentration of carriers, the Hall coefficient can be expressed as a summation of the average values of carrier concentration, \(n_i\) and mobility \(\mu_i\), in \(i\)th layers of thickness \(d_i\). Assuming that there are no circulating currents and that the Hall and conductivity mobility in the \(i\)th layer are equal:

\[
R_H = \frac{d \sum n_i \mu_i^2 d_i}{e(\sum n_i \mu_i d_i)^2} \quad \ldots \quad (3.14)
\]

\[
R_{HS} = \frac{R_H}{d}
\]

The conductivity is expressed by

\[
\sigma = \left(\frac{e}{d}\right) \sum n_i \mu_i d_i \quad \ldots \quad (3.15)
\]

\[
\rho_s = (\sigma d)^{-1}
\]

where \(d = d_i\) and \(n_i\) and \(\mu_i\) are the carrier concentration and mobility in the \(i\)th layer.

The effective Hall mobility is given by:

\[
\mu_H (\mu_{eff}) = \frac{\sum n_i \mu_i^2 d_i}{\sum n_i \mu_i d_i} \quad \ldots \quad (3.16)
\]

\[
\rho_s = \frac{R_{HS}}{R_H}
\]
From this expression, it can be seen that the effective Hall mobility is weighted by the contribution of layers with higher mobility in a different manner than the conductivity mobility $\mu$

$$\mu = \frac{\sum_i n_i \mu_i d_i}{\sum_i n_i d_i} \quad \ldots \quad (3.17)$$

This can lead to lower values of sheet carrier concentration ($n_\text{s}$ or $p_\text{s}$) than would be found from the number $N_\text{d}$ given by $\sum_i n_i d_i$.

In 1966 Buehler\textsuperscript{(172)} pointed out that a more accurate value of $N$ can be determined from the combination of stripping techniques and Hall measurements. The number of carriers in the $i$th layer and their mobility can be found from:

$$\frac{(R_{\text{SH}})_i}{(\rho_s)_i^2} - \frac{(R_{\text{SH}})_i + 1}{(\rho_s)_i^2 + 1} = e n_i \mu_i^2 d_i \quad \ldots \quad (3.18)$$

and

$$\frac{1}{(\rho_s)_i} - \frac{1}{(\rho_s)_i + 1} = e n_i \mu_i d_i \quad \ldots \quad (3.19)$$

giving

$$\mu_i = \frac{\Delta \left[ \frac{R_{\text{SH}}}{\rho_s^2} \right]_i}{\Delta (\frac{1}{\rho_s})_i} \quad \ldots \quad (3.20)$$

and

$$n_i = \frac{\Delta (\frac{1}{\rho_s})_i}{e d_i \mu_i} \quad \ldots \quad (3.21)$$
The quantities \((R_{SH})_i\) and \((\rho_s)_i\) are the sheet Hall coefficient and sheet resistivity measured following the \(i\)th layer removal.

3.6.2.3 Profile Measurement Procedure

For profile measurements, the Van der Pauw geometry\(^{165}\) (clover leaf shapes) was used. Electrical isolation was achieved by forming a p-n junction in the samples or by implanting into SI GaAs. The schematic diagram of the measurement circuit is shown in Fig. 3.6.

As mentioned earlier, to obtain the sheet resistivity of a specimen using the Van der Pauw equation, (equation 3.8) required the measurement of voltage and current in two different configurations with a third necessary to determine the Hall coefficient. Generally the procedure adopted was to keep the current through the specimen constant during the measurements and only monitor the voltage developed between the required pair of contacts.

For greater accuracy, instead of just the basic set of three measurements mentioned above, readings were also taken with the constant current reversed to compensate for slightly non-linear contacts and also with the direction of the magnetic field reversed to reduce the effect of misalignment of the specimen contacts with the field. This required a total of twelve measurements. Our system had a manually operated switching relay box to run through the sequence of measurements which follows the scheme set out below:-
Fig. 3.6  The schematic diagram of the Hall measurement circuit
<table>
<thead>
<tr>
<th>SEQUENCE</th>
<th>CONSTANT CURRENT</th>
<th>MEASURED VOLTAGE</th>
<th>MAGNETIC FIELD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$+ I_{AB}$</td>
<td>$V_{CD}$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>$+ I_{BC}$</td>
<td>$V_{AD}$</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>$+ I_{BD}$</td>
<td>$V_{AC}$</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$+B$</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$-B$</td>
</tr>
<tr>
<td>7</td>
<td>$- I_{AB}$</td>
<td>$V_{DC}$</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>$- I_{BC}$</td>
<td>$V_{DA}$</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>$- I_{BD}$</td>
<td>$V_{CA}$</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$+B$</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$-B$</td>
</tr>
</tbody>
</table>

The clover-shaped sample.

These readings were fed into a computer (calculator) which calculated values for the sheet Hall coefficient ($R_{HS}$), the sheet resistivity ($\rho_s$), the carrier concentration ($n_s$), the sheet mobility ($\mu_s$) using the equations stated earlier (3.8, 3.9, 3.10 and 3.13).

After a set of twelve measurements, the sample was etched in a solution of concentrated sulphuric acid +
hydrogen peroxide + water in the volume ratio 1:1:125, which was agitated continuously with a magnetic stirrer to ensure homogeneity.

The GaAs sample to be stripped was then immersed for typically one minute in the solution which removes about 300 Å of surface material. After rinsing in water to remove all traces of the etchent, the specimen was placed in the sample holder in a beaker of distilled water (this maintained the sample at a constant temperature and also reduced errors due to thermomagnetic effects) and the twelve voltage measurements made as described above. This stripping and measuring cycle was continued until the DVM voltage reading became too unstable.

After the final strip, the specimen was cleaned and the etch rate calculated by measuring the step height using a Rank Taylor Hobson Talystep. Depth profiles of volume carrier concentration (n) and mobility (μ) were computed using calculated etch rate and the values of R_{HS} and ρ_s obtained previously for each etch step (equations 3.20 and 3.21).

3.6.3. **Rutherford Backscattering Analysis Technique**

3.6.3.1 **Rutherford Backscattering**

Rutherford backscattering is an established versatile and non-destructive technique which is being applied increasingly to material surface analysis. It has been widely used for the analysis of semiconductors. Some
of the applications include, location of implanted ions, the extent and density of radiation-induced crystalline disorder, the identification of surface contaminants, monitoring changes in stoichiometry of compounds, obtaining diffusion profiles and examining the effects of annealing. Recently Rutherford backscattering has found applications in new areas such as corrosion science, environmental pollution studies and super conducting film technology.

In this present work the Rutherford backscattering was used for measuring the density of radiation induced crystalline disorder and to examine the effects of annealing.

Several excellent publications \(^{(173-175)}\) have been written concerning the Rutherford backscattering technique. The principle behind the technique is that when a flux of high energy charged particles impinges on a target, some of these projectile ions undergo large angle scattering due to coulombic electrostatic repulsion. The energy of the scattered projectile is always less than its original incident energy. The yield of the projectile ions backscattered into the detector is given by:

\[ Y = N_2 \Phi \sigma R \theta \]

where: \( N_2 \) is the number of target atoms per unit area.
\( \Phi \) is the number of incident ions (He\(^+\)).
\( \theta \) is the solid angle of the detector.
\( \sigma R \) is the Rutherford backscattering cross-section.
From the knowledge of the yield and energy spectrum of the backscattered particles a quantitative information on the atomic composition (of the material under examination) as a function of depth can be obtained. Full description of the equations and the method used for identifying surface constituents and the depth distribution is given by Butcher(176).

In the case of a crystalline target the incident ion beam can be aligned to a crystallographic axis so that channelling occurs. This results in a marked attenuation in the backscattering yield. For a channelled beam large angle scattering is mainly due to interactions with first row atoms not sitting on normal lattice sites. Gradual dechannelling of the beam occurs due to interactions with the lattice atoms as it penetrates the crystal. Therefore the aligned backscattering spectrum can yield information about the atom location and the relative density of the crystalline damage.

In this work, crystalline damage is defined in two different ways:

(i) The quantity of damage is defined as the area under the damaged peak in the aligned spectrum and this is denoted by $X_D$. For an amorphous material $X_D$ is assumed to be 100%.

(ii) The damage is defined as the ratio of the yield integrated over 50 channels behind the damaged peak of the channelled spectrum to the non-channelled spectrum. This is denoted by $X_{\text{min}}$. 
The percentage of atoms which lie on substitutional lattice sites can be determined from the equation:

\[
\text{Percentage substitutional on lattice sites} = \left( 1 - \frac{Y_a}{Y_r} \right) \times 100
\]

where the backscattering yields between the incident beam and the dopant atoms for a channelled and non-channelled incident are denoted by \(Y_a\) and \(Y_r\) respectively.

3.6.3.2 Experimental Details

All the backscattering experiments were carried out on the Department's 2 MeV Van de Graaff accelerator\(^*\).

Figure 3.7 illustrates the experimental set up. Samples were mounted on a 3-axis goniometer in a vacuum chamber which was connected to the beam line. The Van de Graaff provided a 1.5 MeV monoenergetic beam of He ions which impinged on the sample. The backscattered particles detected by the surface barrier detector mounted at 150° to the incident beam (Fig. 3.7). The detector produced signals whose amplitudes were proportional to the energy of each backscattered particle within its field of view. The output of the detector was fed to an amplifier and a pulse height analyser which amplified and processed the data. This was displayed as a spectrum on a CRT screen, or it was recorded in analogue or digital form.
Fig. 3.7 Schematic of Rutherford backscattering Experimental set up
Backscattered spectra were obtained for <100> channelled and non-channelled directions. Each spectrum was taken using a beam current of 2 to 4 nA and the charge collected was either 3 µC or 6 µC. The detector used was an Ortec detector having an energy resolution of 13 keV at FWHM.

For channelling experiments the samples were carefully oriented using the two goniometer controls, $\phi$ and $\theta$ corresponding to the two axis respectively. The backscattered yields were also recorded on an x-ray recorder. The goniometer movement was controlled remotely and had a minimum incremental angular advance of 0.01°. To obtain a channelling direction the sample was carefully adjusted remotely using the $\phi$ and $\theta$ controls, until the chart-recorder indicated a minimum in the backscattered yield.

Instability of the beam energy, counting statistics and pulse pile-up can all contribute to an error in this technique, which was estimated to be about 10 to 20%. 
4.1 Introduction

This chapter is divided into four sections and presents the results of an investigation into the properties of ion implanted gallium arsenide. The first section describes the electrical and the physical properties of thermally annealed zinc implanted GaAs. Sections two and three illustrate the effects of high energy short pulses from a freely generated mode ruby laser and Q-switched ruby laser respectively on the properties of Zn implanted gallium arsenide. The final section describes the properties of cadmium implanted GaAs obtained using Rutherford back-scattering, the Hall effect and sheet resistivity measurements following thermal and laser pulse annealing.

The discussion and interpretation of results will be given in chapter five.

4.2 ELECTRICAL AND PHYSICAL PROPERTIES OF THERMALLY ANNEALED ZINC IMPLANTED GALLIUM ARSENIDE

4.2.1 Annealing Temperature Dependence at 150 keV

In this section the results of annealing in the temperature range 300 to 900°C of 150 keV zinc ions implanted into gallium arsenide at room temperature to a dose of 1x10^{15} ions/cm^2 are presented in the following order:
(a) Electrical Measurements.

(b) Rutherford Backscattering Measurements.

(c) Transmission Electron Microscopy Measurements.

(a) Electrical Measurements

Four-point probe measurements (Fig. 4.1 and table 4.1) showed that the sheet resistivity went through a maximum as the annealing temperature increased from 300°C to 900°C and a peak value of approximately 1x10^6 Ω/□ was measured after annealing at 400°C. Sheet resistivities of about 500 Ω/□ and 100 Ω/□ were recorded after annealing at 700°C and at 900°C respectively.

Sheet electrical properties obtained using Hall effect measurements (table 4.2) indicated that after annealing at 650, 700 or at 800°C, the sheet hole concentration was in the range 1-1.6.10^14 holes/cm^2 and sheet mobilities between 87 and 105 cm^2/V.s. However after annealing at 900°C the sheet hole concentration increased to about 8.6x10^14 holes/cm^2 and the sheet mobility became approximately 96 cm^2/V.s.

The sheet resistivity values measured using a four-point probe and the Van der Pauw technique, after annealing at 650°C and above, were in good agreement (Fig.4.1). The attempts to measure sheet resistivity using the Van der Pauw technique following annealing in the temperature range 300-600°C, were unsuccessful. This was mainly due to the difficulty in making good ohmic contacts to the implanted layers.
Fig. 4.1 Sheet resistivity as a function of annealing temperature for zinc implanted gallium arsenide.
### TABLE 4.1

**Sheet Resistivity as a Function of Annealing Temperature for 150 keV Zn⁺ into GaAs**

Dose: $1.10^{15}$ Ions/cm²

<table>
<thead>
<tr>
<th>Annealing Temp &amp; Time (°C/Min)</th>
<th>Implant Temp. (°C)</th>
<th>Encapsulation</th>
<th>Sheet Resistivity $(\Omega/\square) \rho_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Anneal</td>
<td>R.T.</td>
<td>None</td>
<td>$1.72 \times 10^4$</td>
</tr>
<tr>
<td>No Anneal</td>
<td>200°C ± 10°C</td>
<td>None</td>
<td>$7.8 \times 10^3$</td>
</tr>
<tr>
<td>300/15</td>
<td>R.T.</td>
<td>None</td>
<td>$4.4 \times 10^5$</td>
</tr>
<tr>
<td>400/15</td>
<td>R.T.</td>
<td>None</td>
<td>$1.16 \times 10^6$</td>
</tr>
<tr>
<td>500/15</td>
<td>R.T.</td>
<td>Al</td>
<td>$4.0 \times 10^4$</td>
</tr>
<tr>
<td>600/15</td>
<td>R.T.</td>
<td>Al</td>
<td>$1.08 \times 10^3$</td>
</tr>
<tr>
<td>650/15</td>
<td>R.T.</td>
<td>Al</td>
<td>$6.48 \times 10^2$</td>
</tr>
<tr>
<td>700/15</td>
<td>R.T.</td>
<td>Al</td>
<td>$5.4 \times 10^2$</td>
</tr>
<tr>
<td>800/5</td>
<td>R.T.</td>
<td>Al</td>
<td>$6.4 \times 10^2$</td>
</tr>
<tr>
<td>900/30 sec.</td>
<td>R.T.</td>
<td>Si₃N₄</td>
<td>$1.0 \times 10^2$</td>
</tr>
</tbody>
</table>

(FOUR POINT PROBE MEASUREMENTS)

Estimated error in $T_a$: ± 5°C

$\rho_s$ : ± 50%
### TABLE 4.2

**Sheet electrical properties as a function of annealing temperature of 150 keV 1.10^{15} Zn⁺/cm² implanted into GaAs at room temperature.**

<table>
<thead>
<tr>
<th>Annealing Temperature &amp; Time (°C/min)</th>
<th>Encapsulation</th>
<th>Sheet Electrical Properties</th>
<th>Electrical Activity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \rho_s (\text{cm}^{-2}) )</td>
<td>( \mu_s (\text{cm}^2/\text{V.Sec}) )</td>
</tr>
<tr>
<td>650/15</td>
<td>Al</td>
<td>1.6 .10^{14}</td>
<td>87</td>
</tr>
<tr>
<td>* 700/15</td>
<td>Al</td>
<td>1.6 .10^{14}</td>
<td>88</td>
</tr>
<tr>
<td>800/5</td>
<td>Al</td>
<td>1.2 .10^{14}</td>
<td>105</td>
</tr>
<tr>
<td>** 900/30 sec.</td>
<td>Si₂N₄</td>
<td>8.6 .10^{14}</td>
<td>96</td>
</tr>
</tbody>
</table>

* mean of two measurements  
** mean of four measurements  
Estimated error in  
\( T_a: \pm 5\% \)  
\( \rho_s: \pm 28\% \)  
\( \mu_s: \pm 14\% \)  
\( \rho (\Omega/\square): \pm 2\% \)
As the annealing temperature increased from 650°C to 800°C the electrical profiles became marginally narrower and peak carrier concentration decreased slightly (Fig. 4.2). The peak hole concentration was about $10^{19}$ holes/cm$^3$. Annealing at 900°C resulted in a peak carrier concentration of about $1.5 \times 10^{19}$ holes/cm$^3$ and the profile was very broad compared with those measured following anneals at 650°C to 800°C. This indicates that diffusion of zinc probably occurred at temperatures above 800°C.

Mobilities obtained were about 70 to 200 cm$^2$/V.s (fig. 4.2), after annealing in the temperature range 650°C to 900°C and a minimum near a depth at which the maximum hole concentration occurred.

(b) Rutherford Backscattering Measurements

The aligned spectrum for the as-implanted sample (Fig. 4.3) reached the random level and thus indicated that the implanted layer was amorphous over a depth of about 2000 Å. The spectrum of the sample annealed at 300°C showed that some recovery of crystallinity had occurred at the interface between the amorphous layer and the underlying crystal. This was indicated by the shift in the rear edge of the aligned spectrum towards the GaAs surface. As the annealing temperature was raised, significant reordering of the crystal occurred, as indicated by the continuous reduction in the damaged peak and also by the progressive regrowth from the backface. Annealing in the range 600 to 700°C resulted in a rapid recovery of crystallinity but the backscattering yield
Fig. 4.2 Hole concentration and mobility profiles as a function of annealing temperature for 150 keV 1.10^{15} \text{Zn}^+/\text{cm}^2 into GaAs. $T_i = \text{R.T.}$
was still high compared to unimplanted gallium arsenide, showing that the implanted layers had contained a high level of residual disorder. The aligned spectra were identical for anneals at 700°C and 800°C but annealing at 900°C resulted in a spectrum which was very similar to the unimplanted and unannealed GaAs.

As the annealing temperature increased from 300°C to 600°C, $X_{\text{min}}$ gradually decreased (Fig. 4.4) and above this temperature it was found to drop rapidly indicating another annealing stage in the range 600°C to 700°C. Following annealing at 900°C for 30 seconds, $X_{\text{min}}$ was found to be 4%, which is the same as that for good single crystal GaAs.

Finally $X_D$ behaves in a similar manner to $X_{\text{min}}$ over the annealing temperature range of 300 to 900°C (Fig. 4.4, table 4.3).

(c) Transmission Electron Microscopy

Recrystallization of the amorphous layer formed by the implantation process was structurally studied using transmission electron microscopy. All TEM analyses (sections 4.2.1c and 4.4.3) were carried out in collaboration with the research group (Dr. D. Sadana and Dr. R. Booker) at University of Oxford.

The detailed information about regrowth and residual damage following each anneal step was obtained using cross-section and plan-view TEM specimens. For the plan-view specimens, the thinning was performed from the unimplanted
Fig. 4.3 Rutherford backscattering spectra as a function of annealing temperature for zinc implanted GaAs.
(1.5 MeV He⁺ backscattered). 1 - As implanted (unannealed), 2 - 300°C, 3 - 400°C, 4 - 500°C, 5 - 600°C,
6 - 650°C, 7 - 700°C/800°C, 8 - 900°C/30 sec./Virgin GaAs.
Fig. 4.4 Damage parameters ($X_{\text{min}}$ and $X_D$) as a function of annealing temperature for 150 keV, $1.10^{15}$Zn$^+$/cm$^2$ into GaAs. (RBS measurements).
<table>
<thead>
<tr>
<th>ANNEALING TEMP &amp; TIME (°C/min)</th>
<th>IMPLANT TEMP. (°C)</th>
<th>ENCAPSULATION</th>
<th>$X_{\text{min}}$ (%)</th>
<th>$X_D$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO ANNEAL</td>
<td>R.T.</td>
<td>NONE</td>
<td>58</td>
<td>100</td>
</tr>
<tr>
<td>NO ANNEAL 200 ± 10°C</td>
<td>NONE</td>
<td>9</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>300/15</td>
<td>R.T.</td>
<td>56</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>400/15</td>
<td>R.T.</td>
<td>51.4</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>500/15</td>
<td>R.T.</td>
<td>Al</td>
<td>41</td>
<td>43</td>
</tr>
<tr>
<td>600/15</td>
<td>R.T.</td>
<td>Al</td>
<td>34.6</td>
<td>24</td>
</tr>
<tr>
<td>650/15</td>
<td>R.T.</td>
<td>Al</td>
<td>12.5</td>
<td>9.7</td>
</tr>
<tr>
<td>700/15</td>
<td>R.T.</td>
<td>Al</td>
<td>5.2</td>
<td>2.7</td>
</tr>
<tr>
<td>800/5</td>
<td>R.T.</td>
<td>Al</td>
<td>5.4</td>
<td>2.7</td>
</tr>
<tr>
<td>900/30 sec.</td>
<td>R.T.</td>
<td>Si$_3$N$_4$</td>
<td>4.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Estimated error $T_a : ± 5°C$, $X_{\text{min}} : ± 5\%$, $X_D : ± 2\%$
side only and micrographs obtained from areas sufficiently thick to include all the damage. All specimens were tilted to two-beam conditions for a 220 type reflection and bright field micrographs recorded. In addition, transmission electron diffraction (TED) patterns were obtained from plan-view specimens. The results are summarized below:

For the unannealed specimen, the TED patterns (Fig. T4.1b inset) showed diffuse rings, indicative of amorphous material. From the cross-section micrograph (Fig. T4.1a) the thickness of the amorphous layer was estimated to be about 1600 Å, which is in reasonable agreement with the RBS data (Fig. 4.2).

Following anneal in the range 300°C to 500°C the micrographs (Fig. T4.2a,b and T4.3a,b) showed a similar structure. Damage in the form of dislocation tangles and Moiré fringes was observed (table T4.1). The TED patterns indicated twinned and single crystal structure suggesting imperfect recrystallization.

After annealing at 500 to 600°C the crystallinity was found to be improved i.e. decrease in the number of twins and wider spaced fringes (Fig. T4.4 and table T4.1).

Annealing at 700°C or at 800°C produced similar results again in agreement with RBS measurements. The TED patterns indicated single crystal structure (Fig.T4.5b inset) however the electron micrographs (Fig. T4.5b) showed dislocation lines and small loops of about 100 to 200 Å diameter.
### TABLE T4.1

*PROPERTIES OF 150 keV, $1.10^{15}$ Zn$^+$ IONS/cm$^2$ INTO GaAs T1 = R.T.*

<table>
<thead>
<tr>
<th>Annealing Temp ($^\circ$C)</th>
<th>Encapsulation</th>
<th>Electrical Activity (%)</th>
<th>$X_{\text{min}}$ (%) ±0.5</th>
<th>Transmission Electron Microscopy Measurements - Observations</th>
<th>Electron Micrographs</th>
<th>Electron Diffraction Pattern</th>
<th>Fig.No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>--</td>
<td>0</td>
<td>58</td>
<td>Amorphous 1600Å</td>
<td>Amorphous</td>
<td></td>
<td>T4.1</td>
</tr>
<tr>
<td>300/15</td>
<td>--</td>
<td>0</td>
<td>56</td>
<td>Very fine dislocation tangles</td>
<td>Twins</td>
<td></td>
<td>T4.2</td>
</tr>
<tr>
<td>400/15</td>
<td>--</td>
<td>0</td>
<td>51.4</td>
<td>Very fine dislocation tangles</td>
<td>Twins</td>
<td></td>
<td>Not Shown</td>
</tr>
<tr>
<td>500/15</td>
<td>Al</td>
<td>0</td>
<td>41.0</td>
<td>Narrow Moiré fringes</td>
<td>Twins</td>
<td></td>
<td>T4.3</td>
</tr>
<tr>
<td>600/15</td>
<td>Al</td>
<td>0</td>
<td>34.6</td>
<td>Wider fringes</td>
<td>Twins</td>
<td></td>
<td>T4.4</td>
</tr>
<tr>
<td>650/15</td>
<td>Al</td>
<td>16</td>
<td>12.5</td>
<td>Wider fringes</td>
<td>Twins</td>
<td></td>
<td>Not shown</td>
</tr>
<tr>
<td>700/15</td>
<td>Al</td>
<td>16</td>
<td>5.2</td>
<td>Dislocations</td>
<td>No twins</td>
<td></td>
<td>T4.5</td>
</tr>
<tr>
<td>800/8</td>
<td>Al</td>
<td>12</td>
<td>5.4</td>
<td>Dislocations</td>
<td>No twins</td>
<td></td>
<td>Not shown</td>
</tr>
<tr>
<td>900/30 ( \text{sec.} )</td>
<td>Si$_3$N$_4$</td>
<td>86</td>
<td>4.0</td>
<td>Few dislocations</td>
<td>Perfect recrystallization</td>
<td>T4.6</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** The table data is formatted in a tabular structure, listing the annealing temperature, encapsulation material, electrical activity, minimum transmission electron microscopy measurement, and the corresponding electron micrographs and electron diffraction patterns along with their respective figures.
Unannealed

Fig. T4.1
Ann Temp = 300°C

Fig. T4.2
Ann Temp = 500°C

Fig. T4.3
Ann Temp = 600°C

Plan, DF

Plan, BF

Cross-Section

surface

Fig. T4.4
Ann Temp = 700°C

Plan

Cross-Section

Fig. T4.5
Almost perfect structure was observed (Fig. T4.6) at 900°C anneal, with the exception of a few loops in the range 100-2000 Å diameter (table T4.1).

In summary the TEM measurements indicated that the as implanted sample was amorphous and an annealing temperature of 900°C was needed for perfect recrystallization. This is consistent with the Rutherford backscattering measurements.

4.2.2 Implant Energy Dependence (60-450 keV) for a Dose of 1x10^{15} Zn^+ /cm^2

For room temperature implanted samples the sheet hole concentration (Fig. 4.6) was found to be independent of the implant energy and the annealing temperature in the range 650°C to 800°C. However, for samples implanted at 200°C, the sheet hole concentration increased from about 2x10^{14} holes/cm^2 to approximately 7x10^{14} holes/cm^2, as the implant energy was raised from 60 keV to 450 keV (Fig. 4.6 and table 4.4).

As the ion energy increased from 60 to 450 keV, the peak hole concentration was found to decrease in magnitude, its depth below the surface increased and so the peak became closer to the LSS range (Fig. 4.7 and table 4.5). A similar variation with energy was observed, both for room temperature and for 200°C implants as well as for the three annealing temperatures of 650°C, 700°C and 800°C. Furthermore electrical activities calculated by integrating the area under each of the carrier distribution profiles in Fig. 4.7 were in good agreement with the measured values (table 4.5).
Ann Temp = 900°C

**Plan**

**Cross-Section**

Fig. T4.6
Fig. 4.6 Sheet hole concentration and mobility as a function of ion energy for $1 \times 10^{15}$ Zn$^+$/cm$^2$ into GaAs. Cap-Al.
### Table 4.4

**Electrical Activity as a Function of Annealing Temperature for $1 \times 10^{15}$ Zn/cm² Implanted at Energies of 60, 150 and 450 keV. Cap - Al.**

<table>
<thead>
<tr>
<th>IMPLANT TEMP. ($^\circ$C)</th>
<th>IMPLANT ENERGY (keV)</th>
<th>ELECTRICAL ACTIVITY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60</td>
<td>650$^\circ$C ± 5$^\circ$C</td>
</tr>
<tr>
<td>R.T.</td>
<td>60</td>
<td>15, 17</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>16, 17</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>14, 15</td>
</tr>
<tr>
<td>200 ± 10$^\circ$C</td>
<td>60</td>
<td>15, 15</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>24, 27</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>44, 48</td>
</tr>
</tbody>
</table>
Fig. 4.7 Hole concentration and mobility profiles as a function of implant energy for $1 \times 10^{15}$ Zn$^+$ /cm$^2$ into GaAs. $T_i = R.T.,$ Cap-Al, $T_a = 800^\circ$C/5 mins.
### TABLE 4.5

**ELECTRICAL PROPERTIES OF ZINC IMPLANTED GaAs**

\[ T_i = \text{R.T}, \ T_a = 600^\circ\text{C}/5 \text{ mins.} \ \text{Dose} = 1.10^{15} \text{ ions/cm}^2, \ \text{Cap - Al} \]

Estimated error in \( \bar{p} \): \( \pm 20\% \), \( d_1 \): \( \pm 5\% \), \( p_s \): \( \pm 28\% \), \( \mu_s \): \( \pm 14\% \)

<table>
<thead>
<tr>
<th>IMPLANT ENERGY (keV)</th>
<th>PEAK HOLE CONCENTRATION ( \bar{p} ) (cm(^{-3})) *</th>
<th>DEPTH OF PEAK ( d_1 ) (\AA)</th>
<th>SHEET CARRIER CONCENTRATION ( p_s ) (cm(^{-2}))</th>
<th>ELECTRICAL ACTIVITY (%)</th>
<th>MEASURED</th>
<th>CALCULATED</th>
<th>SHEET HOLE MOBILITY (\mu_s) (cm(^2)/V･sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>(1.2.10^{19})</td>
<td>700</td>
<td>(1.15.10^{14})</td>
<td>12</td>
<td>12</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2.28.10^{20})</td>
<td>(263)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>(7.8.10^{18})</td>
<td>1000</td>
<td>(1.17.10^{14})</td>
<td>12</td>
<td>12</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.37.10^{20})</td>
<td>(595)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>(5.5.10^{18})</td>
<td>1600</td>
<td>(1.64.10^{14})</td>
<td>16</td>
<td>15</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(5.57.10^{19})</td>
<td>(1775)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Values in brackets refer to L.S.S. peak hole concentration and L.S.S. range. (mean of two measurements).

### TABLE 4.6

**ELECTRICAL PROPERTIES OF ZINC IMPLANTED GaAs AS A FUNCTION OF IMPLANT DOSE RATE (ION BEAM CURRENT) \( E = 150 \text{ keV}, \ T_i = \text{R.T.}, \ \text{DOSE} = 1.10^{15} \text{ IONS/cm}^2 \)**

\[ \text{Cap - Al, } T_a = 700^\circ\text{C}/15 \text{ min.} \]

Estimated error in \( p_s \): \( \pm 28\% \), \( \mu_s \): \( \pm 14\% \), \( \rho_s \): \( \pm 2\% \)

| BEAM CURRENT (\(\mu\)A) | IMPLANT DOSE RATE (\(\mu\)A/cm\(^2\)) | \( p_s \) (cm\(^{-2}\)) | \( \mu_s \) (cm\(^2\)/V･s) | \( \rho_s \) (\(\Omega\)/\(\Omega\)) | ELECTRICAL ACTIVITY (\(\%\)) |
|--------------------------|---------------------------------------|-----------------|-----------------|-----------------|---------|-----------|
| 0.1                      | 0.04                                  | \(1.3.10^{14}\) | 80              | 594             | 13      |
|                          |                                       | \(1.1.10^{14}\) | 88              | 627             | 11      |
| 0.87                     | 0.35                                  | \(8.5.10^{13}\) | 91              | 809             | 9       |
| 0.95                     | 0.38                                  | \(1.0.10^{14}\) | 85              | 705             | 10      |
|                          |                                       | \(9.6.10^{13}\) | 93              | 699             | 10      |
| 3.5                      | 1.4                                   | \(1.1.10^{14}\) | 94              | 626             | 11      |
| 9.0                      | 3.6                                   | \(1.0.10^{14}\) | 89              | 687             | 10      |
|                          |                                       | \(1.0.10^{14}\) | 75              | 814             | 10      |

Estimated error in Beam current: \( \pm 0.02 \mu\)A
4.2.3 Implant Temperature Dependence for a Dose of $1 \times 10^{15}$ Zn$^+$/cm$^2$ (60, 450 keV)

At the low implant energy (60 keV) the profiles were very similar both for implants at room temperature and for 200°C, however a peak in the profile was found to be much deeper than the LSS range (Fig. 4.8).

For high energy implants (450 keV), much broader profiles and higher peak carrier concentrations were obtained when the samples were implanted at 200°C rather than at room temperature (Fig. 4.8). Peak hole concentrations of about $4.7 \times 10^{18}$ holes/cm$^3$ and $8.5 \times 10^{18}$ holes/cm$^3$ were measured after annealing at 650°C for the cold (RT) and hot (200°C) implanted samples respectively.

Mobilities lie in the range 60 to 180 cm$^2$/V.s with slightly higher mobilities being measured from samples implanted cold (Fig. 4.8).

A similar trend to Fig. 4.8 was observed following annealing at 700°C and at 800°C of the hot and cold implants.

The above results suggest that at low energy, that is 60 keV, the profile broadening is independent of the implant temperature, whereas at high energy, that is 450 keV, it is dependent on the implant temperature.

4.2.4 Dose Rate Dependence at 150 keV for $1 \times 10^{15}$ Zn$^+$/cm$^2$

The implant was carried out at room temperature using a beam current in the range from 0.1 μA to 9.0 μA, which
Fig. 4.8 Hole concentration and mobility profiles for $1 \times 10^{15} \text{Zn}^+/\text{cm}^2$ into GaAs. Cap-Al.
corresponds to a dose rate of 0.04 μA/cm² to 3.6 μA/cm². Following implantation, samples were encapsulated using evaporated aluminium prior to annealing at 700°C for fifteen minutes.

Hall effect and sheet resistivity measurements (Fig. 4.9) showed that the hole concentration and sheet mobility were independent of the implant dose rate in the range 0.04 μA/cm² to 3.6 μA/cm². The carrier concentration and mobility profiles, over the dose rate investigated were found to be identical.

4.2.5 Dose Dependence of 200°C Implant (150 keV)

The sheet hole concentration increased with increasing dose up to a dose of 1x10¹⁴ ions/cm² and above this dose it reached a constant value of about 1.4x10¹⁴ and 3.4x10¹⁴ holes/cm² after annealing at 650°C and 700°C respectively (Fig. 4.10). However, the sheet mobility was found to remain fairly constant with increasing dose and annealing temperature (Fig. 4.10). Below a dose of 1x10¹⁴ ions/cm² electrical activity was about 70 to 100% while sheet mobility was about 50 to 100 cm²/V.s (table 4.7).

Hole concentration and mobility profiles (Fig. 4.11) showed that, following annealing at 700°C for fifteen minutes, the peak hole concentration increased with increasing dose. As the dose was incremented from 5x10¹³ to 1x10¹⁵ ions/cm² the peak hole concentration increased from about 5x10¹⁸ to 1.5x10¹⁹ holes/cm³ and the profiles became broader. The
Sheet hole concentration and mobility as a function of implant dose rate for 150 keV, $1 \times 10^{15}$ Zn$^+$/cm$^2$. $T_i$ = RT, Cap-Al. $T_a$ = 700°C/15 minutes.
Fig. 4.10  Sheet hole concentration and sheet mobility as a function of dose for 150 keV Zn⁺ ions into GaAs. Cap-Al.
mobilities were found to lie in the range from 40 to 120 cm²/V.s with a minimum near a depth at which maximum hole concentration occurred. Furthermore it was observed that up to a dose of 5x10¹⁴ ions/cm² the peak in the profile was at the LSS range and above this dose it was at a much greater depth than predicted by LSS theory.

Similar results to Fig. 4.11 were observed after annealing at 650°C for fifteen minutes, but the peak hole concentration in this case was slightly lower.

4.2.6 Dose Dependence at High Energy (450 keV) for Hot and Cold Implants.

(a) Sheet Measurements

After annealing the room temperature implanted samples at 800°C for five minutes, the sheet hole concentration was found to increase with increasing dose and reached an approximately constant value of (1-1.7)x10¹⁴ holes/cm² above a dose of 1.10¹⁴ ions/cm² (Fig. 4.12). Below a dose of 1.10¹⁴ ions/cm² the electrical activity was 80 to 100% (table 4.8). The sheet mobility was in the range 90 to 120 cm²/V.s and was almost independent of ion dose.

The electrical activity of samples implanted at 200°C and annealed at 650°C or at 700°C for fifteen minutes (Fig. 4.12) increased linearly with increasing dose. The net electrical activity was 70 to 90% for doses up to 1x10¹⁴ ions/cm² and about 70% up to a dose of 1x10¹⁵ ions/cm².
Fig. 4.11 Hole concentration and mobility profiles as a function of dose for zinc implanted GaAs. Cap-Al, $T_i = 200^\circ C$, $T_a = 700^\circ C/15$ mins.
### Table 4.7

Sheet electrical properties as a function of ion dose for 150 keV Zn⁺ implanted into GaAs at $T_i = 200°C$. Cap - Al

<table>
<thead>
<tr>
<th>ANNEAL TEMP.</th>
<th>ION DOSE (cm⁻²)</th>
<th>SHEET ELECTRICAL PROPERTIES</th>
<th>ELECTRICAL ACTIVITY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$p_s$(cm⁻²)</td>
<td>$μ_s$(cm²/V·sec)</td>
<td>$ρ_s$(Ω·cm)</td>
</tr>
<tr>
<td>5.10¹³</td>
<td>4.6.10¹³</td>
<td>57</td>
<td>2.3.10³</td>
</tr>
<tr>
<td></td>
<td>4.3.10¹³</td>
<td>81</td>
<td>1.8.10³</td>
</tr>
<tr>
<td>1.10¹⁴</td>
<td>5.8.10¹³</td>
<td>66</td>
<td>1.6.10³</td>
</tr>
<tr>
<td></td>
<td>5.3.10¹³</td>
<td>72</td>
<td>1.6.10³</td>
</tr>
<tr>
<td>5.10¹⁴</td>
<td>1.1.10¹⁴</td>
<td>71</td>
<td>831</td>
</tr>
<tr>
<td></td>
<td>1.2.10¹⁴</td>
<td>60</td>
<td>849</td>
</tr>
<tr>
<td>650/15</td>
<td>1.5.10¹⁴</td>
<td>42</td>
<td>1.1.10³</td>
</tr>
<tr>
<td></td>
<td>1.3.10¹⁴</td>
<td>58</td>
<td>847</td>
</tr>
<tr>
<td></td>
<td>2.4.10¹⁴</td>
<td>64</td>
<td>403</td>
</tr>
<tr>
<td></td>
<td>2.7.10¹⁴</td>
<td>78</td>
<td>318</td>
</tr>
<tr>
<td></td>
<td>2.2.10¹⁴</td>
<td>66</td>
<td>429</td>
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<td></td>
<td>1.2.10¹⁴</td>
<td>67</td>
<td>762</td>
</tr>
<tr>
<td></td>
<td>1.1.10¹⁴</td>
<td>74</td>
<td>730</td>
</tr>
<tr>
<td>5.10¹³</td>
<td>5.0.10¹³</td>
<td>118</td>
<td>9.93.10²</td>
</tr>
<tr>
<td></td>
<td>5.0.10¹³</td>
<td>104</td>
<td>1.1.10³</td>
</tr>
<tr>
<td>1.10¹⁴</td>
<td>7.7.10¹³</td>
<td>102</td>
<td>795</td>
</tr>
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<td></td>
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<td>743</td>
</tr>
<tr>
<td></td>
<td>8.4.10¹³</td>
<td>110</td>
<td>673</td>
</tr>
<tr>
<td></td>
<td>8.4.10¹³</td>
<td>112</td>
<td>660</td>
</tr>
<tr>
<td>700/15</td>
<td>5.10¹⁴</td>
<td>2.3.10¹⁴</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>2.1.10¹⁴</td>
<td>71</td>
<td>431</td>
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<tr>
<td></td>
<td>3.6.10¹⁴</td>
<td>45</td>
<td>376</td>
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<tr>
<td></td>
<td>3.7.10¹⁴</td>
<td>58</td>
<td>286</td>
</tr>
<tr>
<td></td>
<td>1.8.10¹⁴</td>
<td>79</td>
<td>428</td>
</tr>
</tbody>
</table>

### Table 4.8

Sheet electrical properties of 450 keV zinc implanted GaAs as a function of dose. $T_i = R.T.$ Cap - Al

<table>
<thead>
<tr>
<th>ANNEAL TEMP.</th>
<th>ION DOSE (cm⁻²)</th>
<th>SHEET ELECTRICAL PROPERTIES</th>
<th>ELECTRICAL ACTIVITY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$p_s$(cm⁻²)</td>
<td>$μ_s$(cm²/V·sec)</td>
<td>$ρ_s$(Ω·cm)</td>
</tr>
<tr>
<td>5.10¹³</td>
<td>3.96.10¹³</td>
<td>121</td>
<td>1.23.10³</td>
</tr>
<tr>
<td></td>
<td>4.15.10¹³</td>
<td>107</td>
<td>1.41.10³</td>
</tr>
<tr>
<td>800</td>
<td>1.10¹⁴</td>
<td>8.57.10¹³</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td>1.0.10¹⁴</td>
<td>94</td>
<td>649</td>
</tr>
<tr>
<td>5.10¹⁴</td>
<td>1.87.10¹⁴</td>
<td>106</td>
<td>314</td>
</tr>
<tr>
<td></td>
<td>1.76.10¹⁴</td>
<td>109</td>
<td>322</td>
</tr>
<tr>
<td>700</td>
<td>5.10¹⁴</td>
<td>5.54.10¹³</td>
<td>110</td>
</tr>
<tr>
<td>650</td>
<td>1.10¹⁵</td>
<td>1.39.10¹⁴</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>1.54.10¹⁴</td>
<td>86</td>
<td>466</td>
</tr>
<tr>
<td>700</td>
<td>1.10¹⁵</td>
<td>2.2.10¹⁴</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2.17.10¹⁴</td>
<td>101</td>
<td>284</td>
</tr>
<tr>
<td>800</td>
<td>1.10¹⁵</td>
<td>9.48.10¹³</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>1.64.10¹⁴</td>
<td>118</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>1.19.10¹⁴</td>
<td>126</td>
<td>414</td>
</tr>
</tbody>
</table>

Estimated error. $T_s : \pm 5\%$, $p_s : \pm 28\%$ $μ_s : \pm 14\%$, $ρ_s : \pm 25\%$
However the activity was lower after annealing at 650°C, being about 50% for doses of $5 \times 10^{13}$ to $1 \times 10^{15}$ ions/cm$^2$ (table 4.9). The sheet mobility was 70 to 100 cm$^2$/V.s at both annealing temperatures.

By comparing the measured sheet hole concentrations, it is observed that up to a dose of $1 \times 10^{14}$ ions/cm$^2$, results from hot (200°C) and cold (RT) implants are very similar after annealing at 700°C or at 800°C. However above this dose, the sheet hole concentration measured from room temperature implanted samples saturates between (1-2)$\times 10^{14}$ holes/cm$^2$, while for samples implanted at 200°C, it continues to increase approximately linearly (Fig. 4.12).

(b) **Electrical Profiles**

For samples implanted at room temperature prior to annealing at 800°C for five minutes, the peak hole concentration (Fig. 4.13) increased as the dose was raised from $5 \times 10^{13}$ to $1 \times 10^{15}$ ions/cm$^2$. The maximum value recorded was about $6.2 \times 10^{18}$ holes/cm$^3$. The mobilities were found to drop from about 170 cm$^2$/V.s near the surface to a minimum of 90 cm$^2$/V.s at about 1770 Å and rise to approximately 220 cm$^2$/Vs deeper in (Fig. 4.13). Furthermore as the ion dose increased the profiles broadened but the peak occurred very close to the LSS range.

For doses up to $1 \times 10^{14}$ ions/cm$^2$ the profiles recorded from samples implanted at 200°C followed by annealing at 700°C (Fig. 4.14) were similar to those obtained
Fig. 4.12  Sheet hole concentration and mobility as a function of ion dose for 450 keV Zn implanted GaAs. Cap-Al.
from room temperature implanted samples annealed at 800°C (Fig. 4.13). However for doses above $1 \times 10^{14}$ ions/cm$^2$ the profiles obtained from samples implanted hot (200°C) were very broad compared with those samples implanted cold (RT). The peak hole concentration was in excess of $1 \times 10^{19}$ holes/cm$^3$, which is much higher than the maximum value for cold implants. The mobilities were higher for cold implants than those measured from hot implants (Figs. 4.13 and 4.14).

The above results suggest that broadening of the carrier profiles is probably due to the increasing diffusion effects as the ion dose increased and is most evident at $1 \times 10^{15}$ ions/cm$^2$ and an implant temperature of 200°C (Fig. 4.14).

4.2.7 The Time Dependence of Annealing at 450 keV

For a dose of $1 \times 10^{15}$ ions/cm$^2$, the effect of varying the annealing time from 5 to 60 minutes at 700°C on the sheet hole concentration and mobility profiles was investigated (Figs. 4.15 and 4.16). The samples were implanted with 450 keV zinc ions at 200°C and annealed using aluminium as the encapsulant.

The sheet hole concentration increased approximately linearly as the annealing time increased from 5 to 15 minutes (Fig. 4.15). When the annealing time was longer than fifteen minutes the sheet hole concentration decreased. The sheet mobility was in the range from 70 to 100 cm$^2$/V.s and improved slightly with increasing annealing time.
Fig. 4.13 Hole concentration and mobility profiles as a function of dose for Cold Zn implanted GaAs. Cap-Al.
Fig. 4.14 Hole concentration and mobility profiles as a function of dose for zinc implanted GaAs at 200°C. \( T_a = 700^\circ C/15 \) mins. Cap-Al.
### Table 4.9

**ELECTRICAL PROPERTIES AS A FUNCTION OF ION DOSE AND**
**ANNEALING TEMPERATURE FOR 450 keV ZINC IONS IMPLANTED**
**INTO GaAs. \( T_a = 200^\circ\text{C}. \) Cap - Al.**

<table>
<thead>
<tr>
<th>ANNEAL TEMP. (°C)</th>
<th>ION DOSE (cm(^{-2}))</th>
<th>SHEET ELECTRICAL PROPERTIES</th>
<th>ELECTRICAL ACTIVITY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>( 5.10^{13} )</td>
<td>( 2.67.10^{13} )</td>
<td>( 92 ) ( \mu_s ) ( \mu_s ) ( 2.53.10^3 ) ( 53 )</td>
</tr>
<tr>
<td></td>
<td>( 1.10^{14} )</td>
<td>( 5.05.10^{13} )</td>
<td>( 103 ) ( \mu_s ) ( \mu_s ) ( 1.19.10^3 ) ( 50 )</td>
</tr>
<tr>
<td></td>
<td>( 5.10^{14} )</td>
<td>( 3.18.10^{14} )</td>
<td>( 76 ) ( \mu_s ) ( \mu_s ) ( 257 ) ( 63 )</td>
</tr>
<tr>
<td></td>
<td>( 9.16.10^{13} )</td>
<td>( 97 ) ( \mu_s ) ( \mu_s ) ( 699 ) ( 18 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 1.10^{15} )</td>
<td>( 4.86.10^{14} )</td>
<td>( 83 ) ( \mu_s ) ( \mu_s ) ( 162 ) ( 48 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 4.37.10^{14} )</td>
<td>( 80 ) ( \mu_s ) ( \mu_s ) ( 176 ) ( 43 )</td>
</tr>
<tr>
<td>700</td>
<td>( 5.10^{14} )</td>
<td>( 4.12.10^{13} )</td>
<td>( 102 ) ( \mu_s ) ( \mu_s ) ( 1.48.10^3 ) ( 82 )</td>
</tr>
<tr>
<td></td>
<td>( 1.10^{14} )</td>
<td>( 6.55.10^{13} )</td>
<td>( 60 ) ( \mu_s ) ( \mu_s ) ( 1.58.10^3 ) ( 65 )</td>
</tr>
<tr>
<td></td>
<td>( 5.10^{14} )</td>
<td>( 3.8.10^{14} )</td>
<td>( 71 ) ( \mu_s ) ( \mu_s ) ( 232 ) ( 76 )</td>
</tr>
<tr>
<td></td>
<td>( 3.5.10^{14} )</td>
<td>( 78 ) ( \mu_s ) ( \mu_s ) ( 210 ) ( 70 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 1.10^{15} )</td>
<td>( 7.29.10^{14} )</td>
<td>( 73 ) ( \mu_s ) ( \mu_s ) ( 116 ) ( 73 )</td>
</tr>
<tr>
<td></td>
<td>( 5.75.10^{14} )</td>
<td>( 72 ) ( \mu_s ) ( \mu_s ) ( 150 ) ( 58 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 7.29.10^{14} )</td>
<td>( 68 ) ( \mu_s ) ( \mu_s ) ( 140 ) ( 73 )</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>( 1.10^{15} )</td>
<td>( 5.1.10^{14} )</td>
<td>( 85 ) ( \mu_s ) ( \mu_s ) ( 143 ) ( 51 )</td>
</tr>
<tr>
<td></td>
<td>( 4.6.10^{14} )</td>
<td>( 88 ) ( \mu_s ) ( \mu_s ) ( 153 ) ( 46 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 5.54.10^{14} )</td>
<td>( 84 ) ( \mu_s ) ( \mu_s ) ( 148 ) ( 55 )</td>
<td></td>
</tr>
</tbody>
</table>

*Estimated error: \( T_a : \pm 5^\circ\text{C}. \) \( p_s : \pm 28\% \) \( \mu_s : \pm 14\% \) \( p_s : \pm 2\% \)*

### Table 4.10

**ELECTRICAL PROPERTIES OF 450 keV ZINC IMPLANTED GaAs**
**AS A FUNCTION ANNEALING TIME. \( T_a = 200^\circ\text{C}. \) Cap - Al.**

<table>
<thead>
<tr>
<th>ANNEALING TIME (MINS)</th>
<th>SHEET ELECTRICAL PROPERTIES</th>
<th>ELECTRICAL ACTIVITY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>( 2.59.10^{14} )</td>
<td>( 78 ) ( \mu_s ) ( \mu_s ) ( 306 ) ( 26 )</td>
</tr>
<tr>
<td></td>
<td>( 2.74.10^{14} )</td>
<td>( 79 ) ( \mu_s ) ( \mu_s ) ( 288 ) ( 27 )</td>
</tr>
<tr>
<td>10</td>
<td>( 4.2.10^{14} )</td>
<td>( 78 ) ( \mu_s ) ( \mu_s ) ( 190 ) ( 42 )</td>
</tr>
<tr>
<td></td>
<td>( 4.6.10^{14} )</td>
<td>( 80 ) ( \mu_s ) ( \mu_s ) ( 169 ) ( 46 )</td>
</tr>
<tr>
<td>15</td>
<td>( 5.76.10^{14} )</td>
<td>( 72 ) ( \mu_s ) ( \mu_s ) ( 150 ) ( 58 )</td>
</tr>
<tr>
<td></td>
<td>( 7.29.10^{14} )</td>
<td>( 73 ) ( \mu_s ) ( \mu_s ) ( 116 ) ( 73 )</td>
</tr>
<tr>
<td>30</td>
<td>( 4.9.10^{14} )</td>
<td>( 80 ) ( \mu_s ) ( \mu_s ) ( 158 ) ( 49 )</td>
</tr>
<tr>
<td></td>
<td>( 5.0.10^{14} )</td>
<td>( 85 ) ( \mu_s ) ( \mu_s ) ( 144 ) ( 50 )</td>
</tr>
<tr>
<td>60</td>
<td>( 3.94.10^{14} )</td>
<td>( 95 ) ( \mu_s ) ( \mu_s ) ( 167 ) ( 39 )</td>
</tr>
<tr>
<td></td>
<td>( 4.22.10^{14} )</td>
<td>( 81 ) ( \mu_s ) ( \mu_s ) ( 183 ) ( 42 )</td>
</tr>
</tbody>
</table>

*Estimated error in \( p_s : \pm 28\% \) \( \mu_s : \pm 14\% \) \( p_s : \pm 2\% \)*
Fig. 4.15  Sheet hole concentration and mobility as a function of annealing time for 450 keV $1.10^{15}$ Zn$^+$/$\text{cm}^2$ implanted into GaAs at 200°C.
Cap-Al.
The hole concentration and mobility profiles show very complicated shapes (Fig. 4.16). A peak concentration in excess of $10^{19}$ holes/cm$^3$ was measured after annealing for 10 or 15 minutes and increasing the annealing time to sixty minutes resulted in a peak concentration of somewhat less (approximately $9\times10^{18}$ holes/cm$^3$).

Mobilities lie in the range 60 to 120 cm$^2$/V.s and the highest mobility was recorded after annealing for a period of sixty minutes.

4.2.8 Summary of Thermally Annealed Results

Rutherford backscattering and transmission electron microscopy measurements indicated increased recrystallization of the amorphous layer, produced by 150 keV, $1\times10^{15}$ Zn$^+/\text{cm}^2$ into gallium arsenide at room temperature, with increasing annealing temperature in the range 300 to 900°C (Figs. 4.3 and T4.1 to T4.5). Perfect recrystallization was observed after annealing at 900°C.

Measurements of $X_{\min}$ and $X_D$ indicated a marked annealing stage in the temperature range 600 to 700°C (Fig. 4.4).

No electrical activation was observed after annealing in the temperature range up to 600°C. However electrical activity of 10 to 20% was measured after annealing at 650°C to 800°C and this increased to about 86% following a thermal pulse anneal to 900°C (Table 4.2).
Hole concentration and mobility profiles as a function of annealing time for 450 keV, 1.10^{15} \text{Zn}^+/\text{cm}^2. Cap-Al.

Fig. 4.16
The sheet hole concentration increased with increasing dose up to a dose of $1 \times 10^{14}$ ions/cm$^2$ and above this dose it reached a constant value between $(1-2) \times 10^{14}$ holes/cm$^2$ when implanted at room temperature (Fig. 4.12).

For samples implanted at 200°C the sheet carrier concentration increased with increasing dose up to a dose of $1 \times 10^{15}$ ions/cm$^2$ (Fig. 4.12).

The sheet hole concentration was found to be independent of the implant energy for room temperature implanted samples but for implants carried out at 200°C, it increased as the implant energy was raised from 60 keV to 450 keV (Fig. 4.6).

Profiles showed that the peak hole concentration increased with increasing dose both for room temperature and for hot implants. A peak carrier concentration of approximately $10^{19}$ holes/cm$^3$ was obtained for a dose of $1 \times 10^{15}$ ions/cm$^2$ implanted at 200°C and for room temperature implanted samples the equivalent value was about $6 \times 10^{18}$ holes/cm$^3$ (Figs. 4.11, 4.13 and 4.14).

For doses up to $1 \times 10^{14}$ ions/cm$^2$ profiles obtained from both cold and hot implants were very similar but above this dose profiles recorded from hot implants were very much broader than those from cold implants (Figs. 4.13 and 4.14).

The diffusion of zinc in gallium arsenide as evident from profile broadening, is dependent on the ion dose, the ion energy, the implant temperature and the annealing temperature.
4.3 LASER ANNEALING OF ZINC IMPLANTED GaAs USING A FREELY GENERATED MODE RUBY LASER

Most of the results presented below correspond to 150 keV, 1x10^{15} Zn^{+}/cm^{2} implanted at room temperature, unless stated otherwise. The effect of a 0.8 m second laser pulse on the properties of gallium arsenide samples has been studied using Rutherford backscattering, Hall effect and sheet resistivity measurements and finally scanning electron microscopy.

4.3.1 Rutherford Backscattering Measurements

The aligned spectrum (Fig. 4.17) obtained after the Si_{3}N_{4} deposition process at 750°C for fifteen seconds show that significant recrystallization of the amorphous layer (see section 4.2.1b) occurred during this process. This was indicated by the reduction in the backscattered yield, the shift in the rear edge of the aligned spectrum towards the GaAs surface and also the disappearance of the amorphous layer. Laser irradiation in the energy density range 0.2 to 0.6 J/cm^{2} on Si_{3}N_{4} coated samples resulted in some recrystallization but a high amount of disorder still remained (Fig. 4.17). As the laser energy density was raised to 3 J/cm^{2} no change in the aligned spectrum was observed, indicating that above 1.6 J/cm^{2} no further annealing took place. The spectrum from uncoated samples irradiated with laser energy density up to 3 J/cm^{2} was very similar to the as-implanted sample (Fig. 4.17) indicating that no annealing had occurred.
Fig. 4.17 Rutherford backscattering spectra as a function of laser energy density. Freely generated mode ruby laser $\lambda = 0.6943 \ \mu m$, Pulse length = 0.8 msec.
Cap - $Si_3N_4$. 1 - as implanted (unannealed),
2 - $Si_3N_4$ deposition - removed,
3 - $Si_3N_4 + 0.2 J/cm^2$. 4 - $Si_3N_4 + 1.6$ to $3.0 J/cm^2$
The Si$_3$N$_4$ deposition process caused appreciable reduction of $X_{\text{min}}$ from 58% to 28% (Fig. 4.18). As the laser energy increased up to 200 mJ, $X_{\text{min}}$ decreased but above this value of laser energy, $X_{\text{min}}$ saturated at 16% (table 4.11), which corresponds to significant amount of residual disorder.

4.3.2 Electrical Measurements

Following laser irradiation of samples coated with Si$_3$N$_4$, in the laser energy range 25 to 190 mJ, the sheet hole concentration was found to be about $2.7 \times 10^{14}$ holes/cm$^2$ and the sheet mobility was about 70 cm$^2$/V.s (Fig. 4.18). As the laser energy was increased to 200 mJ, a sudden increase in the hole concentration was observed and the corresponding mobility decreased. Above this value of laser energy, the sheet hole concentration and sheet mobility saturated at values of about $4.8 \times 10^{14}$ holes/cm$^2$ and 50 cm$^2$/V.s respectively. No electrical measurements were possible on samples irradiated with up to 3 J/cm$^2$ without a Si$_3$N$_4$ coating.

For samples capped with Si$_3$N$_4$, the peak hole concentration increased from about $1 \times 10^{19}$ to $7 \times 10^{19}$ holes/cm$^3$ as the laser energy density was raised from 0.2 J/cm$^2$ to 2.6 J/cm$^2$ (Fig. 4.19 and table 4.11). The peak in the profile moved towards the surface and the profile became slightly narrower as the laser energy density increased.
150 Kev Zn\(^{+}\) (1\(\times\)10\(^{15}\)/cm\(^{2}\)) R.T.
LASER ANNEALED (RUBY)

Fig. 4.18 Sheet hole concentration, sheet mobility and \(X_{\text{min}}\) value as a function of laser energy.
Freely generated mode ruby laser, 0.8msec. pulse, Cap-Si\(_{2}\)N\(_{4}\)
Mobilities were found to lie in the range between 50 to 200 cm$^2$/V.s (Fig. 4.19).

**Implant Temperature Dependence**

For samples implanted with an ion energy of 150 keV, electrical activities of 47% and 34% were measured for cold (RT) and hot (200°C) implants respectively and the sheet mobilities were 49 and 90 cm$^2$/V.s (table 4.12). In the case of 450 keV, electrical activities were 41% and 82% for cold and hot implants respectively (table 4.12).

Hole concentration and mobility profiles (Fig. 4.20) show that by implanting hot rather than cold, profiles became broader with lower peak hole concentrations following laser irradiation with 3 J/cm$^2$. Broader profiles suggest that diffusion may take place which is more in the samples implanted hot than for samples implanted cold.

The measured mobilities are in good agreement with the data of Sze and Irvin$^{160}$ (Fig. 4.21) irrespective of the implant temperature.

**Multiple Irradiation Dependence**

Following a single pulse irradiation in the energy density range 1.7 to 3.0 J/cm$^2$, for 60 keV implants, the electrical activity was about 30% (table 4.13). As the number of pulses increased from one to four, the electrical activity increased from 34% to 89% (table 4.13) and the peak hole concentration increased from about $4\times10^{19}$ holes/cm$^3$ to
Hole concentration and mobility profiles as a function of laser energy density. Freely generated mode ruby laser. Cap-Si$_3$N$_4$. Laser pulse length = 0.8 msec. A - 0.2J/cm$^2$, B - 0.6J/cm$^2$, C - 1.0J/cm$^2$, D - 1.6J/cm$^2$, E - 2.4J/cm$^2$, F - 2.6J/cm$^2$. 

Fig. 4.19 150 Kev Zn$^+$ (1x10$^{15}$/cm$^2$)
### TABLE 4.11

**PROPERTIES OF SAMPLES IMPLANTED AT ROOM TEMPERATURE WITH**

150 keV 1.10¹⁵ Zn⁺ ions/cm² FOLLOWED BY LASER IRRADIATION

FREELY GENERATED RUBY LASER \( \lambda = 0.6943 \mu \text{m} \) PULSE LENGTH = 0.8 msec.

<table>
<thead>
<tr>
<th>Laser Energy (J/cm²)</th>
<th>Encapsulant</th>
<th>Sheet Electrical Properties</th>
<th>Activity (%)</th>
<th>Peak Hole Concent. ( \rho (\Omega \text{cm}) )</th>
<th>( X_{\text{min}} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>Si₃N₄</td>
<td>&gt;&gt; 0</td>
<td>0 (0)</td>
<td>---</td>
<td>58</td>
</tr>
<tr>
<td>---</td>
<td>Si₃N₄</td>
<td>2.7.10⁻¹⁴</td>
<td>10</td>
<td>1789</td>
<td>27</td>
</tr>
<tr>
<td>0.2</td>
<td>Si₃N₄</td>
<td>3.3.10⁻¹⁴</td>
<td>65</td>
<td>284</td>
<td>33</td>
</tr>
<tr>
<td>0.6</td>
<td>Si₃N₄</td>
<td>2.7.10⁻¹⁴</td>
<td>76</td>
<td>297</td>
<td>27</td>
</tr>
<tr>
<td>1.0</td>
<td>Si₃N₄</td>
<td>2.9.10⁻¹⁴</td>
<td>67</td>
<td>325</td>
<td>29</td>
</tr>
<tr>
<td>1.5</td>
<td>Si₃N₄</td>
<td>2.9.10⁻¹⁴</td>
<td>70</td>
<td>305</td>
<td>29</td>
</tr>
<tr>
<td>1.6</td>
<td>Si₃N₄</td>
<td>4.2.10⁻¹⁴</td>
<td>50</td>
<td>293</td>
<td>42</td>
</tr>
<tr>
<td>1.7</td>
<td>Si₃N₄</td>
<td>4.6.10⁻¹⁴</td>
<td>51</td>
<td>263</td>
<td>46</td>
</tr>
<tr>
<td>2.4</td>
<td>Si₃N₄</td>
<td>4.7.10⁻¹⁴</td>
<td>46</td>
<td>290</td>
<td>47</td>
</tr>
<tr>
<td>2.6</td>
<td>Si₃N₄</td>
<td>4.7.10⁻¹⁴</td>
<td>49</td>
<td>279</td>
<td>47</td>
</tr>
<tr>
<td>3.0</td>
<td>Si₃N₄</td>
<td>4.1.10⁻¹⁴</td>
<td>73</td>
<td>211</td>
<td>41</td>
</tr>
<tr>
<td>0.2-2.4</td>
<td>-</td>
<td>---</td>
<td>&gt;&gt; 0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.3</td>
<td>-</td>
<td>1.7.10⁻¹³</td>
<td>1</td>
<td>1.10⁵</td>
<td>2</td>
</tr>
</tbody>
</table>

Estimated error in Energy: ± 10%, \( P_a: \pm 28\% \), \( \mu_a: \pm 14\% \), \( \rho_a: \pm 2\% \), \( \dot{\rho}: \pm 20\% \), \( X_{\text{min}}: \pm 0.5\% \)
(mean of two measurements)

### TABLE 4.12

**ELECTRICAL PROPERTIES OF 1.10¹⁵ Zn ions/cm² INTO GaAs. ENCAPSULANT : Si₃N₄**

LASER ANNEALED WITH FREELY GENERATED RUBY LASER \( \lambda = 0.6943 \mu \text{m} \)

PULSE LENGTH = 0.8 msec ENERGY DENSITY = 3 J/cm²

<table>
<thead>
<tr>
<th>IMPLANT ENERGY (keV)</th>
<th>IMPLANT TEMP (°C)</th>
<th>SHEET ELECTRICAL PROPERTIES</th>
<th>ELECTRICAL ACTIVITY (%)</th>
<th>PEAK HOLE CONCENT. ( \rho (\Omega \text{cm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>RT</td>
<td>3.4.10⁻¹⁴</td>
<td>29</td>
<td>633</td>
</tr>
<tr>
<td>150</td>
<td>RT</td>
<td>4.7.10⁻¹⁴</td>
<td>51</td>
<td>263</td>
</tr>
<tr>
<td>150</td>
<td>200</td>
<td>3.4.10⁻¹⁴</td>
<td>90</td>
<td>210</td>
</tr>
<tr>
<td>450</td>
<td>RT</td>
<td>4.1.10⁻¹⁴</td>
<td>66</td>
<td>235</td>
</tr>
<tr>
<td>450</td>
<td>200</td>
<td>8.2.10⁻¹⁴</td>
<td>68</td>
<td>110</td>
</tr>
</tbody>
</table>

Estimated error in \( T_1: \pm 10°\), \( P_a: \pm 28\% \), \( \mu_a: \pm 14\% \), \( \rho_a: \pm 2\% \)
\( \dot{\rho}: \pm 20\% \), Laser energy density: ± 10%
(mean of two measurements).
Fig. 4.20 Hole concentration and mobility profiles for hot and cold implants. Laser annealed with freely generated mode ruby laser. Cap-Si$_3$N$_4$. 

HOLE CONCENTRATION, $P_V$ (cm$^{-3}$) 

HALL MOBILITY, $\mu_H$ (cm$^2$/v.sec.) 

DEPTH (um) 

$1\times10^{15}$ Zn$^+$/cm$^2$ 

LASER ANN. 3 J/cm$^2$ 

0-2 0-4 0-6 

0 $\times 10^{20}$ $\times 10^{19}$ $\times 10^{18}$ 

R.T. 150 Kev. 

200°C 

R.T. 450 Kev. 

200°C
Fig. 4.21  Hall mobility as a function of carrier concentration for laser annealed zinc implanted GaAs. Ruby laser $\lambda = 0.4963 \mu m$, Pulse length = 0.8 msec, all samples capped with Si$_3$N$_4$ before laser irradiation.
<table>
<thead>
<tr>
<th>NUMBER OF LASER PULSES</th>
<th>LASER ENERGY DENSITY PER PULSE (J/cm²)</th>
<th>CAP</th>
<th>SHEET ELECTRICAL PROPERTIES</th>
<th>ELECTRICAL ACTIVITY (%)</th>
<th>PEAK HOLE CONCENTRATION (p/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>p_s (cm⁻²)</td>
<td>μ_s (cm²/V.s)</td>
<td>ρ_s (Ω·cm)</td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>Si₃N₄</td>
<td>3.5×10¹⁴</td>
<td>13.9</td>
<td>1284</td>
</tr>
<tr>
<td>1</td>
<td>1.7</td>
<td>Si₃N₄</td>
<td>3.2×10¹⁴</td>
<td>60</td>
<td>323</td>
</tr>
<tr>
<td>1</td>
<td>1.8</td>
<td>Si₃N₄</td>
<td>2.9×10¹⁴</td>
<td>43</td>
<td>495</td>
</tr>
<tr>
<td>1</td>
<td>1.9</td>
<td>Si₃N₄</td>
<td>3.1×10¹⁴</td>
<td>42</td>
<td>485</td>
</tr>
<tr>
<td>1</td>
<td>2.8</td>
<td>Si₃N₄</td>
<td>4.4×10¹⁴</td>
<td>52</td>
<td>270</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>Si₃N₄</td>
<td>3.4×10¹⁴</td>
<td>29</td>
<td>633</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>Si₃N₄</td>
<td>4.9×10¹⁴</td>
<td>43</td>
<td>291</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>Si₃N₄</td>
<td>8.9×10¹⁴</td>
<td>29</td>
<td>241</td>
</tr>
</tbody>
</table>

ELECTRICAL PROPERTIES OF SAMPLES IMPLANTED AT ROOM TEMPERATURE WITH 60 keV 1×10¹⁵ Zn⁺/cm², FOLLOWED BY LASER IRRADIATION FREELY GENERATED RUBY LASER λ = 0.6943 μm. PULSE LENGTH = 0.8 ms sec. Estimated Error in Laser Energy density ± 10%, p_s: ± 28%, μ_s: ± 14%, ρ_s: ± 2%, p: ± 20%
$1.6 \times 10^{20}$ holes/cm$^3$ (Fig. 4.22). Also the peak in the profile moved towards the surface. The measured profiles appeared to be slightly broader than the calculated LSS profile (Fig. 4.22).

The mobilities, which are lower than the expected values, lie in the range between 15 to 100 cm$^2$/V.s, have a minimum near the surface and increase to a higher value deeper in.

4.3.3 Scanning Electron Microscopy

The surface topography of laser annealed samples was observed using a scanning electron microscope. No surface effects were perceived on coated and uncoated samples when irradiated in the energy density range 0.2 to 3.0 J/cm$^2$. Above an energy density of about 4 J/cm$^2$, ripples and craters formed at the surface and microcracks probably along cleavage planes were observed both on coated and uncoated samples (Fig. 4.23). As the energy density was increased to 12 J/cm$^2$ the above effects became more enhanced. Also the surface effects were more pronounced on coated samples which indicated that these may have absorbed more energy.

4.3.4 Summary

A freely generated ruby laser pulse of 0.8 m seconds length produced electrical activity from 27% to about 50% and peak hole concentration from $1 \times 10^{19}$ to about $7 \times 10^{19}$
Fig. 4.22 Hole concentration and mobility profiles as a function of laser pulses. Cap- Si$_3$N$_4$. Freely generated mode ruby laser.
**S.E.M. PHOTOGRAPHS OF LASER ANNEALED ZINC IMPLANTED GaAs** (Freely generated mode)

<table>
<thead>
<tr>
<th>Pulse length</th>
<th>Energy density</th>
<th>100x</th>
<th>500x</th>
<th>2000x</th>
<th>5000x</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8 ms</td>
<td>6.5 J/cm²</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **(a)**
  - Fractures along cleavage planes
  - No Si₃N₄

- **(b)**
  - Craters, ripples
  - Si₃N₄

- **(b)**
  - Crack lines
  - Si₃N₄

*(200x)*
holes/cm$^3$ for laser energy densities between 0.2 to 3 J/cm$^2$ on coated samples. Rutherford backscattering measurements showed that significant residual damage still remained after laser irradiations (Fig. 4.17 to 4.19).

The maximum electrical activity of 89% and hole concentration of 1.6x10$^{20}$ holes/cm$^3$ were recorded following irradiation with four pulses of 3 J/cm$^2$ (Fig. 4.22). However the mobility in this case was rather low ($\sim$ 20 to 60 cm$^2$/V.s).

Profiles broadened during laser irradiations and were found to be more for hot implants than for cold implants.

4.4 LASER ANNEALING OF ZINC IMPLANTED GaAs USING A Q-SWITCHED RUBY LASER

The physical and electrical properties of gallium arsenide implanted with 150 keV, 1x10$^{15}$ Zn$^+$/cm$^2$ at room temperature and annealed using a Q-switched ruby laser are presented below.

The results are divided into four sections:-

(a) Rutherford Backscattering Measurements (4.4.1).
(b) Electrical Measurements (4.4.2).
(c) Transmission Electron Microscopy (4.4.3).
(d) Surface Topography (4.4.4)
4.4.1 Rutherford Backscattering Measurements

Laser irradiation of uncoated samples, (using the City University Laser), with an energy density of 0.3 J/cm² caused significant recrystallization, which is indicated by the reduction in the backscattering yield (Fig. 4.24). As the energy density was raised recrystallization of the implanted GaAs increased. The spectrum obtained following irradiation with 1.2 J/cm², showed a high backscattering yield and a large gallium peak compared with unimplanted unannealed GaAs (Fig. 4.24). Later it was found that the large gallium peak resulted from the excess gallium present at the gallium arsenide surface (refer to TEM section 4.4.3).

Annealing of Si₃N₄ coated samples with energy densities in the range from 0.3 to 1.2 J/cm² produced spectra which were identical to the virgin GaAs, indicating that complete recrystallization had occurred. (Fig. 4.24).

Somewhat different results were obtained when annealing was accomplished using Surrey University laser (results shown in Fig. 4.25). The aligned spectrum recorded following irradiation with 0.2 J/cm² of the uncoated sample was identical to the unimplanted unannealed GaAs, indicating that complete annealing had occurred. However this is inconsistent with the earlier results of Fig. 4.24 (possible reasons are given in the discussion chapter, section 5.3).
Fig. 4.24 Rutherford backscattering spectra as a function of laser energy density. Q-switched ruby laser (City University laser). \( \lambda = 0.6943 \text{ \(\mu m\)} \).

Pulse length = 15 nsec. 1, 2 – no anneal, 3 – 0.3J/cm\(^2\), 4 – 0.6J/cm\(^2\), 5 – 1.2J/cm\(^2\); 6 – 0.3 – 1.2J/cm\(^2\), Si\(_2\)N\(_4\); 1, 3–5 uncapped.
Following irradiation with laser energy densities greater than 0.2 J/cm$^2$, the gallium arsenide surface became non-stoichiometric, that is an excess of gallium at the surface. This was evident with the Ga peak being higher than the arsenic peak (Fig. 4.25). Furthermore the ratio of Ga to As appeared to increase as the laser energy was raised from 0.3 J/cm$^2$ to 1.6 J/cm$^2$. However the gallium peak was found to reduce (Fig. 4.25) after etching the laser annealed sample in HCl, which indicated that excess Ga was present at the gallium arsenide surface as found earlier. After the HCl etch the GaAs surface was approximately stoichiometric (Fig. 4.25).

In general the magnitude of $X_{\text{min}}$ for capped and uncapped samples decreased as the laser energy density was increased (Fig. 4.26). The decrease in $X_{\text{min}}$ was gradual in the case of samples irradiated with the City University laser but it was abrupt in the case of our own laser (tables 4.14, 4.14a and Fig. 4.26). $X_{\text{min}}$ measured from samples capped with Si$_3$N$_4$, from non-capped samples and samples boiled in HCl for five minutes was in the range 4-5% (table 4.14 and 4.14a).

4.4.2 Electrical Measurements

Sheet Results

The electrical activity increased with increasing laser energy density both for coated and uncoated samples (table 4.14, 4.14a and Fig. 4.26). The activity went through a maximum and then decreased as the laser energy
Fig. 4.25 RBS spectra of laser annealed zinc implanted GaAs after irradiating with Surrey University laser, $\lambda = 0.694 \mu m$, Pulse length 25 nsec. Q-switched ruby laser. All samples un-capped.
density was raised from 0.2 J/cm$^2$ to 1.6 J/cm$^2$. For the maximum electrical activity a slightly higher energy density was needed for uncoated samples than for samples coated with Si$_3$N$_4$. Following irradiation with an energy density of 0.3 J/cm$^2$ some of the uncapped samples did not become electrically active, others were about 20% active, however, the capped samples produced 60% electrical activity. 100% activity was recorded for Si$_3$N$_4$ capped samples following irradiation with 0.6 J/cm$^2$.

**Hole concentration Profiles**

The profiles for capped samples annealed with energy densities of 0.3 J/cm$^2$ and 1.2 J/cm$^2$ were similar (Fig. 4.27). Profiles from noncapped samples irradiated with 1.2 J/cm$^2$ were also similar to the above profiles, except that the peak concentrations were displaced towards the surface. For samples coated with Si$_3$N$_4$, the peak hole concentration increased from 5x10$^{19}$ holes/cm$^3$ to 1x10$^{20}$ holes/cm$^3$ as the laser energy density was incremented from 0.3 to 0.6 J/cm$^2$ and the profiles became broader (Fig. 4.27).

In accord with the sheet measurements the electrical activity calculated by integrating the area under the profiles in Fig. 4.27, goes through a maximum.
TABLE 4.14 (CITY UNIV. LASER)

PROPERTIES OF SAMPLES IMPLANTED AT ROOM TEMPERATURE WITH 150 keV 1.10^{15} Zn^+/cm^2 FOLLOWED BY LASER IRRADIATION WITH Q-SWITCHED RUBY LASER $\lambda = 0.6943 \mu$m Pulse Length = 15 nsec.

Estimated errors in laser energy: $\pm 50\%$, $p_0: \pm 28\%$, $\mu_0: \pm 14\%$, $\rho_0: \pm 2\%$, $\rho_g: \pm 20\%$, $X_{min}: \pm 0.5\%$

<table>
<thead>
<tr>
<th>Laser Energy Density (J/cm²)</th>
<th>Encapsulation</th>
<th>SHEET ELECTRICAL PROPERTIES</th>
<th>ELECTRICAL ACTIVITY (%)</th>
<th>PEAK HOLE CONC. $\rho_g$ (cm⁻²)</th>
<th>$X_{min}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>$p_e$ (cm⁻²)</td>
<td>$\mu_e$ (cm²/V.s.)</td>
<td>$\rho_g$ (cm²/V.s.)</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>Si₃N₄</td>
<td>$2.7.10^{14}$</td>
<td>10</td>
<td>$1.8.10^{3}$</td>
<td>27</td>
</tr>
<tr>
<td>0.3</td>
<td>Si₃N₄</td>
<td>$6.0.10^{14}$</td>
<td>45</td>
<td>228</td>
<td>60</td>
</tr>
<tr>
<td>0.6</td>
<td>Si₃N₄</td>
<td>$1.0.10^{15}$</td>
<td>14</td>
<td>448</td>
<td>100</td>
</tr>
<tr>
<td>1.2</td>
<td>Si₃N₄</td>
<td>$3.9.10^{14}$</td>
<td>30</td>
<td>525</td>
<td>100</td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>H.R.</td>
</tr>
<tr>
<td>0.6</td>
<td>-</td>
<td>$1.7.10^{14}$</td>
<td>10</td>
<td>$3.5.10^{3}$</td>
<td>17</td>
</tr>
<tr>
<td>1.2</td>
<td>-</td>
<td>$6.6.10^{14}$</td>
<td>26</td>
<td>355</td>
<td>66</td>
</tr>
</tbody>
</table>

* $X_{min}$ 4% after etching the laser annealed sample in HCl for 5 minutes. (Mean of two, three or four measurements).

TABLE 4.14A (SURREY UNIVERSITY LASER)

PROPERTIES OF SAMPLES IMPLANTED AT ROOM TEMPERATURE WITH 150 keV 1.10^{15} Zn^+/cm² FOLLOWED BY LASER IRRADIATION WITH Q-SWITCHED RUBY LASER $\lambda = 0.6943 \mu$m Pulse Length = 25 nsec. Estimated errors in Energy: $\pm 10\%$, $p_0: \pm 28\%$, $\mu_0: \pm 14\%$

Estimated errors in laser energy: $\pm 50\%$, $p_0: \pm 28\%$, $\mu_0: \pm 14\%$, $\rho_0: \pm 2\%$, $\rho_g: \pm 20\%$, $X_{min}: \pm 0.5\%$

<table>
<thead>
<tr>
<th>LASER ENERGY DENSITY (J/cm²)</th>
<th>SHEET ELECTRICAL PROPERTIES</th>
<th>ELECTRICAL ACTIVITY (%)</th>
<th>$X_{min}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>$p_e$ (cm⁻²)</td>
<td>$\mu_e$ (cm²/V.s.)</td>
<td>$\rho_g$ (cm²/V.s.)</td>
</tr>
<tr>
<td>0.2</td>
<td>$1.6.10^{14}$</td>
<td>19</td>
<td>$1.9.10^{3}$</td>
</tr>
<tr>
<td>0.3</td>
<td>$2.0.10^{14}$</td>
<td>24</td>
<td>$1.3.10^{3}$</td>
</tr>
<tr>
<td>0.5</td>
<td>$2.8.10^{14}$</td>
<td>32</td>
<td>683</td>
</tr>
<tr>
<td>0.84</td>
<td>$2.8.10^{14}$</td>
<td>20</td>
<td>$1.1.10^{13}$</td>
</tr>
<tr>
<td>1.0</td>
<td>$4.8.10^{14}$</td>
<td>9.7</td>
<td>$1.3.10^{3}$</td>
</tr>
<tr>
<td>1.6</td>
<td>$1.4.10^{14}$</td>
<td>52</td>
<td>850</td>
</tr>
</tbody>
</table>

* $X_{min}$ 4% after etching the laser annealed sample in HCl for 5 minutes. (Mean of two, three or four measurements).
Sheet hole concentration, sheet mobility and $X_{\min}$ as a function of laser energy density for laser annealed zinc implanted GaAs. Q-switched ruby laser, $\lambda = 0.6943 \, \mu m$. Pulse length 15/25 nsecs.
Mobility Profiles

The magnitude of the mobility is low compared with that expected from good crystalline gallium arsenide\(^{160}\) (Fig. 4.27). Fig. 4.28 shows that the mobility values are about 0.7, 0.6 and 0.2 of the expected values for 0.3 J/cm\(^2\), 1.2 J/cm\(^2\) and 0.6 J/cm\(^2\) respectively.

Implants at 200°C

Electrical activities of 70% and 75% were measured from samples capped with Si\(_3\)N\(_4\) and irradiated with energy densities of 0.3 J/cm\(^2\) and 0.6 J/cm\(^2\) respectively (table 4.15). Irradiation with 1.2 J/cm\(^2\) of the uncapped samples produced 38% electrical activity and the sheet mobility was 49 cm\(^2\)/V.s.

A peak hole concentration of 1x10\(^{20}\) holes/cm\(^3\) (Fig. 4.29, table 4.15) was measured from a sample coated with Si\(_3\)N\(_4\) and irradiated with 0.6 J/cm\(^2\). However the mobility was low, being about 8 to 100 cm\(^2\)/V.s. The minimum value of mobility corresponds to the maximum hole concentration.

4.4.3 Transmission Electron Microscopy

TEM measurements on zinc implanted gallium arsenide showed that the as implanted samples were amorphous (Fig. T4.7a) and the Si\(_3\)N\(_4\) deposition process caused partial recrystallization (Fig. T4.8a and table T4.2). These observations are in agreement with the RBS results (Fig. 4.24).
Fig. 4.27 Hole concentration and mobility profiles as a function of laser energy density. Q-switched ruby laser, 15 nsec. pulse length.

- A - 0.3J/cm²
- B - 0.6J/cm²
- C - 1.2J/cm²

A and B capped with Si₃N₄. C - Un-capped.
Hall mobility as a function of carrier concentrations for laser annealed zinc implanted GaAs.

- 0.3 J/cm²
- 0.6 J/cm²
- 1.2 J/cm²

Si₃N₄ Cap.
No Cap.

--- ZE and IRVIN.
150 keV Zn⁺ (1×10¹⁵ cm⁻²) R.T.
150 keV Zn$^+$ 1.10$^{15}$/cm$^2$
\[ T_i = 200^\circ C \]

LASER ANNEALED

1.2J/cm$^2$

UNCAPPED

1.10$^{19}$

\[ \text{HOLE CONCENTRATION } P_V \text{ (cm}^{-3}) \]

0.6J/cm$^2$

Si$_3$N$_4$ Capped

0.1

1.10$^{18}$

\[ \text{DEPTH IN } (\mu\text{m}) \]

0.3

1.10$^{17}$

HALL MOBILITY (cm$^2$/V.s)

100

60

20

200

Fig. 4.29 Hole concentration and mobility profiles for laser annealed zinc implanted GaAs. Q-switched ruby laser. $\lambda = 0.6943 \mu$m, Pulse length 15 nsecs.
In general, following laser annealing of both capped and uncapped samples, the concentration of defects in the implanted layer decreased as the laser energy density was increased from 0.3 J/cm² to 1.2 J/cm² (Figs. T4.7, T4.8 and table T4.2). Micrographs, from the capped samples irradiated with laser energy densities of 1.2 J/cm² or 1.6 J/cm², showed that the material was single crystal and that the only defects present were small dislocation loops (Fig. T4.8d). In contrast micrographs from uncapped samples showed a series of dark blobs (Fig. T4.7b) after laser irradiation in the energy density range 0.6 to 1.6 J/cm². The transmission electron diffraction pattern indicated that the small blobs were not crystalline while the surrounding regions were single crystal. Subsequently these samples were etched in HCl for five minutes and re-examined in the TEM, the dark spots were no longer present. Therefore the small dark blobs observed prior to HCl treatment, are probably gallium at the GaAs surface. Thus it seems that arsenic is lost from the gallium arsenide surface.

In conclusion the TEM results are in good agreement with Rutherford backscattering measurements (section 4.4.1).

4.4.4 Surface Topography

The physical effects of the laser irradiation on the gallium arsenide surface were examined using a scanning electron microscope. Following laser irradiation with energy density of 0.3 J/cm², no surface effects were visible with
### TABLE 4.15

Properties of samples implanted at 200°C with 150 keV 1.10^{15} Zn⁺ ions/cm² followed by laser annealing with Q-switched ruby laser. λ = 0.6943 μm. Pulse length 15 nsec.

<table>
<thead>
<tr>
<th>Laser Energy Density (J/cm²)</th>
<th>Encapsulant</th>
<th>Sheet Electrical Properties</th>
<th>Electrical Activity (%)</th>
<th>Peak Hole Concent. (x)</th>
<th>p/cm³</th>
<th>( \mu_m ) (cm²/V·sec)</th>
<th>( \rho_0 ) (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 Si₃N₄</td>
<td>7.3.10^{14}</td>
<td>6</td>
<td>1.46.10³</td>
<td>73</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.6 Si₃N₄</td>
<td>7.5.10^{14}</td>
<td>23</td>
<td>354</td>
<td>75</td>
<td>1.10^{20}</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>1.2 Si₃N₄</td>
<td>3.8.10^{14}</td>
<td>49</td>
<td>336</td>
<td>38</td>
<td>1.5.10^{19}</td>
<td>7.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Estimated error in laser energy density: ± 50%, \( p_0 ± 28% \), \( \mu_m ± 14% \), \( \rho_0 ± 2\% \)

\( p ± 20\% \), \( x_{min} ± 0.5\% \)

(Mean of two measurements)

### TABLE T4.2

TEM data for GaAs implanted with 150 keV, 10^{15} Zn⁺/cm² at RT and annealed with Q-switched ruby laser.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>Fine dotty structure</td>
<td>Amorphous</td>
<td>T4.7a</td>
<td></td>
</tr>
<tr>
<td>- Si₃N₄</td>
<td>Fine + coarse damaged structure</td>
<td>Twins</td>
<td>N/S</td>
<td>T4.8a</td>
<td></td>
</tr>
<tr>
<td>0.3 Si₃N₄</td>
<td>Coarse damage and dislocations</td>
<td>Twins</td>
<td>Twins</td>
<td>N/S</td>
<td>T4.8b</td>
</tr>
<tr>
<td>0.6 Si₃N₄</td>
<td>Moire fringes and dislocations</td>
<td>Twins</td>
<td>Twins</td>
<td>T4.8b</td>
<td></td>
</tr>
<tr>
<td>1.2 Si₃N₄</td>
<td>Dark blobs (Ga)</td>
<td>Single crystal</td>
<td>N/S</td>
<td>T4.7b</td>
<td></td>
</tr>
<tr>
<td>1.6 Si₃N₄</td>
<td>Single dislocations and loops</td>
<td>Single crystal</td>
<td>Single crystal</td>
<td>T4.8c</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>- * No blobs</td>
<td>Single crystal</td>
<td>Single crystal</td>
<td>T4.7c *</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>Small dislocation loops</td>
<td>Single crystal</td>
<td>Single crystal</td>
<td>T4.8d</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>Few dislocation loops</td>
<td>Single crystal</td>
<td>Single crystal</td>
<td>T4.8e</td>
<td></td>
</tr>
</tbody>
</table>

* After HCl treatments
LASER ANNEALING OF UNCOATED, Zn⁺ IMPLANTED GaAs (10⁻¹⁵/㎝², 150 keV, R.T)
Fig. T4.8
the naked eye. When these samples were viewed under an optical microscope or scanning electron microscope the surfaces appeared to be slightly blemished. For example, the flat surfaces gave the appearance of being slightly marked with small etch pits. At an energy density of 0.6 J/cm² the surface effects were visible with the naked eye and when examined using the SEM, gave the appearance of having flowed slightly, that is melting probably occurred. At an energy density of 1.2 J/cm² craters were formed, the surfaces became rippled (Fig. 4.30) and the effects were more prominent on samples coated with Si₃N₄. Some craters of about 1000 Å deep were measured (Fig. 4.31) by scanning the GaAs surface with a talystep.

4.4.5 Summary

A single pulse from a Q-switched ruby laser in the energy density range 0.2 to 1.6 J/cm² produced complete recrystallization \( X_{\text{min}} \sim 4 \) to 5\% of the amorphous gallium arsenide (Figs. 4.24 - 4.26).

High electrical activities up to 100\% were measured (table 4.14 and 4.15) for both hot and cold implants.

Peak carrier concentrations of about \( 1 \times 10^{20} \) holes/cm³ were recorded both for hot and cold implanted samples following irradiation with 0.6 J/cm², provided the samples were coated with Si₃N₄ (Figs. 4.27 and 4.29).

Profiles broadened during laser annealing and the mobilities were found to be exceptionally low (Figs. 4.27 and 4.28).
S.E.M. PHOTOGRAPHS OF LASER ANNEALED ZINC IMPLANTED GaAs (Q-Switched)

Pulse length 15 \text{ns} \text{sec.} \quad \text{Energy density} \quad 1.2 \text{ J/cm}^2

200 \times \quad 500 \times \quad 2000 \times \quad 5000 \times

(a) [Images of process effects at different magnifications]

(b) [Images showing the effects of Si$_3$N$_4$ blowing off]

Fig. 4.30
150 keV, 1.10^-15 zn+/-cm^2 into GaAs, Ti = RT.

Fig. 4.31 Crater measured by scanning the surface of the GaAs sample with a taly-step following irradiation with a Q-switched ruby laser.
4.5 PROPERTIES OF CADMIUM IMPLANTED GALLIUM ARSENIDE

4.5.1 Introduction

Results of Hall effect and sheet resistivity measurements (sections 4.2 to 4.4) indicated that diffusion of zinc in gallium arsenide probably occurred during the annealing processes. To study this diffusion, cadmium was implanted into GaAs and annealed in the same way as the Zn implanted gallium arsenide. Cadmium ions were chosen because:

(a) They are acceptors in GaAs
(b) Zinc and cadmium behave similarly in GaAs
(c) The high mass of Cd compared with gallium arsenide and Zn, which made it possible to study the distribution of cadmium in GaAs using the Rutherford backscattering technique.

All the results presented below correspond to 150 keV Cd implanted into GaAs to a dose of $1 \times 10^{15}$ ions/cm$^2$ at room temperature.

4.5.2 Thermal Annealing

An investigation of annealing in the temperature range 300 to 900°C of Cd implanted gallium arsenide is presented below. Rutherford backscattering measurements and ion channelling have been used to study the implantation damage and the distribution of cadmium in GaAs before and
after annealing. Hall effect and sheet resistivity measurements have been used to obtain the profiles of the electrically active carriers following annealing.

(a) **Electrical Properties**

After annealing at 500°C for fifteen minutes a sheet hole concentration of $1 \times 10^{13}$ holes/cm$^2$ and sheet mobility of about $10$ cm$^2$/V.s was measured. As the annealing temperature increased, the sheet hole concentration and sheet mobility were found to increase (Fig. 4.32). The maximum hole concentration of $6 \times 10^{14}$ holes/cm$^2$ was measured following annealing at 900°C for 30 seconds and the maximum mobility was about $65$ cm$^2$/V.s. No Hall effect measurements were possible in the annealing temperature range 300°C to 500°C, due to the difficulty in making good ohmic contacts to the implanted layer.

For comparison, samples were annealed using both aluminium and Si$_3$N$_4$ as the encapsulant. Hall effect and sheet resistivity measurements on these samples annealed at 800°C for five minutes (Fig. 4.32) were very similar.

Following annealing at 700°C for fifteen minutes or at 800°C for five minutes, the peak hole concentrations were very similar but the profiles became broader with increasing annealing temperature from 700 to 800°C, (Fig. 4.33). Further profile broadening occurred following an anneal at 900°C and the peak hole concentration increased to about $2.9 \times 10^{19}$ holes/cm$^3$. Profiles were very broad compared
150 Kev Cd$^+$ (1x10$^{15}$/cm$^2$) R.T.

Cap - Al.

Si$_3$N$_4$

From ref. (30)

Fig. 4.32 Sheet hole concentration and mobility as a function of annealing temperature for Cd implanted GaAs at room temperature.
with the calculated ISS profile which suggested that
diffusion of cadmium probably occurred during annealing
and increased as the annealing temperature increased.

Mobilities were in the range from 35 to 120
cm²/V·s and the minimum mobility corresponded to a depth
of 1250 Å on the profile obtained after 900°C anneal.

(b) **Rutherford Backscattering Properties**

Rutherford backscattering measurements (Fig. 4.34)
indicated that the as-implanted sample was amorphous over
a depth of about 1600 Å. The aligned spectrum of the
sample annealed at 300°C showed that significant annealing
of the radiation damage took place. As the annealing
temperature increased further reordering of the crystal
occurred. Following annealing at 600°C the gallium and the
arsenic peaks were found to be resolved but the back-
scattering yield was still high compared with the unimplanted,
unannealed GaAs. Increasing the annealing temperature to
900°C, resulted in a spectrum which was similar to the
virgin GaAs (Fig. 4.34), indicating that complete annealing
had been obtained.

Random and aligned spectra were collected to
observe the changes in the cadmium distribution as a function
of annealing temperature. The atomic profiles of Cd over
100 channels (channel numbers 220 to 320) showed that after
annealing at 300°C or at 400°C the distribution of cadmium
in gallium arsenide was the same as that for as-implanted
samples. As the annealing temperature increased the Cd peak
Fig. 4.33 Hole concentration and mobility profiles as a function of annealing temperature for cadmium implanted GaAs.
Fig. 4.34 Rutherford backscattering spectra as a function of annealing temperature for Cd implanted GaAs. 1 - Unannealed, 2 - 300°C, 3 - 400°C, 4 - 500°C, 5 - 600°C, 6 - 700°C, 7 - 800°C, 8 - 900°C/Virgin GaAs.
decreased which is consistent with an indiffusion of cadmium (see section on electrical measurements of Cd).

\[ X_{\text{min}} \] decreased with increasing annealing temperature and became about 4 to 5% in the range 800 to 900°C (Fig. 4.35).

The number of cadmium atoms occupying substitutional lattice sites increased from 8%, for the as-implanted sample, to 90% for samples annealed at 700 to 900°C (Fig. 4.35, table 4.17).

4.5.3 Laser Annealing of Cadmium Implanted GaAs

The results of annealing cadmium implanted gallium arsenide samples using single and multiple pulses from a Q-switched ruby laser are presented in this section. Rutherford backscattering, Hall effect and sheet resistivity measurements were employed to assess the effects of the laser irradiations.

(a) Laser Energy Density Dependence

The aligned spectrum from the uncoated sample, following irradiation with a single pulse of energy density of 0.3 J/cm\(^2\) showed that significant annealing of the amorphous layer had occurred (Fig. 4.36). As the laser energy density was increased, further recrystallization took place. The backscattering yield obtained following irradiation with an energy density of 1.2 J/cm\(^2\) was still high compared with unimplanted unannealed gallium arsenide, indicating that a significant amount of disorder remained.
Fig. 4.35 Relative damage ($X_{\text{min}}$) and percentage Cadmium substitutionals on lattice sites as a function of annealing temperature.
Fig. 4.36 also shows the random backscattering spectra in the region of the impurity (cadmium) peak. The atomic profiles for energy densities 0.3 to 1.2 J/cm$^2$ indicates that there is a significant out-diffusion of Cd towards the surface. The height of the cadmium peak was found to be reduced as the laser energy density was increased from 0.6 to 1.2 J/cm$^2$. This may be due to a combination of out-diffusion and evaporation of Cd during laser irradiation (Fig. 4.36).

As the laser energy density was increased, $X_{\text{min}}$ decreased and the percentage of cadmium occupying substitutional lattice sites increased (Fig. 4.37). Following irradiation with 1.2 J/cm$^2$, $X_{\text{min}}$ was about 7% and the percentage of Cd on lattice sites was 78% (Fig. 4.37, table 4.18). After etching the sample in H$_2$O the $X_{\text{min}}$ reduced to about 4%, in agreement with the results on laser annealed zinc implanted gallium arsenide (section 4.4).

Following the Si$_2$N$_4$ deposition process and after irradiation with laser energy density in the range 0.3 to 1.2 J/cm$^2$ (Fig. 4.38), the aligned spectra were identical to the virgin gallium arsenide. $X_{\text{min}}$ was found to be between 4 and 5% (table 4.18), indicating complete recrystallization had occurred. The percentage of Cd on lattice sites was found to be in the range between 80 and 90% (table 4.18).

Electrical measurements on uncoated samples irradiated in the energy density range 0.3 to 1.2 J/cm$^2$
Fig. 4.36  Rutherford backscattering spectra as a function of laser energy density for Cd implanted GaAs. Irradiation with Q-switched ruby laser, Pulse length = 15 nsec. All samples un-capped.

2 - 0.3J/cm², 3 - 0.6J/cm², 4 - 1.2J/cm²

5 - Virgin GaAs.
150 keV Cd\(^+\) (1 \times 10^{15}/\text{cm}^2)\) R.T.
LASER ANNEALED (Q-Switched ruby)
UNCAPPED

Fig. 4.37 \(X_{\text{min}}\) value and the percentage Cd\(^+\) substitutionals on lattice sites as a function of laser energy density.
### TABLE 4.17

**PROPERTIES OF SAMPLES IMPLANTED AT ROOM TEMPERATURE WITH 150 keV 1.10^{15} \text{Cd}^+ \text{IONS/cm}^2 FOLLOWED BY THERMAL ANNEALING.**

<table>
<thead>
<tr>
<th>ANNEAL TEMP. °C</th>
<th>ENCAPSULANT</th>
<th>SHEET ELECTRICAL PROPERTIES $\mu_e$ (cm$^2$/V·sec)</th>
<th>ELECTRICAL ACTIVITY $\chi$ (°)</th>
<th>SUBSTITUTIONAL Cd+ (%)</th>
<th>TOTAL Cd+ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\rho_e$ (cm$^2$·V·sec$^{-1}$)</td>
<td>$\rho_e$ (n·Ω·cm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>$&gt;&gt;0$</td>
<td>0</td>
<td>50</td>
<td>8</td>
</tr>
<tr>
<td>$500/15$</td>
<td>$\text{Si}_2\text{N}_4$</td>
<td>n-type 0.3</td>
<td>2092</td>
<td>0</td>
<td>4.3</td>
</tr>
<tr>
<td>$400/15$</td>
<td></td>
<td>$&gt;&gt;0$</td>
<td>0</td>
<td>0</td>
<td>42.5</td>
</tr>
<tr>
<td>$600/15$</td>
<td>$\text{Al}$</td>
<td>$7.7 \times 10^{12}$</td>
<td>3.1</td>
<td>2.6 $\times 10^{5}$</td>
<td>0.8</td>
</tr>
<tr>
<td>$700/15$</td>
<td>$\text{Al}$</td>
<td>$6.7 \times 10^{13}$</td>
<td>38</td>
<td>2.4 $\times 10^{3}$</td>
<td>7</td>
</tr>
<tr>
<td>$800/5$</td>
<td>$\text{Al}$</td>
<td>$1.7 \times 10^{14}$</td>
<td>60</td>
<td>622</td>
<td>17</td>
</tr>
<tr>
<td>$800/5$ $\text{Si}_2\text{N}_4$</td>
<td>$3.5 \times 10^{14}$</td>
<td>66</td>
<td>268</td>
<td>35</td>
<td>4.3</td>
</tr>
<tr>
<td>$900/30$ sec $\text{Si}_2\text{N}_4$</td>
<td>$6.0 \times 10^{14}$</td>
<td>51</td>
<td>202</td>
<td>60</td>
<td>4.3</td>
</tr>
</tbody>
</table>

(Mean of two measurements)

### TABLE 4.18

**PROPERTIES OF SAMPLES IMPLANTED AT ROOM TEMPERATURE WITH 150 keV 1.10^{15} \text{Cd}^+ \text{IONS/cm}^2 FOLLOWED BY LASER IRRADIATIONS Q-SWITCHED RUBY LASER $\lambda = 0.6943 \text{μm}$ PULSE LENGTH = 15 or 25 nsec.**

<table>
<thead>
<tr>
<th>LASER ENERGY DENSITY (J/cm$^2$)</th>
<th>ENCAPSULANT</th>
<th>SHEET ELECTRICAL PROPERTIES $\mu_e$ (cm$^2$/V·sec)</th>
<th>ELECTRICAL ACTIVITY $\chi$ (°)</th>
<th>SUBSTITUTIONAL Cd+ (%)</th>
<th>TOTAL Cd+ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td>$&gt;&gt;0$</td>
<td>0</td>
<td>50</td>
<td>8</td>
</tr>
<tr>
<td>$0.3$ $\text{Si}_2\text{N}_4$</td>
<td>$6.7 \times 10^{15}$</td>
<td>0.3</td>
<td>2.1 $\times 10^{3}$</td>
<td>0</td>
<td>4.3</td>
</tr>
<tr>
<td>$0.6$ $\text{Si}_2\text{N}_4$</td>
<td>$3.6 \times 10^{14}$</td>
<td>22</td>
<td>758</td>
<td>36</td>
<td>4.7</td>
</tr>
<tr>
<td>$1.2$ $\text{Si}_2\text{N}_4$</td>
<td>$6.2 \times 10^{14}$</td>
<td>9.2</td>
<td>1.1 $\times 10^{3}$</td>
<td>62</td>
<td>5.4</td>
</tr>
<tr>
<td>$1.2$ $\text{Si}_2\text{N}_4$</td>
<td>$3.0 \times 10^{14}$</td>
<td>4.4</td>
<td>2.10$^4$</td>
<td>30</td>
<td>4.0</td>
</tr>
<tr>
<td>$0.3$ High resistance</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>19.1</td>
</tr>
<tr>
<td>$0.6$ High resistance</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>9.3</td>
</tr>
<tr>
<td>$1.2$ High resistance</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>7.1</td>
</tr>
</tbody>
</table>
were found to be highly unstable. However for samples coated with Si$_3$N$_4$ electrical activities measured were 36, 62 and 30% following irradiation with energy densities of 0.3, 0.6 and 1.2 J/cm$^2$ respectively.

Only one profile from a coated sample was measured and showed that for 0.3 J/cm$^2$ a maximum hole concentration of about $4 \times 10^{19}$ holes/cm$^3$ occurred. The high hole concentration at the surface (Fig. 4.39) is consistent with the RBS results (Fig. 4.38). The electrical profile differs in shape and is broader than the theoretical LSS profile. This indicates that diffusion of cadmium occurred during laser irradiations.

The mobilities lie in the range between 20 to 30 cm$^2$/V.s. which are low and are about 0.3 of the values quoted by Sze and Irvin\textsuperscript{(160)} (Fig. 4.39), for similar carrier concentrations.

(b) Multiple Pulse Irradiations

Following irradiation with one or five pulses of 0.3 J/cm$^2$ the aligned spectra were identical. As the number of pulses increased to ten, the aligned spectrum showed a decrease in the backscattering yield and the value of $X_{\text{min}}$ reduced from 19% to about 8.4% (Fig. 4.40, table 4.19). The atomic profiles (Fig. 4.40) show that out-diffusion of cadmium occurred which was more marked as the number of pulses was increased.
Fig. 4.38 RBS spectra of laser annealed Cd implanted GaAs. Encapsulation - Si$_2$N$_4$. Irradiation with Q-switched ruby laser with various energy densities. $\lambda = 0.6943$ $\mu$m, Pulse length = 15 nsec. (1.5 MeV He$^+$ RBS) 1 - as implanted, 2 - Si$_2$N$_4$ (750°C/15 sec), 3 - 0.3J/cm$^2$, 4 - 0.6J/cm$^2$, 5 - 1.2J/cm$^2$. 
Fig. 4.39 Hole concentration and mobility profiles for cadmium implanted GaAs. Laser annealed with Q-switched ruby laser (Surrey Univ.). Pulse length 25 nsecs.
Fig. 4.40 RBS spectra as a function of multiple laser irradiations using Q-switched ruby laser on non-capped samples. Laser energy density 0.3 J/cm². 1 - As implanted. 2 and 3 - laser annealed.
The same effect as above was also observed when the number of incident pulses was kept constant (five) but the energy density was increased from 0.3 J/cm$^2$ to 0.6 J/cm$^2$ (Fig. 4.41, table 4.19).

Fig. 4.42 shows the effects of irradiating with a laser beam on the backsurface of the implanted sample. The aligned spectra after irradiating with 1, 2, 3 and 8 pulses of energy density 2.6 J/cm$^2$ per pulse, were very similar. $X_{\text{min}}$ decreased from 50% to 36%, indicating some reordering of the crystal had occurred (Fig. 4.42 table 4.20).

4.5.4 Summary

For 150 keV, 1x10$^{15}$ ions/cm$^2$ of cadmium implanted into gallium arsenide, an increased recrystallization and electrical activation occurred as the annealing temperature was increased. Annealing at 900°C for 30 seconds, caused perfect recrystallization (Fig. 4.33), incorporated 85% of cadmium on lattice sites and caused 60 percent of the implanted atoms to become electrically active (table 4.17).

Maximum peak hole concentrations of about 3x10$^{19}$ holes/cm$^3$ were measured after annealing at 900°C and the electrical profiles were very broad (Fig. 4.32) which is evidence of diffusion of Cd in GaAs.

Samples coated with Si$_3$N$_4$ and non-coated samples were annealed successfully using single and multiple pulses from a Q-switched ruby laser. A maximum electrical activity
Fig. 4.41 RBS spectra as a function of laser energy density at multiple pulses. Each sample irradiated with 5 pulses of 25 nsec length per pulse. Q-switched ruby laser.

1 - as implanted. 2 and 3 - laser annealed.
### Table 4.19

Properties of 150 keV $1.10^{15}$ Cd$^+$ Ions/cm$^2$ into GaAs. Laser Annealed Ruby Laser $\lambda = 0.6943$ μm. Pulse Length = 15 or 25 nSec.

<table>
<thead>
<tr>
<th>Laser Energy Density (J/cm$^2$)</th>
<th>Number of Pulses</th>
<th>$X_{\text{min}}$ (%)</th>
<th>Substitutional Cd$^+$ (% of 100 Chns.)</th>
<th>Total Cd$^+$ Substitutional (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>50</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>0.3</td>
<td>1</td>
<td>19.1</td>
<td>57</td>
<td>65</td>
</tr>
<tr>
<td>0.3</td>
<td>5</td>
<td>19.1</td>
<td>57</td>
<td>65</td>
</tr>
<tr>
<td>0.3</td>
<td>10</td>
<td>8.4</td>
<td>65</td>
<td>80</td>
</tr>
<tr>
<td>0.6</td>
<td>1</td>
<td>9.3</td>
<td>57</td>
<td>65</td>
</tr>
<tr>
<td>0.6</td>
<td>5</td>
<td>5.5</td>
<td>65</td>
<td>69</td>
</tr>
<tr>
<td>1.2</td>
<td>1</td>
<td>7.1</td>
<td>62</td>
<td>78</td>
</tr>
</tbody>
</table>

Estimated error in laser energy density: ± 10%, $X_{\text{min}}$: ± 0.5%

### Table 4.20

Properties of Samples Implanted at Room Temperature with 150 keV $1.10^{15}$ Cd$^+$ Ions/cm$^2$ Followed by Laser Irradiation with Q-Switched Ruby Laser on to the Back Surface of the Sample.

<table>
<thead>
<tr>
<th>Laser Energy Density (J/cm$^2$)</th>
<th>Number of Pulses</th>
<th>Electrical Activity (%)</th>
<th>$X_{\text{min}}$ (%)</th>
<th>Substitutional Cd$^+$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>0</td>
<td>50</td>
<td>8</td>
</tr>
<tr>
<td>2.6</td>
<td>1</td>
<td>0</td>
<td>36</td>
<td>20</td>
</tr>
<tr>
<td>2.6</td>
<td>2</td>
<td>0</td>
<td>36</td>
<td>24</td>
</tr>
<tr>
<td>2.6</td>
<td>4</td>
<td>0</td>
<td>37</td>
<td>24</td>
</tr>
<tr>
<td>2.6</td>
<td>8</td>
<td>0</td>
<td>36</td>
<td>20</td>
</tr>
</tbody>
</table>

Estimated error in laser energy density: ± 10%, $X_{\text{min}}$: ± 0.5%

Percentage Cd$^+$ Substitutionals: ± 5%
Fig. 4.42 RBS spectra as a function of multiple irradiations on the back surface of the Cd implanted GaAs. Q-switched ruby laser, Pulse length = 25 nsec, laser energy density 2.6J/cm². 2 - 1 pulse, 3 - 2, 4, 8 pulses.
of 62% was recorded after irradiating the coated sample with 0.6 J/cm².

Out-diffusion of cadmium was observed which was found to be dependent both on the laser energy density and the number of irradiations.

4.6 CONCLUSIONS

For zinc and cadmium implanted gallium arsenide, the results presented in this chapter indicate that high electrical activation and peak hole concentrations in excess of \(10^{19}\) holes/cm\(^3\) can be obtained following annealing using either the conventional thermal annealing process or the newly developed laser annealing method.

Diffusion of both Zn and Cd in GaAs was evident from the broadening of the electrical and the atomic profiles. The results suggest that the diffusion is dependent on:

(a) The implant temperature.
(b) The annealing temperature.
(c) The implant ion energy.
(d) The ion dose.
(e) The type of laser used for annealing.
(f) The laser pulse energy density.
(g) The number of irradiations.
5. DISCUSSION AND ANALYSIS OF RESULTS

The results presented in chapter four are discussed and analysed in this chapter.

5.1 Conventional and Thermal Pulse Annealing

5.1.1 Crystalline Damage

Following implantation with 150 keV, 1x10^{15} ions/cm^2 of Zn or Cd at room temperature into GaAs, the peak in the aligned RBS spectrum reached a random level thus indicating that the gallium arsenide surface layer became amorphous. The amorphous layers were estimated to be about 1600 Å and 2000 Å thick in the cases of Cd and Zn implants respectively.

The calculated \(^{(178)}\) projected range and standard deviation both for zinc and cadmium in GaAs are listed below (table 5.1). It can be seen (Figs. 4.3 and 4.34) that the

<table>
<thead>
<tr>
<th>ION</th>
<th>PROJECTED RANGE ( R_p )</th>
<th>STANDARD DEVIATION ( \Delta R_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>595</td>
<td>284</td>
</tr>
<tr>
<td>Cd</td>
<td>412</td>
<td>179</td>
</tr>
</tbody>
</table>

Table 5.1. For 150 keV Zn and Cd into GaAs, implant direction 8° to the \(<100>\) surface normal. Dose 1x10^{15} ions/cm^2.
measured thickness of the disordered region extends to depths considerably larger than $R_p + \Delta R_p$. Similar effects have been observed by Campisano et al (143) for Te implanted into GaAs. Furthermore they believe that at a distance of three times the standard deviation from the projected range, the concentration of implanted tellurium was still larger than $10^{12}$ atoms/cm$^2$, which is sufficient to create a heavy damage layer. This is also true for our experiments and as the accelerated ions slow down in the host material they may cause displacements, resulting in further interactions which may also be partially responsible for the extended amorphous layer thickness observed. These ideas are consistent with the findings of Gamo et al (56), where a 100 keV, $3 \times 10^{13}$ Zn$^+$/cm$^2$ implant produced an amorphous layer in gallium arsenide.

When the GaAs samples were implanted with zinc ions at a substrate temperature of about 200°C, the amount of damage caused by the implant was quite small. The $X_{\text{min}}$ value measured was about 9%, which is significantly higher than the value of 4% observed for a single crystal GaAs.

In general the results (section 4.2.1) suggest that increased reordering of the implanted gallium arsenide occurs with increasing annealing temperature. For samples implanted at room temperature with zinc or cadmium ions, annealing at temperatures up to 700°C does not cause complete recovery. For perfect recrystallization an annealing temperature of 900°C was necessary. However for the implantation performed at 200°C, subsequent annealing
in the temperature range 650 to 800°C produced a damage free crystal as measured by RBS.

5.1.2 Annealing Behaviour of Zinc Implanted GaAs (RT-900°C).

The room temperature sheet resistivity results of Fig. 4.1 suggest that there are four distinct annealing stages and these are:-

(1) RT to 400°C.
(2) 400°C to 650°C.
(3) 650°C to 800°C.
(4) 800°C to 900°C.

1st Annealing Stage (RT to 400°C)

This stage corresponds to a progressive increase in sheet resistivity and can be explained in terms of a hopping mechanism.

For amorphous semiconducting materials the process of thermally activated hopping of carriers is dominant\(^{180}\). For completely disordered gallium arsenide, the activation energy of hopping was calculated by Kato et al\(^{179}\) to be 0.087 eV and the hopping distance \(R_D\) 55 Å.

The RBS and TEM analyses (section 4.2.1, Figs. 4.3 and T4.1) suggest that the unannealed specimen is amorphous and therefore the electrical conductivity in this sample is probably due to the thermally assisted hopping mechanism associated with localized states within the
forbidden gap. The increase in sheet resistivity is thought to be due to the decrease in the number of localized states. Upon annealing at 300°C/400°C, the GaAs became more ordered (section 4.2.1 RBS and TEM measurements) and it is likely that the number of localized states reduced. This increased the hopping distance and the mobility decreased which resulted in an increased resistivity (reduced conductivity) that is seen in Fig. 4.1.

The data in the range from room temperature to 400°C is further examined by plotting \( \ln \rho_{Ta}/\rho_{RT} \) versus the reciprocal annealing temperature (Fig. 5.1).

\[
\ln(\rho_{Ta}/\rho_{RT}) \propto \exp(-E_a/kT_a) \quad (179) \quad ... \quad (5.1)
\]

where \( \rho_{RT} \) and \( \rho_{Ta} \) are the sheet resistivities of the as-implanted material and after annealing at a temperature of Ta respectively. E\(_a\) is the activation energy.

The activation energy estimated from Fig. 5.1 was about 0.14 eV which is somewhat different to the value of 0.35 eV reported by Kato et al\((179)\) for both N\(^+\) and S\(^+\) ions implanted into gallium arsenide.

**2nd Annealing Stage (400 to 650°C)**

This stage is associated with a rapid decrease in sheet resistivity (Fig. 4.1) which is probably due to hopping conduction in addition to the contribution from the normal semiconductor conduction process.
150 keV Zn$^+$ $1.10^{15}$ Ions/cm$^2$

$T_i = RT$

$T_a = RT$ to 400°C

Activation energy

$E_a = 0.14$ eV

Fig. 5.1 Log of sheet resistivity ratio versus reciprocal annealing temperature.
The variation of sheet resistivity with reciprocal annealing temperature is shown in Fig. 5.2. In the annealing temperature range 400 to 650°C ln $\rho_s$ of the implanted layer shows a $T^{-1}$ dependence and so the sheet resistivity can be expressed as follows:

$$\rho_s = \rho_0 \exp\left(\frac{E}{kT}\right) \quad \ldots \quad \ldots \quad (5.2)$$

From fig. 5.2

$E = 1.6$ eV and $\rho_0 = 1.3 \times 10^{-6}$ $\Omega/\square$

This value of 1.6 eV may be associated with the occupation of substitutional lattice sites by the implanted zinc ions during the annealing process (400 to 650°C). If this is so, then the normal semiconductor conduction process may account for the decrease in resistivity. However, conduction via defect states (i.e. hopping conduction) should not be excluded as disorder (residual damage), evident from RBS and TEM observations in the temperature range 400 to 650°C, is still present. The activation energy of 1.6 eV is very similar to the value of 1.5 eV reported by Okabayashi(49) for zinc implanted GaAs$_{1-x}$P$_x$.

3rd Annealing Stage (650 to 800°C)

This is indicated by the constant sheet resistivity (about 500 $\Omega/\square$) which is in agreement with the Hall measurements showing a constant electrical activation of about 15% from 650 to 800°C. The material is single crystal and the gross disorder encountered at lower temperatures is no longer present (see section 4.2.1 RBS and TEM).
150 keV $1.10^{15}$ Zn$^+$/cm$^2$ INTO GaAs

$T_i = RT$

$\text{Cap} = \text{Al}$

$T_a = 400^\circ C$ to $650^\circ C$

**Fig. 5.2.** Sheet resistivity versus reciprocal annealing temperature
It seems that the electrical activity in this annealing stage is due to a small fraction (~15%) of the implanted zinc ions occupying gallium sites. The remaining fraction (approximately 85%) of Zn ions are most probably associated with either single dislocations or loops that are present, or defects that are too small to detect with TEM, for example small clusters or complexes. The carrier mobility (Fig. 5.3) is equivalent to good quality GaAs\(^{160}\) with the exception of the 650°C anneal, and thus is unaffected by the presence of dislocation lines and loops.

**4th Annealing Stage (800 to 900°C)**

In this final stage a large decrease in the sheet resistivity occurs from about 500 Ω/□ to 100 Ω/□ (Fig. 4.1). The electrical activity approaches 100% (table 4.2) and carrier profiles (Fig. 4.2) become very broad. This suggests that the majority of zinc ions which were bound up with defects and did not contribute to the carrier concentration at 700 and 800°C now diffuse into the specimen, occupy lattice sites and contribute to the carrier concentration. This indiffusion of zinc is in accord with the published data showing that the profiles became increasingly deep as the annealing temperature increases from 850 to 950°C\(^{30}\).

Cadmium implants have not been studied in such detail as the zinc implants. However, the properties of cadmium implanted GaAs (RBS and electrical section 4.5.2) as a function of annealing temperature changed in a manner
Fig. 5.3 Hall mobility as a function of carrier concentrations for zinc implanted GaAs.
similar to zinc implants. The variation of sheet carrier concentration with reciprocal annealing temperature is plotted in figure 5.4. It can be seen that there exists a linear relationship with an activation energy of about 0.6 eV.

The Hall mobilities measured from Cd implanted samples are much lower than those for the Zn implants and those predicted by the Sze and Irvin data (160) (Fig. 5.5). This may be related to the large mass of cadmium and the implantation damage it produces. Even after annealing at 900°C there may be defects present which have not annealed out completely. However partial encapsulation (Si₃N₄) failure may also have caused a lowering of the mobility.

In summary, four distinct annealing stages have been identified. The initial stage RT to 400°C fits a hopping conduction model and the final stage 800 to 900°C is related to the diffusion of zinc in gallium arsenide.

5.1.3 Electrical Properties (annealing temp. 650 to 900°C)

In this section the electrical properties obtained from Zn implanted gallium arsenide are compared with the published data and the differences are discussed.

(i) Sheet Measurements

For cadmium implanted into GaAs at room temperature followed by annealing in the temperature range room temperature to 900°C, our results are in accord with those of other groups (30) (Fig. 4.32). For zinc implanted gallium
150 keV 1.10^{15} \text{Cd}^+ / \text{cm}^2 \text{ INTO GaAs}

\text{T}_i = RT, \quad \text{Cap - Al}/\text{Si}_3\text{N}_4

Activation energy

0.63 \text{eV.}

**Fig. 5.4** Dependence of sheet hole concentration on annealing temperature
Fig. 5.5  Hall mobility as a function of carrier concentration for Cd implanted GaAs
arsenide, our results for doses below $1 \times 10^{14}$ ions/cm$^2$ are consistent with published work$^{(17, 30, 45, 47)}$. However, above this dose the results agree with Littlejohn et al$^{(47)}$ but disagree with Yuba et al$^{(17)}$. We have recorded similar electrical activities ($\sim 100\%$) to Zolch et al$^{(30)}$ following a thermal pulse anneal at $900^\circ$C for 30 seconds, even though he$^{(30)}$ annealed samples for thirty minutes. This suggests that at high annealing temperatures, the annealing time employed is not so critical. This is in accord with the results on donors in GaAs where it was reported$^{(180)}$ that the time required to obtain a saturation percentage electrical activity, decreased with increasing annealing temperature.

The discrepancy between our results and those of other groups$^{(17, 45, 47)}$ may be related to:

(a) The thermal stability and preparation of the substrate material.

(b) Variation in the implantation parameters such as the dose rate.

(c) The type of encapsulant used and the method of deposition.

(d) The method of forming ohmic contacts.

Each of these points is briefly discussed below:--

(a) **Substrate Stability**

The thermal stability of the substrate material was investigated in order to ensure that results were not
influenced by changes in its electrical properties.

The unimplanted n-type bulk GaAs samples \( (n \sim 10^{16} \text{ cm}^{-3}) \) were annealed at 700\(^{\circ}\)C for fifteen minutes and at 800\(^{\circ}\)C for five minutes after encapsulating with aluminium layers. Hall effect and sheet resistivity measurements showed that the concentrations in the gallium arsenide samples remained unchanged from their values prior to annealing. This indicates that no unusual redistribution of the background impurity occurred during the annealing process.

However, no mention has been made in the literature\(^{17,30,45,47}\) of the thermal stability of the substrate material used. In the early stages of ion implantation into GaAs, the quality of the material commercially available was not very good compared with that currently available\(^{181}\). Therefore this may have had a significant effect on the results reported in earlier publications.

(b) **Dose Rate**

It was found (see section 4.2.4) that the sheet hole concentrations and sheet mobilities were unaffected by the implant dose rate in the range 0.04 \( \mu \text{A/cm}^2 \) to 3.6 \( \mu \text{A/cm}^2 \).

The dose rate used by other workers\(^{17,30,45,47}\) is not known.
In the early work on the heat treatment of GaAs, SiO$_2$ was the popular choice of encapsulant, but subsequent findings have indicated that SiO$_2$ permits out-diffusion of gallium atoms.$^{(2,182)}$

Sealy et al.$^{(10)}$ and Hemment et al.$^{(182)}$ have found that SiO$_2$ is a poor encapsulant for implanted donors in GaAs. It is possible that this may also be true for acceptors in gallium arsenide as Benson et al.$^{(8)}$ have observed the formation of Zn$_3$As$_2$ and ZnGa$_2$O$_4$ in SiO$_2$ capped samples which had been implanted with $1\times10^{15}$ Zn$^+$/cm$^2$ and annealed at 600°C and 800°C respectively. They believed$^{(8)}$ that this effect was due to outdiffusion of As or Ga and indiffusion of oxygen from the SiO$_2$ layer.

It is well known that Si$_3$N$_4$ is a superior encapsulant to SiO$_2$$^{(5,10,182)}$ and furthermore Sealy and Surridge$^{(15)}$ have reported that evaporated aluminium layers can give very similar results to Si$_3$N$_4$ for donor ions implanted into gallium arsenide.

For comparison purposes, GaAs samples implanted with 150 keV, $1\times10^{15}$ ions/cm$^2$ of Zn and Cd, were encapsulated with Si$_3$N$_4$ layers deposited at 750°C for fifteen seconds. Annealing was performed at 700°C for 15 minutes or at 800°C for five minutes in a manner similar to aluminium encapsulated samples. Table 5.2 below summarises the results.
<table>
<thead>
<tr>
<th>ION CAP</th>
<th>ANNEALING TEMP. (°C)</th>
<th>SHEET ELECTRICAL PROPERTIES $\rho_s$ (Ω/cm)</th>
<th>ELECTRICAL ACTIVITY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>700</td>
<td>$1.7 \cdot 10^{14}$</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.5 \cdot 10^{14}$</td>
<td>93</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>700</td>
<td>$3.4 \cdot 10^{14}$</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3.1 \cdot 10^{14}$</td>
<td>84</td>
</tr>
<tr>
<td>Al</td>
<td>800</td>
<td>$2.3 \cdot 10^{14}$</td>
<td>67</td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td>$3.5 \cdot 10^{14}$</td>
<td>65</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>800</td>
<td>$2.9 \cdot 10^{14}$</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 5.2: Electrical properties of 150 keV, $1 \times 10^{15}$ ions/cm$^2$ of Zn/Cd implanted into gallium arsenide and annealed at 700/800°C.

Annealing with Si$_3$N$_4$ or Al capping layers produces slightly different electrical properties (table 5.2). The higher electrical activities in the case of Si$_3$N$_4$ capped samples may be due to the extra thermal pulse anneal (750°C for thirty seconds) received by these samples during the Si$_3$N$_4$ deposition process. However, taking into account the experimental errors involved in the measurements (see appendix 7.A.1) both Si$_3$N$_4$ and aluminium capping layers produce very similar results. Previously we have observed similar results for magnesium implanted gallium arsenide. Therefore it is probable that aluminium layers are more efficient as encapsulants than are SiO$_2$ layers.
SiO$_2$ has been employed by other groups$^{(17,45,47)}$ for protecting zinc implanted GaAs during annealing. In these cases post implantation annealing may have caused out-diffusion of gallium into the SiO$_2$ leaving behind an arsenic rich layer. Since p-type dopants (Be, Mg, Zn and Cd) in GaAs occupy gallium sites, it is possible that the formation of Ga vacancies (arsenic rich GaAs) may have enhanced the electrical activation observed by others$^{(17,45,47)}$. To some extent this has been confirmed by Zölch et al$^{(30)}$ who have obtained higher electrical activities with SiO$_2$ than with Si$_3$N$_4$ coatings, for zinc implanted gallium arsenide.

(d) Contacts

The method employed for making ohmic contacts can also affect the electrical activities. The results reported on Mg and Zn implanted GaP showed large differences in the measured values of sheet carrier concentrations which were mainly due to the material used and the method employed for making ohmic contacts$^{(42)}$.

In our study we observed that by evaporating gold at room temperature, followed by an annealing cycle at 400°C for five minutes, the GaAs became very conducting with an apparent electrical activity of greater than 100%. This suggests that gold diffuses into the gallium arsenide surface layers enhancing the activity. The damage caused by the implantation process increases this effect.
The method employed for fabricating ohmic contacts by other groups\(^{(17,30,45,47)}\) is not known in detail. However, we have made ohmic contacts to p-type layers by evaporating gold at room temperature without any subsequent alloying cycle (section 3.5). So there is no possibility for the diffusion of gold during contact fabrication.

From our investigations we conclude that the differences between our results and those of other researchers\(^{(17,30,45,47)}\) are mainly due to different encapsulants (SiO\(_2\)) and to different methods of making ohmic contacts.

\[\text{(ii) Electrical Profiles}\]

Profiles obtained from implants carried out at 200°C are broader (Fig. 4.14) than those measured for samples implanted at room temperature (Fig. 4.13), which is indicative of diffusion of zinc during annealing. The differences between cold and hot implants disagree with the conclusions of Donnelly\(^{(162)}\), who summarised that for cadmium and zinc, hot implants decrease diffusion compared with cold implants. Itoh and Oana\(^{(48)}\) reported that the p-n junction depth in Zn implanted GaAs\(_{(1-x)^P_X}\) decreased with increasing implant temperature. Similar results have been obtained for Cd into GaAs\(^{(70)}\) and GaP\(^{(60)}\).

The apparent differences between our results and published data are probably due to the technique employed in characterisation. The depth of the p-layer has been
measured (16, 48, 70) by estimating the p-n junction depth using mostly the technique of angle lapping and staining. In our study the carrier profiles were calculated using differential Hall and sheet resistivity measurements. Figure 5.6 illustrates the differences in the results one would expect, depending on which of the two analysis techniques is used. The carrier profile from the hot implant is broader (Fig. 5.6) than that from the cold implant, thus indicating more diffusion in the case of hot implant. However, the p-n junction depths (Fig. 5.6, depths extrapolated) suggest more diffusion in the case of cold implants. So our results (p-n junction depths) are in agreement with the published data, implying more diffusion in the case of cold implants.

To investigate whether the diffusion (Section 4.2) of the implanted zinc in GaAs occurs during the annealing process or during implantation, an experiment was conducted in which 450 keV, 1x10^{15} Zn^+ /cm^2 was implanted into 4x8 mm GaAs sample (double) held at 200°C. Following implantation about 0.4 um of the implanted region was removed from one half of the sample. This corresponds to the region where about 95% of the zinc ions come to rest. The whole of the sample was encapsulated with aluminium and annealed at 700°C for fifteen minutes. Hall effect and sheet resistivity measurements on two halves of the sample indicated electrical activities of about 2% and 53% for the etched and the unetched samples respectively. An electrical activity of about 2% indicated that no diffusion of Zn took place during the ion implantation. Therefore the diffusion occurred during the annealing process.
Fig. 5.6  Extrapolated junction depths for hot and cold implants in GaAs.
5.2 Laser Annealing with Millisecond Pulses

The gallium arsenide samples implanted with $1.10^{15}$ zinc ions/cm$^2$ and coated with Si$_3$N$_4$ layers annealed successfully when irradiated with millisecond pulses. However, the uncoated samples remained electrically non-conducting. In contrast no measurable electrical activation was observed from gallium arsenide samples implanted with donors (Se, Te and Sn) and annealed in a similar way to the Zn implanted GaAs.

The results of RBS measurements suggest that although Si$_3$N$_4$ deposition process caused significant recrystallization there was damage remaining at the sample surface (Fig. 4.17). The electrical measurements on these samples showed that 28% of the implanted Zn ions became electrically active during the Si$_3$N$_4$ deposition process but the sheet mobility was very low (approximately 10 cm$^2$/V.s).

As the laser energy or the number of irradiations was increased, improvement in the electrical properties was observed (Fig. 4.18). The electrical activity estimated by integrating the area under the carrier concentration profiles (Fig. 4.19) increased as the laser energy density was increased (Fig. 5.7). The difference in the calculated and the measured electrical activity (Fig. 5.7), is due to the effect of residual damage and to the poor ohmic contacts which were not very stable with time during the profile measurements.
Fig. 5.7 Percentage electrical activity versus laser energy density from freely generated mode ruby laser.
Properties of laser annealed GaAs implanted with 150 keV, \(1.10^{15}\) Zn\(^+\)/cm\(^2\) at room temperature. Annealed with freely generated mode ruby laser. Cap - Si\(_3\)N\(_4\)

<table>
<thead>
<tr>
<th>LASER ENERGY DENSITY (J/cm(^2))</th>
<th>MEASURED</th>
<th>CALCULATED</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>33</td>
<td>10</td>
</tr>
<tr>
<td>0.6</td>
<td>27</td>
<td>23</td>
</tr>
<tr>
<td>1.0</td>
<td>29</td>
<td>27</td>
</tr>
<tr>
<td>1.5</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td>1.6</td>
<td>42</td>
<td>36</td>
</tr>
<tr>
<td>1.7</td>
<td>46</td>
<td>37</td>
</tr>
<tr>
<td>2.4</td>
<td>47</td>
<td>43</td>
</tr>
<tr>
<td>2.5</td>
<td>47</td>
<td>46</td>
</tr>
<tr>
<td>3.0</td>
<td>41</td>
<td>40</td>
</tr>
</tbody>
</table>
In comparison with conventional thermal annealing at 700°C or at 800°C, laser irradiation produced high electrical activation (from 30 to 80% compared with 10 to 20%), narrow profiles and much greater peak hole concentrations. The highest peak hole concentration recorded was about $1 \times 10^{20}$ holes/cm$^2$ following irradiation with four pulses (Fig. 4.22) or about $7 \times 10^{19}$ holes/cm$^2$ after irradiation with a single pulse (Fig. 4.19). These are about three to five times of that obtained following the thermal anneal at 900°C for thirty seconds. Similar results to the above have been reported by Bogatyrev et al(139) who used a 5 millisecond pulse of 50 J/cm$^2$ energy density from a ruby laser to anneal GaAs samples implanted at 200°C with 35 keV, $1 \times 10^{16}$ Zn$^+/cm^2$.

Bertolloti et al(183), using RBS and RHEED techniques reported that for ion implanted silicon only an amorphous to polycrystal transition is possible when irradiating with a ruby laser in the freely generated mode. This is consistent with our RBS measurements on GaAs (Fig. 4.17) where residual damage ($X_{\text{min}} \sim 16\%$) remained after laser annealing. However the measured electrical properties are similar to good single crystal GaAs (Fig. 5.8)(160) and furthermore the mobilities are in good agreement with the mobilities observed after thermal anneals (compare Figs. 5.3 and 5.8).

From our results it appears that the annealing mechanism may be linked with the Si$_3$N$_4$ capping layer.
Fig. 5.8 Hall mobility as a function of carrier concentrations for laser annealed GaAs. Freely generated mode ruby laser. All samples capped with Si$_3$N$_4$. 
Experiments carried out on InSb\(^{184}\) suggested that the Si\(_3\)N\(_4\) layer was acting as an antireflection coating. However this is not the correct explanation for our results as some experiments were carried out in which the Si\(_3\)N\(_4\) layer was deposited at 750\(^\circ\)C for fifteen seconds, followed by removal of this layer and subsequent annealing with a laser energy density of about 3 J/cm\(^2\). Electrical measurements indicated that the sheet hole concentration was 2.7x10\(^{14}\) holes/cm\(^2\) and the sheet mobility was 74 cm\(^2\)/V.s, which are similar to the values measured for capped samples. Therefore from these observations we conclude that the antireflection properties of the Si\(_3\)N\(_4\) layer are not solely responsible for the annealing affect during irradiation with a freely generated pulse from a ruby laser.

The reason why only the capped samples became electrically active is due to the sample structure before annealing. The difference between capped and uncapped samples prior to laser irradiation is illustrated in Fig. 5.9. The uncoated sample is amorphous over a depth of about 2000 \(\AA\) and the Si\(_3\)N\(_4\) capped sample contains residual damage close to the surface. Therefore a higher energy density (energy threshold) will be needed for the sample structure shown in Fig. 5.9a, than for the structure shown in Fig. 5.9b, for recrystallization (see section 2.2.2). The maximum energy density employed during this investigation was about 3 J/cm\(^2\) which is significantly lower than the threshold value of 10 to 100 J/cm\(^2\) reported by Smirnov et al\(^{185}\) and about 40 J/cm\(^2\) per pulse and a total of 64
Sample structure prior to laser irradiation of zinc implanted GaAs, 150 keV $1.10^{15}$ ions/cm$^2$, $T_i = RT$. (RBS measurements)
pulses used by Regolini et al. to recrystallize amorphous silicon.

However an energy density of about 3 J/cm$^2$ was found to cause significant electrical activation with some recrystallization (Fig. 5.9b) in samples which had received Si$_3$N$_4$ deposition treatments prior to laser irradiation. For as-implanted samples this energy density was insufficient to cause a measureable change in electrical properties and structure.

An earlier publication suggested that laser annealing is accompanied not only by heating but also by effective ionization, shock waves and quenching. Some of these are discussed below:

(i) **Possible Thermal Effect**

The temperature rise of the GaAs sample surface following irradiation with a laser pulse was calculated using the following method:

For the one-dimensional case

$$T_s(0,t) = \left( \frac{2F_0}{K'} \right) \left( \frac{K''t}{\pi} \right)^{\frac{1}{2}}$$

Where:

- $T_s$ = Surface temperature °C.
- $F_0$ = Flux absorbed W/cm$^2$.
- $K'$ = Thermal conductivity W/cm deg.
- $K''$ = Thermal diffusitivity.
- $t$ = Length of the laser pulse in seconds.
\[ F_0 = F_i (1-R) \quad \ldots \ldots \ldots \ldots \quad (5.4) \]

\[ F_i \text{ = Incident flux W/cm}^2 \]

\[ R \text{ = Reflection coefficient.} \]

From Carslaw and Jaeger (187):

\[ K'' = \frac{K'}{C_v} \quad \ldots \ldots \ldots \ldots \quad (5.5) \]

\[ \rho' = \text{density g/cm}^3 \]

\[ c_v = \text{specific heat cal g}^{-1} \text{deg}^{-1} \]

Combining equations 5.3 to 5.5:

\[ T_s (0,t) = 2F_i (1-R) \left( \frac{t}{K' \rho' C_v} \right)^{1/2} \quad \ldots \ldots \quad (5.6) \]

For gallium arsenide at \( \lambda = 0.6943 \mu \text{m} \), from reference 137:

\[ R = 0.3 \]

\( \alpha = \text{absorption coefficient} = 2 \times 10^4 \text{ cm}^{-1} \)

\[ K' = 0.44 \text{ W/cm deg} \]

\[ C_v = 0.074 \text{ cal g}^{-1} \text{deg}^{-1} \]

\[ \rho' = 5.3 \text{ g/cm}^3. \]

The pulse duration, \( t \), and the energy density used were 0.8 ms and 3 J/cm\(^2\) respectively.

\[ F_i = 3.75 \times 10^3 \text{ W/cm}^2, \text{ corresponding to } 3 \text{ J/cm}^2. \]

Also, we make the assumption that \( R, K', \rho' \text{ and } C_v \) remain constant with time and temperature.
The calculated temperature rise of the gallium arsenide surface following each laser pulse was found to be about 200°C (from equation 5.6) by assuming that the freely generated pulse train consisted of a square wave of amplitude $3.75 \times 10^3 \text{ W/cm}^2$. This is an ideal case. However, in a practical situation, the temperature rise will be much less than 200°C as some of the heat will be lost deeper into the semiconductor by the normal thermal conduction mechanism. Also by taking account of the spiking nature of the pulse, the probable surface temperature cannot exceed the above temperature by more than a factor of three$^{(183)}$. Therefore the major annealing effect may not be associated with a rise in temperature or a rapid quenching affect.

(ii) **High Ionization**

The mechanisms by which laser irradiation is absorbed at the surface of the semiconductor are believed to be$^{(183, 188)}$:

(a) Absorption by free carriers in the conduction and valence bands.

(b) Absorption through the creation of electron-hole pairs across the forbidden gap.

(c) Absorption at the recombination centres at the surface.

The electromagnetic energy absorbed through these three different processes is subsequently given to the lattice. Ionization in a semiconductor takes place via process b$^{(183)}$. 
Electron-hole pair production requires an energy $\varepsilon_{eh}$ of about $3E_g$ per pair (189) where $E_g$ is the band gap energy. For GaAs, $\varepsilon_{eh} = 4.2$ eV at room temperature (189). The absorption coefficient of gallium arsenide for ruby laser light (1.785 eV) is about $2 \times 10^4$ cm$^{-1}$ (137), i.e. most of the light is absorbed within the first 5000 Å.

If the GaAs sample was irradiated with 3 J/cm$^2$ then allowing for surface reflection, the energy transmitted will be about 2.1 J/cm$^2$. Assuming this is absorbed over 5000 Å, the energy input becomes equal to about $2.6 \times 10^{23}$ eV/cm$^3$. Since the density of GaAs is $2.21 \times 10^{22}$ atoms/cm$^3$ (190), then the energy input is about 11.9 eV/atom. This is approximately three times the energy required for production of an electron-hole pair. Assuming that (a) the surface reflectivity of the gallium arsenide remains constant during the period at which the laser pulse energy is transmitted into the GaAs and (b) that there will be some recombination of electrons-hole pairs as they are created, then there will be approximately $10^{22}$ e-h pairs per cm$^3$ created (191). This enormous concentration of e-h pairs may assist in the annealing of zinc implanted gallium arsenide.

We suggest that the annealing in the case of the freely generated mode ruby laser may be caused by (i) the stress set up near the surface of the gallium arsenide both laterally and internally due to the temperature gradient and (ii) to the production of a large number of electron-hole pairs.
In conclusion the major differences between conventional thermal annealing and laser annealing in the freely generated mode are that:-

(i) The laser irradiation produces much higher electrical activities, up to 100% and greater peak hole concentrations, up to $1 \times 10^{20}$ holes/cm$^3$.

(ii) Laser annealing results in narrow carrier concentration profiles, indicative of less diffusion compared with the broader profiles resulting from the conventional thermal annealing.

(iii) The annealing process is associated with the stress set up near the surface of the GaAs.

5.3. Laser Annealing with Nanosecond Pulses

In general laser irradiation with nanosecond pulses produced high electrical activation of the implanted Zn and Cd, up to 100% (section 4.4 table 4.14). These values are considerably higher than those measured following thermal annealing in the temperature range 650 to 800°C (section 4.2) or after irradiation with a millisecond pulse from a freely generated mode ruby laser (section 4.3).

For 150 keV, $1 \times 10^{15}$ Zn$^+$/cm$^2$, the peak carrier concentrations recorded were about $1 \times 10^{20}$ holes/cm$^3$ from both hot and cold implants (Fig. 4.27). This is an order of magnitude higher than the values obtained following annealing
at 900°C for thirty seconds or about 1.5 times those observed after irradiation with a single pulse of 0.8 ms length. However, the measured carrier concentration profiles are broader (Fig. 4.27) than the other two cases (sections 4.2 and 4.3), suggesting that more diffusion of zinc in GaAs occurred during this annealing process.

The high peak carrier concentrations (about $10^{20}$ cm$^{-3}$) (Fig. 4.27) are an order of magnitude higher than those (about $10^{19}$ cm$^{-3}$) reported for donor implanted GaAs annealed using a Q-switched ruby laser(144-147).

The measured mobilities were substantially lower when compared with, the conventional thermal anneal results, (section 4.2) the millisecond pulse anneals, (section 4.3) and the Sze and Irvin(160) data for good crystalline GaAs (Fig. 4.28). However these results are similar to the published work on donor implanted gallium arsenide annealed with a Q-switched ruby laser(144-148). Some forms of defects are probably responsible for the low values of the mobility observed.

Figure 5.10 illustrates the laser energy density threshold obtained using RBS measurements, for an amorphous layer of about 2000 Å thick. Results indicate a sharp and a gradual transition with energy densities of 0.2 J/cm$^2$ and 1.2 J/cm$^2$ corresponding to Surrey University and City University lasers respectively. The difference between the results (Fig. 5.10) is due to the high spatial non-uniformity in the City University laser beam compared with the Surrey
Fig. 5.10 Illustration of laser energy density threshold for 150 keV, $1 \times 10^{15} \text{ Zn}^+/\text{cm}^2$ implanted into GaAs at room temp. Laser irradiation with Q-switched ruby laser.
University laser beam and also due to the different method employed for measuring laser energy (section 3.4.3). Threshold energy densities of 0.2 J/cm$^2$ and 1.2 J/cm$^2$ are consistent with those of other groups (Italian group, Oak Ridge and Bell Labs) who have reported values in the range 0.2 to 1.4 J/cm$^2$ (section 2.2.3). However, we believe that the most likely value of threshold energy density is about 0.2 to 0.3 J/cm$^2$.

To obtain the maximum electrical activity, more energy was needed for non-coated samples (Fig. 4.26 tables 4.14 and 4.14A). The maximum electrical activities recorded were 100% and 66% from capped and un-capped samples following irradiation with 0.6 J/cm$^2$ and 1.2 J/cm$^2$ respectively. The difference in the energy threshold may be due to the sample structure (damage) prior to laser annealing; that is, the uncapped samples were amorphous and the Si$_3$N$_4$ capped samples were partially crystalline (section 5.2). Thus to be consistent with published data$^v$ (93,143,150) more energy would be required for the former than for the latter samples.

The Hall effect and sheet resistivity measurements on zinc and cadmium implanted gallium arsenide indicated that it is possible to overanneal (tables 4.14, 4.14A and 4.18). This is apparent from the electrical properties which degrade following irradiation at energy densities in excess of about 1 J/cm$^2$ (Fig. 4.26). The SEM micrographs (section 4.4.4) show undulating regions and craters on the GaAs surface following laser annealing. The depth of the craters increased with increasing laser energy density. Above an
energy density of about 1 J/cm$^2$ the surface topographic features were very pronounced and laser induced damage may have occurred in this case which degraded the electrical properties of the implanted GaAs. In ion implanted silicon laser induced damage has been observed using TEM following irradiation with an energy density just above the threshold value.

Decomposition of the gallium arsenide occurred during annealing with the Q-switched ruby laser. This is evident from the large gallium peak in the aligned RBS spectrum (Fig. 4.25) and the amorphous blobs in the TEM micrographs (Fig. T4.7b).

In the case of uncapped GaAs samples implanted with Zn or Cd ions and irradiated with an energy density in the range 1.2 to 1.6 J/cm$^2$, a $X_{\text{min}}$ value of about 7% was measured (tables 4.14, 4.14A and 4.18). Associated with this high value of $X_{\text{min}}$ was a large gallium peak (see Figs. 4.24, 4.25 and 4.36). After etching these samples in HCl for five minutes, $X_{\text{min}}$ becomes about 4%, the excess gallium peak disappeared and the RBS yield became similar to the value for good crystalline gallium arsenide (Fig. 4.25). In contrast, the Si$_3$N$_4$ coated samples had $X_{\text{min}}$ values of 4 to 5% for energy densities in the range 0.3 to 1.2 J/cm$^2$ (Figs. 4.24 and 4.38). The differences between $X_{\text{min}}$ values of capped and uncapped samples are associated with the fact that prior to RBS measurements, all the capped samples were etched in HF after laser irradiation whereas the uncapped samples were not. Therefore if excess gallium i.e. loss of
arsenic, occurred in the case of capped samples, this would not have been observed because it would have been removed by the HF acid. These results are in agreement with the TEM studies on zinc implanted GaAs (section 4.4.3) which showed that both capped and uncapped samples had small amorphous blobs at the gallium arsenide surface. These precipitates, believed to be gallium, disappeared following etching in HCl or HF acid.

Similar effects to the above have been observed by Barnes et al.\textsuperscript{(156)} using RBS on Te implanted GaAs annealed using a Q-switched Nd:YAG laser. Loss of arsenic from the Te implanted gallium arsenide surface was also reported\textsuperscript{(153-155)} following irradiation with a frequency doubled Nd:YAG laser. Venkatesan et al.\textsuperscript{(154)} used time resolved reflectivity and channelling measurements to show that the above effect occurred during annealing.

An important conclusion is that both capped and uncapped samples dissociate during laser annealing (Q-switched) and the amount of decomposition is governed by the laser energy density.

The electrical profiles (Figs. 4.27 and 4.39) were found to be considerably different to the as implanted profile after annealing with a Q-switched ruby laser. A redistribution of the implanted impurity (Cd and Zn) occurred both towards the surface of the GaAs and also deeper into the crystal. This is in agreement with the cadmium atomic profiles (Figs. 4.36, 4.38 and 4.40) obtained using RBS,
which indicated a large Cd peak at the GaAs surface and fairly uniform concentration of cadmium deeper in. The redistribution appeared to be dependent upon the laser energy density as well as on the number of successive irradiations (pulses). The broadening of the electrical (Fig. 4.27) and the atomic profiles (Fig. 4.36) suggests that diffusion of zinc and cadmium occurred during laser annealing. Figure 5.11 illustrates the calculated diffusion profile together with the as-implanted profile (ISS) and the measured profile after laser irradiation. The diffusion coefficient of Zn in GaAs ($\sim 10^{-4}$ cm$^2$/s) estimated from figure 5.11 strongly suggests that the surface melts. Similar results have been reported for ion implanted silicon (see section 2.2 and compare Figs. 2.11 and 5.11). Also it has been shown for Si, that liquid phase epitaxial growth occurs as a result of irradiating with Q-switched ruby and Nd:YAG lasers. So liquid phase epitaxial regrowth may also have occurred in our studies. If the gallium arsenide were to have remained solid, unrealistically long times would be required for the observed redistribution of Zn and Cd to occur (Fig. 5.11). The estimated times required for such redistribution to occur in the solid phase are 3 to $4 \times 10^3$ seconds. These times are enormously long compared to 15 or 25 nanoseconds during which laser energy is deposited. Further evidence is available from our SEM results (section 4.4.4) which show that after laser annealing the gallium arsenide surfaces were rippled, suggesting melting may have occurred.
Fig. 5.11 Carrier concentration profiles before and after laser annealing with a Q-switched ruby laser. Pulse length 15 nsec. Cap - Si$_3$N$_4$.

Shown also diffusion profile calculated.
Finally, we conclude that for zinc and cadmium implanted gallium arsenide irradiated with Q-switched ruby laser, recrystallization and electrical activation of impurities occurs because the surface melts. The regrown layer is free from defects and the dopant profiles are consistent with diffusion in liquid GaAs.
5.4 Redistribution of Implanted Impurity

5.4.1 Introduction

The electrical and atomic profiles of zinc and cadmium in gallium arsenide presented in sections 4.2 to 4.5 indicated that redistribution of the implanted impurity occurred which was shown (section 5.1) to be the result of diffusion during annealing. In this section the diffusion of ion implanted Zn and Cd in GaAs is discussed.

It is well known that the normal diffusion of zinc in gallium arsenide is very complicated. The generally accepted mechanism is the interstitial-substitutional mechanism. In the case of ion implantation no information has been reported on the diffusion mechanism of zinc in GaAs, but it appears that the diffusion is even more complex than that for non-implanted materials (section 2.1.9). However in the following a rather simplified model is adopted to evaluate the diffusion of zinc and cadmium that occurred during annealing. It must be stressed that the calculated diffusion coefficients and the activation energies are qualitative rather than quantitative.

5.4.2 Calculations of Diffusion Coefficients

Diffusion of zinc and cadmium in GaAs can be described by the following equation:

\[ D \propto C V_{Ga} V_{As} V_{I} \exp(-E/kT) \]  

\[ (5.7) \]

\[ D = \text{Diffusion coefficient, cm}^2/\text{s}. \]
\( C \) = Concentration, \( \text{cm}^{-3} \) (Zn or Cd).

\( V_{Ga} \) = Concentration of gallium vacancies

\( V_{As} \) = Concentration of arsenic vacancies

\( V_I \) = Concentration of interstitial vacant sites.

\( E \) = Activation energy, eV.

\( k \) = Boltzmann constant, \( 1.380 \times 10^{-23} \text{ J/K} \).

\( T \) = Temperature, K.

Assuming that the diffusion coefficients of Zn and Cd are independent of their concentrations, then equation 5.7 becomes:

\[
D \propto V_{Ga} V_{As} V_I \exp(-E/kT) \tag{5.8}
\]

The solution of equation 5.8 can be obtained using a simplified diffusion equation.

Assume that a thin film containing \( 1 \times 10^{15} \text{ zinc or cadmium atoms/cm}^2 \) lies on the gallium arsenide surface and takes part in diffusion. The diffusion equation assuming limited source conditions is(193):

\[
C(x,t) = \frac{M}{(\pi D t)^{3/2}} \exp(-x^2/4Dt) \tag{5.9}
\]

\( M \) = Diffusing impurity, \( \text{cm}^{-2} \) (in this case \( M=10^{15} \text{ cm}^{-2} \)).

\( x \) = Depth in cm.

\( t \) = Time in seconds.
Using equation 5.9 the theoretical diffusion profiles are matched to the tail of the experimental profiles from which the diffusion coefficient \( D \) is estimated.

Figure 5.12 illustrates the measured zinc profiles in GaAs together with the theoretical diffusion profiles calculated for the annealing temperature range 650°C to 900°C. It can be seen that the experimental profiles are very much different from the as-implanted LSS profile, indicative of diffusion during annealing. The diffusion coefficients estimated are very similar \( \sim 10^{-13} \text{ cm}^2/\text{s} \) for temperatures in the range 650°C to 800°C. As the annealing temperature is increased to 900°C, the diffusion coefficient increased by two orders of magnitude (Fig. 5.12). The estimated value of about \( 2 \times 10^{-11} \text{ cm}^2/\text{s} \) at 900°C is about three orders of magnitude smaller than the values reported for normal thermal diffusion (approximately \( 5 \times 10^{-8} \text{ cm}^2/\text{s} \)) of Zn in GaAs\(^{67}\). The difference can be explained in terms of the diffusion conditions and the diffusion environment in which zinc atoms diffuse. Also some disagreement may be related to the more simplified diffusion model used in this investigation.

A much higher value of diffusion coefficient \( \sim 10^{-4} \text{ cm}^2/\text{s} \), than the value measured following a thermal anneal was observed (section 5.3, Fig. 5.11), when the annealing was accomplished using a Q-switched ruby laser. Reasons for such a high value are that the gallium arsenide probably melts under these conditions and the implanted atoms diffuse in liquid GaAs.
Fig. 5.12  As implanted profile, measured profiles and the calculated diffusion profiles as a function of annealing temperature. The calculated diffusion profiles are matched to the tail of the experimental profiles and hence the diffusion coefficients.
The diffusion data is analysed by plotting the diffusion coefficient versus the reciprocal annealing temperature (Fig. 5.13). The diffusion of Zn in GaAs does not seem to be dependent on the annealing temperature in the range 650 to 800°C. However, between 800 and 900°C the diffusion coefficient is strongly dependent on the annealing temperature (Fig. 5.13). From figure 5.13 the activation energy is estimated to be about 3.5 ± 1.5 eV and the diffusion coefficient can be described by the following relationship:

\[ D \propto 4.7 \times 10^{10} \exp\left(-\frac{3.5 \pm 1.5}{kT}\right) \]  \hspace{1cm} (5.10)

The calculated activation energy (3.5 ± 1.5 eV) is not very much different to the value of 2.43 eV reported for normal thermal diffusion of zinc in gallium arsenide (195). Allowing for the fact that in the ion implanted case, there will be disorder, vacancies and interstitials which may have a significant effect on the diffusion of Zn in GaAs, the agreement between our values to the published values is reasonable.

The activation energy for interstitial diffusion of zinc in GaAs is reported to be about 1 eV or less (194) and for substitutional diffusion in the As sublattice it is about 4 eV, which is much larger than that in the gallium sublattice, about 2.5 eV (194).

In view of the small number of data points in figure 5.13 it is difficult to draw a definite conclusion about the diffusion mechanism. However if one takes the
Fig. 5.13. Log of diffusion coefficient versus reciprocal annealing temperature.
activation energy to be a maximum of about 5 eV, that is 3.5 + 1.5 eV, the diffusion of zinc may have occurred via the arsenic sub-lattice and interstitials\(^{(194)}\). For example after implantation most zinc atoms may occupy As sites and upon annealing at 900\(^\circ\)C become interstitials and migrate until they come across gallium vacancies which they can occupy and act as acceptors.

On the other hand if one takes the activation energy to be a minimum of about 2 eV, that is 3.5 - 1.5 eV, a reasonable agreement with the activation energy for diffusion via the gallium sublattice is obtained\(^{(194)}\).

For ion implanted cadmium, somewhat less diffusion is observed (Fig. 5.14) compared with that for zinc (Fig. 5.12). It can be seen that increasing the annealing temperature from 700\(^\circ\)C to 900\(^\circ\)C resulted in an increase in the diffusion coefficient by two orders of magnitude. At 900\(^\circ\)C the estimated diffusion coefficients are about 2x10\(^{-11}\) and 5x10\(^{-12}\) cm\(^2\)/s for Zn and Cd in ion implanted GaAs respectively. For cadmium implanted gallium arsenide Zolch et al\(^{(30)}\) reported a diffusion coefficient which is an order of magnitude smaller than the values found above. The difference may be due to the different method used for evaluating diffusion by this author\(^{(30)}\).

The log of the diffusion coefficient versus the reciprocal annealing temperature (Fig. 5.15) exhibits a linear relationship in the temperature range 700\(^\circ\)C to 900\(^\circ\)C. The activation energy for diffusion was estimated to be
Fig. 5.14 As implanted, measured and the calculated diffusion profiles of Cd in GaAs as a function of annealing temperature.
about 2.3 eV, which is much less than the value obtained
for zinc diffusion in GaAs (3.5 ± 1.5 eV) but is similar
to the value (2.3 eV) observed by Zölch et al\(^{(30)}\). These
values are in excellent agreement with the activation
energy value of 2.49 eV found for normal thermal diffusion
of Cd in GaAs\(^{(195)}\). For cadmium implanted gallium
arsenide the diffusion coefficient in the temperature
range 700 to 900°C can be described by the following
equation:–

\[
D = 1.3 \times 10^{-2} \exp(- \frac{2.3}{kT}) \text{ cm}^2/\text{s} \quad \ldots \quad (5.11)
\]

A similar expression has been reported by other
groups\(^{(30,195)}\). The activation energy of about 2.3 eV
suggests that diffusion of cadmium in GaAs may be occurring
via the gallium sublattice. Further support for the above
suggestion comes from the RBS measurements on Cd implanted
GaAs. After annealing in the temperature range 600 to 900°C
about 75 to 90% of the implanted cadmium was found to occupy
substitutional lattice sites.

However, before arriving at some positive
conclusions one must not overlook the fact that after
implantation the diffusion mechanisms may be very complex
and may be affected by radiation damage, defects, vacancies
and Zn and Cd may occupy any position in the gallium
arsenide crystal, i.e. As sites, Ga sites or interstitial
sites. Thus during annealing it may be possible for Zn/Cd
atoms to diffuse via any of the above three positions.
Fig. 5.15 Log of diffusion coefficient versus reciprocal annealing temperature
In light of the work on thermal diffusion (section 2.1.9) we feel that the diffusion of zinc in the ion implanted case occurs by the substitutional-interstitial mechanism. That is zinc occupies gallium sites and during annealing gains enough thermal energy to occupy interstitial sites, migrate via these interstitial sites until it comes across a gallium vacancy which it fills and finally becomes electrically active. This mechanism is consistent with our mean value of the activation energy of $3.5 \text{ eV}$. For cadmium the diffusion is likely to take place substitutionally via the gallium sublattice. The difference between the diffusion mechanisms of Zn and Cd are not understood but it may be related to the difference in the atomic radius of the Cd, Zn, Ga and As. This could be the subject of future study.

5.4.3 Profile Broadening

In chapter 4 the Hall effect and sheet resistivity measurements showed that the zinc and cadmium profiles were broader than the as-implanted profiles. Later in section 5.1 it was concluded that profile broadening occurred during annealing. These ideas are further examined in this section.

Profile broadening occurred as a result of diffusion of Zn and Cd in GaAs. This took place more readily with increasing annealing temperature and increasing ion dose and is consistent with results of other groups who have observed similar behaviour for Be, Cd and Zn implanted gallium arsenide (section 2.2). The two explanations for the above effects are, firstly, diffusion
of Zn is known to be concentration dependent and therefore above a certain concentration rapid diffusion will result. Our results show that diffusion occurs only above a dose of $10^{14}$ ions/cm$^2$, and increases with increasing annealing temperature. Therefore it seems that the above behaviour is similar to the unimplanted GaAs.

When annealing was accomplished using a Q-switched ruby laser, profile broadening was observed once again. This is an expected result as laser energy densities above a threshold value, melt the surface layer and the implanted impurity is able to diffuse in molten GaAs. Increasing the pulse energy density and using a number of successive irradiations has the effect of increasing the thickness of the layer that is melted and therefore the implanted ions can diffuse deeper into the material. Thus the overall result is an increased diffusion and broadening of the profile. Following laser annealing both the electrical and the cadmium atomic profiles showed a large peak at the GaAs surface. It is not understood why and how this large Cd peak occurs, but it may be related to the outdiffusion of cadmium.

More broadening of the profiles was observed from samples which were implanted hot rather than cold. Profile broadening in this case may be related to the radiation damage, since for hot implants most of the damage anneals out during ion implantation (section 5.1).

For zinc and cadmium implanted GaAs it has been reported$^{50,70,71}$ (section 2.1.9), that the additional implantation of arsenic creates large numbers of gallium
vacancies and slows down the diffusion of Zn and Cd in GaAs. This may also be true for our cold implants where the radiation damage may have created a sufficiently large number of vacancies compared with a hot implant and slowed down the diffusion of zinc. Less profile broadening observed in this case may be related to the fact that some of the zinc ions may have been trapped by the vacancies and thus less diffusion occurred.

5.4.4 **Solubility**

Plotted in figure 5.16 is the measured peak hole concentration as a function of ion dose for zinc implants in gallium arsenide. All samples had been coated either with aluminium or with Si$_3$N$_4$ and annealed in the temperature range 700°C to 900°C. The results indicate that for the three implant energies of 60, 150 and 450 keV, the peak hole concentration saturates at about $1.5 \times 10^{19}$ holes/cm$^3$. This is probably the solubility limit in ion implanted gallium arsenide. However, this value is an order of magnitude lower than the value of $1.7 \times 10^{20}$ cm$^{-3}$ at 800°C reported following diffusion of radioactive zinc in gallium arsenide(196). The difference is due to the different experimental conditions.

The peak carrier concentrations and thus the solubility were found to be greatly increased ($\sim 10^{20}$ cm$^{-3}$) following irradiation with a Q-switched ruby laser. This is most likely due to the melting of the GaAs and the very fast quench that takes place in this process.
Fig. 5.16 The peak hole concentrations as a function of implant dose, measured from zinc implanted GaAs.
CONCLUSIONS

The properties of zinc and cadmium implanted into gallium arsenide have been investigated as a function of ion dose, ion energy and the temperature of the substrate during implantation. This chapter states the main conclusions which can be drawn from this work.

The ion implantation process was found to produce gross lattice damage in the surface layer of the gallium arsenide. This damage had to be annealed out in order to establish electrical activity of the implanted ions. This was accomplished using conventional thermal annealing, thermal pulse annealing and laser pulse annealing.

(i) Thermal Annealing

Doses of $1 \times 10^{15}$ ions/cm$^2$ of 150 keV Zn and Cd ions implanted at room temperature into GaAs were found to create an amorphous layer of about 2000 Å and 1600 Å thick respectively. It was shown that annealing at 900°C was required for good electrical activation ($\sim 90\%$) and perfect recrystallization. Broadening of the carrier profiles was shown to occur during annealing and not during implantation.

Following an anneal in the temperature range 650 to 800°C, the sheet hole concentration increased with increasing dose up to a dose of $1 \times 10^{14}$ Zn$^+$/cm$^2$ and above this dose it reached a constant value between $(1-2) \times 10^{14}$ holes/cm$^2$ when implanted at room temperature.
For samples implanted at 200°C the sheet carrier concentration increased with increasing dose up to a dose of $1 \times 10^{15}$ Zn$^+$ /cm$^2$.

The sheet hole concentration was found to be independent of the implant energy for samples implanted at room temperature but for samples implanted at 200°C the sheet carrier concentration increased as the implant energy increased from 60 keV to 450 keV.

It was shown that the peak hole concentration increased with increasing dose up to a dose of $5 \times 10^{14}$ Zn$^+$ /cm$^2$ for both room temperature and for hot implants. Above this dose a saturation value of about $(1-2) \times 10^{19}$ holes /cm$^2$ was measured. It was postulated that the saturation was caused by the solubility of zinc in ion implanted gallium arsenide.

For doses up to $1 \times 10^{14}$ Zn$^+$ /cm$^2$ profiles obtained from both cold and hot implants were very similar but above this dose profiles recorded from hot implants were very much broader than those for cold implants. It is believed that the narrow profiles in the former case were related to the effects of radiation damage.

The annealing process caused significant redistribution of the ion implanted zinc ions and the electrical profiles were shown to depend on the implantation temperature, the ion dose, ion energy and the annealing temperature. The diffusion coefficient was estimated by comparison of the calculated (theoretical) diffusion profiles with the experimental profiles. The diffusion in
this case was concluded to be about three orders of magnitude smaller than the normal thermal diffusion of zinc in GaAs. The diffusion mechanism of the ion implanted Zn in GaAs was suggested to be the substitutional-interstitial mechanism, with zinc atoms probably occupying gallium sites, diffusing interstitially and finally residing in gallium vacancies.

In comparison with zinc less diffusion was observed in the case of Cd ions implanted into GaAs. The activation of diffusion was estimated to be about 2.3 eV. This value is believed to be consistent with the diffusion of Cd in gallium arsenide via the gallium sublattice.

(ii) **Laser Annealing**

It has been shown that short pulses from a ruby laser can be used successfully to anneal both capped and uncapped amorphous, crystalline or partially crystalline ion implanted layers in gallium arsenide.

Annealing using a Q-switched ruby laser leads to complete removal of defects in the ion implanted GaAs by the mechanism of liquid phase epitaxial regrowth. Complete annealing was accompanied by up to 100% incorporation of dopants (Zn or Cd) into electrically active substitutional lattice sites. Laser irradiation caused significant dopant redistribution and the final electrical and atomic profiles of Zn and Cd respectively were shown to depend on the laser pulse energy density, the number of successive pulses and the type of laser used (Q-switched or freely generated mode).
The estimated diffusion coefficient of zinc and cadmium in GaAs following irradiation with a Q-switched ruby laser suggested that the sample surface was molten during annealing.

Laser annealing leads to decomposition of the capped (Si$_3$N$_4$) and the non-capped gallium arsenide and it was shown that this could be minimised by choice of laser energy density.

(iii) A comparison of Thermal and Laser Annealing Results.

In general some of the major differences between laser annealing and conventional thermal annealing of ion implanted gallium arsenide are that laser irradiation produces:

(a) Higher electrical activation (up to 100%) and higher peak carrier concentrations ($\sim 10^{20}$ cm$^{-3}$).
(b) Greater redistribution of the implanted impurity.
(c) Regrowth of the implanted layer occurs via melting and liquid phase epitaxy.

From certain aspects the laser annealing process appears to be superior to the conventional thermal annealing process.

Finally, rapid progress in applying pulsed or cw laser beams to semiconductor processing holds out considerable hope for its application to device fabrication. Once the
strengths and weaknesses of the process are fully identified and understood by the semiconductor industry, laser processing together with ion implantation will have an enormous impact on the semiconductor industry!
A.1 ERROR CONSIDERATIONS

A.1.1 Introduction

The effects of the annealing processes (sections 4.2 to 4.5) on the ion implanted gallium arsenide was assessed mainly by using the Hall effect and sheet resistivity measurements. Therefore the errors related to this system are briefly discussed in this section. The electrical profiles reported in sections 4.2 to 4.5 are the mean of two, three or four profiles unless stated otherwise.

The source of errors in the Hall measurements, the maximum uncertainties in the current, magnetic field, measured voltage and the etch rate are examined. Inaccuracies due to galvanomagnetic and thermomagnetic effects were considered to be small and were further reduced by changing the direction of the current and the magnetic field (see section 3.6.2).

A.1.2 Errors related to the Hall Effect and Sheet Resistivity Measurements

(a) Hall Scattering Factor $r$

The main source of error in the Hall measurements may be due to the Hall scattering factor $r$. The value of $r$ has been reported to be dependent on the magnetic field,
impurity content, the temperature and the scattering mechanism\textsuperscript{(167-170)}. Normally r is taken to be unity as it is very difficult to calculate the precise value because several scattering mechanisms can be acting simultaneously.

In view of the uncertainty in the exact value of r which should be used for a given GaAs sample at a given temperature, we have employed $r=1$ in equation 3.13. According to the results of Stillman et al\textsuperscript{(170)} the error made in the calculated value of $n$ due to this procedure will be less than 15\% at room temperature and possibly 5\% at 77K.

(b) Measurement Current

The main error in the measurement current arises from the surface leakage ($I_s$) and the junction leakage ($I_j$) (shown below).

Sample with various current components
\[ I_m = I + I_s + I_j \]

\( I_m \) = Measurement current

\( I \) = Current in the implanted layer

\( I_s \) = Surface leakage current

\( I_j \) = Junction leakage current

The surface leakage \((I_s)\) depends upon the surface cleanliness and is expected to be small, say approximately 1 \(\mu\)A and should remain fairly constant; this can lead to a maximum error of about 1.5% assuming \(I_m = 70 \mu\)A.

The junction leakage \((I_j)\) can vary from one measurement to the next and also it varies as a function of stripping, as this increases the resistance of the implanted region as successive layers are removed (section 3.6.2). Maximum leakage occurs near the end of the profile, this is when the junction characteristics are degraded and so the leakage current can lead to a maximum error up to about 5%.

(c) **Magnetic Field**

A field of \(\pm 5 \) kG was used throughout when measuring the Hall voltages and this corresponded to a DVM reading of 141.00 mV. The reproducibility of the magnetic field was good i.e. better than 1% which gives rise to an uncertainty of about 1%.

(d) **Voltage Measurements**

The measured voltages were typically of the order of 0.1 to 100 mV and hence prone to errors due to spurious pick-up. This undesirable affect was reduced by the use of
coaxial cables for all inter-connections.

However the maximum error occurred when voltages of the order of 0.1 mV were measured and the maximum uncertainty was calculated to be about 5%.

(e) **Step Height Measurements**

After stripping the step height was measured using a Rank-Taylor Hobson Talystep. Two separate stylus traces were taken at each corner, giving a total of eight step height determinations per sample. The mean of these readings was used to calculate the etch rate which had an error estimated to be about 5%.

A.1.3 **Experimental Errors**

The maximum errors in $\rho_s$, $R_{hs}$, $\mu$, $n_s$ ($p_s$) and $n_i$ are considered below and it is shown how these affect the profile determination.

By using partial differentiation on equations 3.8, 3.9, 3.10, 3.13, 3.20 and 3.21 and assuming a small error in the various components the following uncertainty equations are derived:

The uncertainty in the sheet resistivity measurement value (worst case):-

$$
\frac{\Delta \rho_s}{\rho_s} = \frac{1}{2} \left[ \frac{\Delta R_{AB,CD}}{R_{AB,CD}} \right] \quad \text{(7.1)}
$$

where $\Delta R_{AB,CD}$ is the small error in the calculated resistance value ($V$ and $I$).
Similarly:

\[
\frac{\Delta R_{HS}}{R_{HS}} = \frac{1}{2} \left[ \frac{2 \Delta V_{AC}}{V_{AC}} + \frac{2 \Delta I_{BD}}{I_{BD}} + \frac{\Delta B}{B} \right]
\]

where \( \Delta I_{BD}, \Delta V_{AC} \) and \( \Delta B \) are the small errors in current, voltage and the magnetic field respectively.

Also:

\[
\frac{\Delta \rho_H}{\rho_H} = \frac{\Delta R_{HS}}{R_{HS}} + \frac{\Delta \rho_s}{\rho_s} \quad \ldots \ldots \quad (7.3)
\]

and:

\[
\frac{\Delta n_s}{n_s} = \frac{\Delta r}{r} + \frac{\Delta R_{HS}}{R_{HS}} \quad \ldots \ldots \quad (7.4)
\]

where \( \frac{\Delta r}{r} \) is the uncertainty in the Hall scattering factor.

\[
\frac{\Delta \mu_i}{\mu_i} = \frac{\Delta R_{SH}}{R_{SH}} + 3 \frac{\Delta \rho_s}{\rho_s} \quad \ldots \ldots \quad (7.5)
\]

\[
\frac{\Delta n_i}{n_i} = \frac{\Delta \rho_s}{\rho_s} + \frac{\Delta d_i}{d_i} + \frac{\Delta \mu_i}{\mu_i} \quad (7.6)
\]

where \( \frac{\Delta d_i}{d_i} \) is the uncertainty in the step height measurement.

Finally, taking the data obtained from sample number 138/8 and using the above equations (7.1 to 7.6) typical errors occurring in the Hall measurements have been calculated and plotted as a function of depth (see Figs. 7.1 to 7.3).
A.1.4 Conclusion

The results indicate that the Hall effect and sheet resistivity measurements may be used to determine the number of carriers/cm\(^2\) \((n_s)\) with an accuracy of 1 to 13 percent. However this is the experimental accuracy, for it was assumed that the depth dependence effects are negligible and the \(\frac{\mu_H}{\mu}\) ratio was known. In ion implanted samples the carrier concentration and mobility are depth dependent and the choice of a unity mobility ratio, can lead to an error of 1 to 28 percent (Fig. 7.1).

By using a combination of Hall measurements and layer removal techniques, the carrier concentration \((n_i)\) and mobility \((\mu_i)\) with depth are accurate to 5 to 21\% (Figs. 7.2 and 7.3).
Fig. 7.1 Uncertainty as a function of depth in the value of the sheet carrier concentrations for sample no. 138/8.
Fig. 7.2 Uncertainty as a function of depth in the value of the hole concentration and the mobility for sample No. 138/8.

\[
\frac{\Delta n_i}{n_i} = \frac{\Delta \rho_S}{\rho_S} + \frac{\Delta d_i}{d_i} + \frac{\Delta \mu_i}{\mu_i}
\]

\[
\frac{\Delta \mu_i}{\mu_i} = 3 \frac{\Delta \rho_S}{\rho_S} + \frac{\Delta R_{HS}}{R_{HS}}
\]
Fig. 7.5 Hole concentration and mobility profiles for 450 keV Zn ions implanted at room temperature to a dose of $1.10^{15}$ ions/cm$^2$ and annealed at 800°C/5 mins. (sample no. 138/8)
The published results and also the investigations carried out during the course of this study indicated that laser irradiation was unsuccessful in annealing gallium arsenide samples implanted with low doses of donor and acceptor ions. It was found that no electrical measurements were possible on uncapped GaAs samples implanted with 150 keV, $1 \times 10^{13}$ or $1 \times 10^{14}$ Zn$^+$/cm$^2$ when annealed with Q-switched ruby laser in the energy density range 0.2 to 1.2 J/cm$^2$.

In view of the above results we feel that a more detailed study is needed on the above topic. Also it would be interesting to investigate:

(i) Laser irradiation of gallium arsenide samples at elevated temperatures.

(ii) Laser annealing of dual implants. For example Zn + He (low dose of zinc plus high dose of helium or Zn + Ar).

(iii) Laser processing of implanted or deposited contacts on gallium arsenide.

(iv) Investigation of the diffusion mechanism of ion implanted cadmium in gallium arsenide under conventional annealing and laser pulse annealing.
7.A.3  List of Publications Resulting from this Study

1. S.S. Kular, B.J. Sealy and K.G. Stephens,
   Electrical profiles from zinc implanted GaAs,

2. S.S. Kular, B.J. Sealy and K.G. Stephens,
   Comparison of electrical profiles from hot and cold
   implantation of zinc ions in GaAs,

3. S.S. Kular, B.J. Sealy, K.G. Stephens, D.R. Chick,
   Q.V. Davis and J. Edwards,
   Pulsed laser annealing of zinc implanted GaAs,

   and G.R. Booker,
   Laser annealing of ion implanted GaAs,
   Presented at International Conference on Ion Beam
   Modification of Materials,

   Pulse annealing of ion implanted GaAs,
   Inst. Phys. Conf. Ser. No. 46 (1979) P.476,
   Nice (France), September, 1978.

6. B.J. Sealy, S.S. Kular, K.G. Stephens, R. Croft and
   A. Palmer,
   Electrical properties of laser annealed donor implanted
   GaAs.
7. B.J. Sealy, M.H. Badawi, S.S. Kular and K.G. Stephens, 
Laser Annealing of Ion Implanted GaAs, 
Int. Symp. on Laser-Solid Interactions and Laser 
Processing, Boston 1978, Eds. S.D. Ferris, H.J. Leamy 

8. S.S. Kular, B.J. Sealy and K.G. Stephens, 
Electrical and Physical Properties of Laser Annealed 
Zinc Implanted GaAs, 
Presented at Conference on Laser Annealing of Ion 
Implanted Semiconductors, 
University of Surrey (Guildford), January, 1979.

9. S.S. Kular, B.J. Sealy, M.H. Badawi, K.G. Stephens, 
D. Sadana and G.R. Booker, Laser annealing of Capped 
and Un-Capped GaAs, Electronics Letters, 15, 413 (1979).

10. S.S. Kular and B.J. Sealy, 
Electrical Properties of Mg Ion Implanted GaAs, 
to be published.

11. S.S. Kular, B.J. Sealy, K.G. Stephens, D. Sadana and 
G.R. Booker, 
Electrical, RBS and TEM studies of Zinc Implanted GaAs, 
to be published.

12. S.S. Kular and B.J. Sealy, 
Laser Annealing of Zinc Implanted GaAs, 
to be published.

13. S.S. Kular, B.J. Sealy and K.G. Stephens, 
Electrical and RBS Properties of Cd Implanted GaAs, 
to be published.
REFERENCES


41. S.S. Kular and B.J. Sealy, to be published.


164. E.H. Hall, Amer. J. Maths, 2, 1 (1879).


191. A.M. Stoneham, private communication.
192. B.J. Sealy, private communication.