ANNEALING OF ZINC AND SELENIUM

IMPLANTED GALLIUM ARSENIDE

by

N.J. BARRETT

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A study of ion implanted zinc in GaAs has been made using four annealing techniques: e-beam, graphite strip heating, furnace annealing in an arsine ambient and laser annealing. The highest hole concentrations, \(7-8 \times 10^{19} \text{ cm}^{-3}\), were obtained using electron beam annealing. Graphite strip heating and electron beam annealing were able to electrically activate 100\% of the implanted dose. Laser annealing produced surface decomposition during irradiation which was reduced by using a diffuser. The effect of strain on the activation of the zinc has been demonstrated by comparing chemical vapour deposited Si\(_3\)N\(_4\) with reactively evaporated AlN encapsulants. A model for the activation of zinc in GaAs has been formulated to take into account the different annealing techniques used for solid phase recrystallisation.

The electrical and structural properties of \(1 \times 10^{14} \text{ Se}^+ \text{ cm}^{-2}\), 100-400 kV and \(5 \times 10^{12} \text{ Se}^{++} \text{ cm}^{-2}\), 350 kV implants into (100) semi-insulating GaAs have been studied. Peak carrier concentrations of \(5 \times 10^{18} \text{ cm}^{-3}\) have been measured and mobilities of \(4000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}\) obtained for low dose implants \((n = 1-2 \times 10^{17} \text{ cm}^{-3})\) by annealing samples on a graphite strip heater. Si\(_3\)N\(_4\) and AlN have been used as encapsulants. Comparisons are made with capless annealing in an arsine ambient. A model for the activation of selenium in GaAs relates the activation energy of diffusion with the rate of electrical activation of selenium.
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This thesis is dedicated to my wife and parents.
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Chapter 1

ANNHEALING OF ZINC AND SELENIUM IMPLANTED GaAs

1. INTRODUCTION AND LITERATURE SURVEY

The considerable efforts directed at improving both the material properties of GaAs and the processing techniques, result from the strong interdependence of high frequency GaAs circuit performance upon substrate quality (1,2,3). Recent developments in the liquid encapsulated Czchralski (LEC) growth technique for semi-insulating GaAs (for integrated circuit applications) have resulted in significant improvements in the quality and quantity of GaAs material suitable for device fabrication. LEC material has dislocation densities between $10^4$ and $10^5 \text{ cm}^{-2}$, which arise from the large thermal gradients within the boule as it is pulled from the melt. This may cause degradation of devices if dislocations pass through electrically active layers (4). To lower the defect concentration, it is possible to dope with impurities which increase the bonding energy of the crystal lattice. It has been established that this can be achieved by B(5), Al and N(6) and In and Sb(7).

The horizontal Bridgeman (HB) method produces material which has a lower dislocation density than LEC material due to the lower temperature gradients used in that growth technique. However HB material has a higher impurity concentration.

Ion implantation results in the chemical doping of the GaAs surface to depths of the order 0.1 to 2 $\mu$m with an estimated concentration uniformity of about ±1% over 75mm diameter wafers. Dose precision is very good although its accuracy may be no better than about 20% depending on the geometry of the implant chamber. Statistical models of the ion-stopping process in amorphous targets yield reasonable first approximations to the implanted atomic distribution in misaligned single-crystal wafers. The
orientation of the implanted substrate with respect to the ion beam
during the implantation influences the carrier concentration profile of the
implanted species due to channeling of the ion beam. In most applications
the crystal orientation is aligned such that it is random to the direction
of the beam. Wilson and Deline (8) extensively investigated these effects
for Se, Si, S and Te implants into GaAs.

The species, dose and energy used for ion implantation depends on the
desired properties of the resulting layer and the availability of the ion
species in the implantation machine. The majority of the studies of n-type
implants into GaAs have used Se, Si, S, Te, Sn and Ge. Gibbons et al (9)
have published implant range data in tabular form, which allows the
calculation of the predicted atomic concentration profile for a large
number of species in different substrate materials.

The early investigations of n-type implantation into GaAs employed
Te since it is a useful n-type species and is significantly heavier than the
GaAs substrate. This allows the use of Rutherford backscattering
spectrometry (RBS) (10,11,12) to investigate the crystalline properties of
the implanted regions. These measurements include a determination of the
implant-induced damage and the efficiency with which the dopant species is
located on lattice sites. The use of Te as an implant species for the
formation of channel regions is limited since the projected range of Te at
400 keV is 0.092mm.

The species most often used for the channel-region implants are Se,
Si and S. The species have sufficient range to produce the necessary
carrier concentration deep enough for the channel regions for MESFETs. S
produces high mobility layers with good doping efficiencies but during the
anneal cycle can exhibit undesirable fast diffusion rates. The inconsistent
profile shape limits the usefulness of S as an implant species. Carrier
concentration profiles for Si implanted layers produce consistent results
for integrated circuit fabrication. Se is one of the heavier implant species commonly used and requires higher energies than Si to obtain the same implant range.

One attraction of using this heavier ion is that the standard deviation ($\Delta R_p$) of the atomic distribution is smaller than for lighter ions (e.g., Si, S). Thus more abrupt impurity (and electrical) profiles are produced (13). In contrast to S (14), the Se diffusion coefficient in GaAs is lower (15), minimizing profile broadening during annealing. Unlike Si (16), Se is not amphoteric in GaAs. A disadvantage of using a heavier ion is that considerably more damage is introduced into the host crystal during implantation (17, 18), but this can be alleviated by implanting at elevated temperatures (19).

Elevated temperature implants do not produce an amorphous layer but essentially preserve the crystallinity within the implanted region, despite the large number of crystal defects (mainly loops and point defects) which are generated (20). In contrast, room temperature implants can produce an amorphous layer, but the degree and nature of the implant damage was found, in early studies (21, 22) to be very sensitive to the ion dose and dose rate. More recent experiments (23, 24) have indicated that considerable dynamic annealing can take place during room temperature implantation, resulting, in some cases, in an implant layer containing part amorphous and part crystalline damage (25).

Many selective area ion implantation processes used for GaAs integrated circuit fabrication, employ photoresist as a masking medium which restricts the temperature at which implantation can occur to less than 120°C compared to the required temperature of greater than 150°C. Therefore, as well as the technical difficulties of 'hot implants' in a production environment, in some cases it is not possible to elevate the substrate temperature during implantation. Therefore, in order to use room temperature
Se implants an improvement in the post ion implantation anneal is necessary in order to increase hole and carrier concentration and limit diffusion.

The first realisation that high carrier concentrations were possible was initiated by Kachurin et al in 1976 (26) who demonstrated that ion implant damage in GaAs could be successfully removed by pulsed laser annealing. The electrical activation of an implanted dopant by liquid phase epitaxy occurs in an energy density window below which the sample does not recrystallise and above which the sample decomposes and the electrical properties are degraded. This energy density window may be observed by RBS (27) or transmission electron microscopy where an energy density of about 0.5 J cm\(^{-2}\) produces defect free single crystal material but energy densities of about 1 J cm\(^{-2}\) introduce large concentrations of dislocations (28,29). Doses less than or equal to \(1 \times 10^{14}\) cm\(^{-2}\) for n-type dopants, are not readily electrically activated (30).

Laser annealing Se and Zn implants at doses of \(1 \times 10^{15}\) cm\(^{-2}\) produce electrically active layers of \(10^{19}\) cm\(^{-3}\) (27) and \(10^{20}\) cm\(^{-3}\) (31) respectively. However standard furnace anneals for room temperature implants with the same doses have hole concentrations of about \(2 \times 10^{19}\) cm\(^{-3}\) for Zn (32) and for Se implants annealed at 1000°C for 15 minutes Lidow et al (33) obtained similar carrier concentrations to those obtained following laser annealing but with a lower activation efficiency. Typically even 'hot' implants of Se only yield carrier concentrations of mid \(10^{18}\) cm\(^{-3}\) after furnace annealing (34).

The major problem of annealing with Q-switched lasers is the loss of material when the surface melts. A sample irradiated through a glass slide in close contact with its surface loses some material which deposits on the glass slide. At energy densities of about 0.2 J cm\(^{-2}\) a very thin layer is visible increasing in thickness as the energy density increases.
At energy densities of about 0.5 J cm\(^{-2}\) and above, the surface becomes rich in gallium due to the preferential loss of arsenic \((32)\). The degree of decomposition has been quantified by measuring the mass of a sample before and after laser irradiation \((35,36)\).

The bibliography by Stevens \((37)\) contains references on the general topic of laser processing of semiconductors prior to 1979. The investigation at Lincoln Laboratories \((38)\) and Hughes \((39)\) using continuous wave (CW) laser radiation, indicated that the use of these lasers was not promising. This was due to the narrow range of parameters over which reasonable dopant activation occurs without severe surface damage.

The majority of methods used for annealing ion implanted damage in GaAs is directed towards solid phase epitaxy which takes place typically between 800\(^\circ\)C and 1100\(^\circ\)C depending on the implant dose. This is well in excess of the GaAs congruent sublimation temperature of about 650\(^\circ\)C \((40)\). Consequently, steps must be taken to prevent the preferential loss of As\(_2\), which would give rise to a Ga rich surface. To protect the surface an encapsulant \((41)\) is generally used. Al, SiO\(_2\), Si\(_3\)N\(_4\), AlN and Si\(_3\)N\(_4\)/SiO\(_2\) are some encapsulants which have been used to date \((42-46)\). The main encapsulant dealt with in this thesis will be pyrolytically deposited Si\(_3\)N\(_4\), first reported by Donnelly et al \((47)\), however some comparisons will be made with AlN which is capable of withstanding higher temperature cycles than Si\(_3\)N\(_4\).

The use of capless \((48,49)\), proximity \((50,51)\) and controlled As pressure \((52,53,54)\) anneal procedures has proved useful in producing good results in many laboratories.

Experimental research on thermal pulse annealing, which anneals in the solid phase, started approximately at the same time as laser annealing. However due to the problem of surface damage with laser annealing and the relatively small area which could be annealed uniformly, the thermal pulse
Annealing systems have superseded laser annealing in the majority of applications. Thermal pulse annealing has many advantages over conventional furnace annealing without the disadvantages of laser annealing effects as times at temperatures are kept short, thus reducing diffusion or chemical reaction. Also the indiffusion of Si (46, 55) and interactions between the \( \text{Si}_2\text{N}_4/\text{GaAs} \) interface (56) impurity diffusion (57) and gettering (58) will be reduced. A recent application is the limiting of intermixing of heterojunction layers (59-62) during annealing.

Anneal cycles range between 1s and \( 3 \times 10^2 \)s for rapid annealing systems such as scanned electron beams, graphite strip heaters and optical furnaces and \( 3 \times 10^2 \)s to about \( 10^4 \)s for standard furnace anneals. Shah et al (63) showed the first results of GaAs activation by scanned electron beam with further work quickly following on (64-69). The first report however of anneal times in the order of seconds was by Surridge et al (44) using a furnace method who showed that the percentage of ions becoming electrically active increased with time at a given temperature up to some maximum. This maximum value increased as the temperature was increased from 700 to 900°C but the time needed to achieve this maximum decreased as the annealing temperature increased. The time and temperature dependence of the activation of dopants is a research area which has not been studied in any detail. Graphite strip heating initially designed by Donnelly (70) has increasingly been used to obtain high temperature/short time anneals (71, 72, 73). The highest anneal temperature which has been reported is 1140°C for 10s by Chapman et al (55) using a composite \( \text{Si}_2\text{N}_4/\text{SiO}_2 \) encapsulant. The implant was at 300°C with \( 10^{15} \) cm\(^{-2} \) of 400 keV Se\(^+\) ions yielding sheet resistivities of 25\( \Omega/\square \). Recently Patel et al (74) have investigated anneals up to 1090°C obtaining sheet resistivities of 37\( \Omega/\square \) and 28\( \Omega/\square \) for room temperature implants of Se and Sn respectively, with carrier concentrations of the order of \( 1 \times 10^{19} \) cm\(^{-3} \) which is approaching
the carrier concentrations obtained by laser annealing.

In recent years there has been considerable interest in incoherent light sources. The first realisation of the potential of the method was by activating implants in the light cavities of lasers (75). This progressed to focussed systems (76,77) and now to linear arrays of lamps (78,79,80) for annealing wafers uniformly. For GaAs a susceptor, either carbon or silicon is used to absorb the radiation from the commonly used tungsten halogen lamps which have a peak light intensity of 0.9 $\mu$m.

The prospect of carrier concentrations as high as $1 \times 10^{19}$ cm$^{-3}$ has received increased attention over the last few years due to the prospect of making non alloyed ohmic contacts by implantation. In order to achieve a low resistance ohmic contact at a metal/high-band gap semiconductor interface, the free carrier concentration at the interface must be sufficient to reduce the barrier width to a few tens of angstroms in order to allow majority carriers to tunnel across the interfacial region (81). The major improvement to be gained from nonalloyed contacts is that the same metal used for the MESFET gate can be used for the ohmic contacts. This simplifies the process and would improve the performance and reliability of the integrated circuits.

Be, Mg, Zn and Cd have all been investigated as p-type dopants in GaAs (82,83) with maximum electrical activation being obtained between 800°C and 900°C, except Be which was 600°C. Electron diffraction analyses indicate (84) that for room temperature implants of $1 \times 10^{15}$ ions cm$^{-2}$ of Zn and Cd an amorphous region formed while the lighter ions, Be and Mg produced defected crystalline material. It should be noted that an observation of crystalline material implanted with Mg using electron diffraction analyses may not necessarily mean that it is crystalline when observed by Rutherford backscattering. This is due to RBS accurately quantifying the implanted damage peak as it is a very sensitive method for
analysing highly damaged material. Consequently within the departments Ion Implantation group using RBS, Mg generally gives an amorphous layer.

For the applications of Zn implanted GaAs in integrated circuits (85-89) it is important to control the diffusion of Zn, especially lateral diffusion (90). Zn is a commonly used p-type dopant often introduced by diffusion, whilst only a limited amount of work has been carried out on the use of ion implantation.

Previous work on the annealing of Zn implanted GaAs has demonstrated that the zinc diffuses very rapidly at high temperatures (91,92,93). However, annealing in an AsH$_3$ ambient limits the diffusion producing very abrupt electrical profiles (86,91,94,95,96). This is also true for dual implants of Zn and As (91,97,98,99). Electron beam annealing (68) optical furnace annealing (100,101) and laser annealing (102) have provided an additional means of limiting diffusion because of the short annealing times used. Recent open tube furnace diffusion has shown good control over the Zn profile (103).

Four annealing methods have been used to activate room temperature Zn implants in this study: (a) graphite strip heater (GSH), (b) electron beam (EB), (c) laser annealing (LA) and (d) furnace annealing with an AsH$_3$ over-pressure. Room temperature Se implants have been electrically activated using methods (a) and (d). These annealing methods together with the measurement techniques are discussed in Chapter 2. The results of Zn and Se implants into GaAs are in Chapter 3. This chapter also covers work on the annealing of unimplanted GaAs. The discussion of the results in Chapter 4 includes models for the electrical activation and diffusion of Zn and Se. The conclusions of the work are in Chapter 5 with discussions for future work.
Chapter 2

APPARATUS AND EXPERIMENTAL TECHNIQUES

2.1 Introduction

Four annealing techniques have been used for unimplanted and implanted GaAs; laser, conventional furnace, electron beam annealing (EBA) and the graphite strip heater (GSH). The study of unimplanted GaAs was necessary in order to understand the changes that occurred to the material properties after an anneal cycle. Surface effects to the GaAs were very much dependent on the annealing process and the encapsulant, if one was used. Thus the assessment of unimplanted GaAs gives a quantitative value to the physical limitations of the annealing system. $^{64}$Zn$^+$ and $^{78}$Se$^+$ ions were implanted into LEC pulled (100) GaAs at room temperature. Three types of bulk material were used; undoped semi-insulating (SI), Cr doped SI and n-type. The implant direction was 7° from the surface normal in order to minimise the effect of channelling.

The anneal cycles for zinc or selenium implanted GaAs have been studied using differential Hall and strip measurements, electrical resistivity measurements, Rutherford backscattering spectrometry (RBS), ellipsometry, secondary ion mass spectrometry (SIMS) and transmission electron microscopy (TEM). SIMS was carried out on an Atomika at Imperial College and TEM was carried out in collaboration with Oxford University.

2.2 Ion Implantation

The modification of material surface properties by ion beam is a relatively recent technology. Considerable development work has been carried out world wide on machines for isotopic separation of elements and some of the current ion implantation machines can be traced directly to these separators (104). The development of machines capable of producing
energetic, focused ion beams (105) are closely connected with the evolution of ion implantation and radiation damage studies.

Ions which penetrate a solid lose energy in a series of collisions with the target atoms until they come to rest. The energy loss at each collision may be interpreted statistically over many collisions, with a given amount of energy being lost per unit distance travelled in the material. At low energies, the energy loss is approximately linearly dependent upon energy. However, as the ion energy increases, there is a power law dependence upon energy with decreasing exponent until the energy loss decreases with increasing energy. This is due to the variation of scattering cross section. When a high energy ion first penetrates the surface of a solid, it initially transfers energy to the lattice relatively slowly. As the ion slows down, the rate of energy loss first increases and then decreases linearly with the ions' retained energy. This effect may lead to a buried amorphous layer as the radiation damage is less at the surface of the crystal than further in. This radiation damage is annealed out during subsequent heat treatment. The range of an ion is determined by the rate at which it loses energy. In a randomly orientated crystal or an amorphous layer the ion distribution may be approximated by a Gaussian shaped distribution but in a channelling direction the ions do not make a random sequence of collisions as the crystal structure has a role in the determination of the range of the ion.

The Gaussian distribution of implanted ions is generally predicted using the theory of Lindhard, Scharff and Schiott (106) usually referred to as LSS which may be described by the equation

\[ N(x) = N_0 \exp \left( \frac{-(x-R_p)^2}{2(\Delta R_p)^2} \right) \]

\[ \frac{1}{(2\pi)^{1/2} \Delta R_p} \] 2.1
where \( x \) = the perpendicular distance into the substrate
\( N_i \) = ion dose
\( R_p \) = the theoretical projected range
\( \Delta R_p \) = the standard deviation of the implanted profile

Deeper profiles are obtained by the ion beam channelling along a major axis within the crystal structure (107). To achieve reproducible depth profiles crystalline targets are generally aligned between 5 and 10 degrees off from the channelling direction so that the crystal appears randomly arranged to the ion beam. Even with these precautions, deflected ions may still channel producing a long tail in the profile (108).

Target atoms which receive sufficient energy may be ejected from the target. This may lead to surface erosion by sputtering and thereby modifying the atomic profile of the dopant. Fortunately this is a relatively small effect and may be neglected, but for high dose implants \(( \geq 10^{15} \text{ cm}^{-2})\) close to the surface, then this effect becomes significant.

Implants were carried out using the Department's 500keV heavy ion accelerator (Figure 2.1). Solid sources of selenium and zinc were vaporised in a modified Nielson type source using electrical heating. The vapour was ionised by electron collisions in crossed electric and magnetic fields.

The ion beam was extracted and focussed by an Einzel lens which was floating on the bun high voltage potential together with the ion source and power supplies. The ion beam was accelerated in a graded accelerator tube using a resistor chain to reduce the terminal voltage in equal steps.

Impurities in the beam or ions with the incorrect charge states are removed from the high energy beam when it is deflected through ninety degrees by an electro-magnet. The required dopant is selected by using the magnet as a momentum analyser. With a field stability of better than 0.1% and a correct adjustment on the slits, just beyond the magnet, then the
Figure 2.1: Schematic diagram of the 500 kV Heavy Ion Implanter.
isotopes of zinc and selenium are readily distinguished. The slits, as well as acting as an aperture also may be used for a feedback signal to stabilize the magnet as each slit intersects with the outer edges of the beam.

After the slits the beam is raster scanned by a triangular waveform on $X$ and $Y$ electrostatic deflection plates. The peak potential applied to the deflection plates is varied according to the energy of the ion to ensure the beam is completely scanned across the aperture in front of the sample which is orientated at $7^\circ$ to the beam axis. Superimposed on the raster scanned signal is a dc deflection to align the beam.

2.3 Encapsulation

An encapsulant Si$_3$N$_4$ or AlN was generally used during the post ion implantation anneal to prevent the dissociation of the GaAs.

2.3.1 Silicon Nitride

A sample to be encapsulated was placed on the graphite strip. The chamber was pumped down to $10^{-4}$ mbar before being let up to nitrogen. Silane and ammonia were then introduced in the ratio 1:24:75 (SiH$_4$:NH$_3$:N$_2$). The gases flowed through the system for five minutes before the GSH was brought up to temperature. Samples were encapsulated with 900-1200Å of silicon nitride grown by the pyrolytic decomposition of silane and ammonia between 635°C and 650°C for thirty to forty seconds.

The optimum thickness of the silicon nitride (109) deposited at 635°C for a range of times was determined by investigating the thermal conversion (110,111) of Si material by measuring the sheet resistivity following a 900°C anneal for 25s at temperature.
2.3.2 Aluminium Nitride

A few samples were coated with 300Å - 600Å of aluminium nitride by reactively evaporating aluminium in an ammonia gas atmosphere at 10^{-3} mbar (45).

2.4 Annealing Apparatus

2.4.1 Graphite Strip Heater (GSH)

The GSH consisted of a 1 mm thick carbon strip resistively heated by a 100 amp ac current. A thermocouple positioned in a small hole (≈0.3 mm) at the back of the carbon strip was used to control the temperature. The rate of rise in temperature was about 70°C s⁻¹ and anneal times were measured once the graphite strip had reached temperature. The temperature-time curves for the systems are shown in Figure 2.2. After a sample was placed on the strip, the chamber was pumped down to 10⁻⁴ m bar before it was let up to N₂ or NH₃ for Si₃N₄ capped samples and AlN capped samples respectively. The NH₃ produced better surfaces than N₂ if the AlN was Al rich.

2.4.2 Electron Beam

A Lintech Instruments 1 kW multiply scanned electron beam annealer was used to activate the implanted ions. The electron beam diameter was 0.4 mm, its energy 30 keV and the scanning frequencies were 30 Hz and 30 kHz for frame and line respectively.

Electron beam annealing (EBA) is a direct heating method and, as a result, it has the ability to heat samples very quickly. The power absorbed by the sample is dependent upon the current and the energy of the electron beam. Heat is lost by conduction and radiation effects, including electrons scattered from the surface. Before annealing, the samples were coated on the back surface with graphite paste to prevent the formation of a reflecting
Figure 2.2: Temperature time curves for G.S.H. The temperature rise times increased by up to 40% over the duration of this work.
layer on the sample holder due to the sublimation of GaAs. Such a deposit would reflect back radiation, causing the sample to heat up quicker, but not reproducibly. Samples were mounted over an indentation in an aluminium block with just the corners in thermal contact. The aluminium block heated up slowly due to its large thermal mass, reaching a maximum temperature of 400°C for long anneal cycles. A programme was written to calculate the temperature-time curves of a sample. The principal conditions used for the programme are presented in Appendix 1.

EBA was investigated by irradiating about fifty unimplanted uncapped samples with energy densities from 7 Wcm$^{-2}$ up to 100 Wcm$^{-2}$ and times between 1 and 700s. Optical microscopy was used to observe the time at which surface blemishes become visible. A selection of these samples were studied using a Cambridge Instruments S250 SEM. Some samples were also GSA for comparison. Zn Implanted samples with a Si$_3$N$_4$ encapsulant were also annealed and assessed by Hall and strip electrical measurements.

2.4.3 Furnace Annealing in an Arsine Ambient

A GSI hydride reactor (at GEC HRC) running at a partial pressure of 7 x 10$^{-3}$ atm was used for capless annealing. The anneal cycle was approximately 20 minutes.

2.4.4 Q switched Ruby Laser

A Q switched ruby laser (25 ns pulse $\lambda = 0.69 \mu$m) built by J.K. Lasers was used to anneal uncapped samples. For the activation to take place using one pulse, the surface must be melted and consequently surface evaporation takes place (36) which results in the loss of some of the Zn. The anneals were carried out in air and, so, after an anneal, samples had to be boiled in HCl to remove the Ga rich surface.
The ruby laser energy density was spatially non-uniform because of the presence of high intensity spikes. This problem was later alleviated by incorporating a diffuser into the system. The diffuser consisted of a quartz rod with a 90° bend in it, using the same design as Cullis et al (112). The laser pulse entered one end which had an unpolished surface to diffuse the light. The 90° bend added to the mixing effect of the beam cross section. The energy intensity was thought to be increased by the tapering of the rod. It then exited through a polished surface. The samples were placed within 1 mm of the exit as the beam was very divergent. To prevent any evaporated material coating the diffuser, a cover glass slide was placed between the sample and diffuser before operating the laser.

To achieve a high power output the laser must be operated in the Q-switched mode resulting in a single pulse with a duration of 25 nano-seconds, which contains most of the energy stored in the ruby rod. This is achieved by the operation of a high speed shutter in the form of an electro-optic device called a Pockel's Cell which is inserted into the optical resonator between the laser rod and the 100% reflecting mirror (Fig. 2.3). The shutter is initially closed thereby preventing laser action, so that the stored energy in the laser rod builds up to release a single nano-second pulse when the shutter is opened.

2.4.5 Q switched Nd-glass laser

A Nd-glass Q switched laser was used on a few samples. The longer wavelength (\( \lambda = 1.06 \, \mu m \)) is not so readily absorbed in GaAs and so the energy is absorbed throughout the sample. Although it is an adiabatic situation it is one step closer to a thermal pulse anneal. Consequently, the surface is left in a much better condition compared with the ruby laser.
Figure 2.3: Schematic diagram of the Q switched ruby laser.
2.5 Measurement Techniques

2.5.1 Electrical Measurements

Electrical resistivity measurements for unimplanted material were made after the Si$_3$N$_4$ cap was removed in hydrofluoric acid and Au contacts evaporated on two edges of an approximately square sample. The resistance between the contacts was measured in the dark, using a high impedance electrometer. The aspect ratio was measured to convert this resistance into a sheet resistivity value.

Electrical analysis of ion implanted samples was carried out using Hall effect measurements and the Van der Pauw technique (113) in conjunction with chemical etching. From these results the hole and carrier concentration and mobility profiles were calculated.

Samples were cut into clover leaf shapes with the encapsulant still in place. A mild steel clover-leaf shaped mask was held in position with dental wax on a sample mounted on a glass slide with the same wax. The unwanted GaAs was cut away with a jet of nitrogen containing alumina abrasive powder from a Comco Inc. microblaster. The residual wax was removed in toluene and then the samples were cleaned in methanol before removing the encapsulant in hydrofluoric acid. The samples were then rinsed in distilled water and cleaned in boiling methanol.

Tin contacts for n-type implants were alloyed in a gas stream of 5% hydrogen in nitrogen bubbled through concentrated hydrochloric acid to prevent oxides forming during the 350°C temperature cycle. The GaAs was kept at temperature for ten seconds after the tin melted. Gold was evaporated onto the GaAs clover leaves through a mask for contacts to p-type layers. The clover leaves were then waxed down to a glass slide which was connected to an edge connector. A conducting paint (silverdag) was used to connect the contacts to the edge connector. To check that the contacts were ohmic current/voltage measurements were made on each pair of contacts.
using a curve tracer.

Theory of Hall Measurements

Currents which flow in a conductor with a mean electron velocity $\overline{V}$ in the presence of a magnetic field $B$ experience a force $q\overline{V} \times B$ which acts directly on the moving charge $q$. This sets up a non-uniform charge density which gives rise to an electric field, $E$ (see Fig. 2.4). In equilibrium the force due to this field balances the force due to the magnetic field so that, the net force $F$ is:

$$F = qE + q\overline{V} \times B = 0 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 2.2$$

The current density $j = nq\overline{V}$ where $n$ is the number of particles of charge $q$ per unit volume.

$$E = -\overline{V} \times B$$

$$= -(j \times B)/nq \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 2.3$$

$$= -R_H (j \times B)$$

where $R_H$ is known as the Hall Coefficient which is negative for electrons of charge $-q$. By combining measurements of the conductivity ($\sigma = nq\mu$) and the Hall effect, it is possible to find both $nq$ and the mobility $\mu$.

The general expressions for the Hall coefficient and conductivity are

$$R_H = \frac{-r}{|q|} \frac{(n_e\mu_e/n_h^2 - n_h)}{(n_e\mu_e/n_h) + n_h} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 2.4$$

$$\sigma = \frac{|q|}{n_e\mu_e + n_h\mu_h} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 2.5$$

where the subscripts $e$ and $h$ refer to electrons and holes respectively. $r$ is the Hall scattering factor which is discussed below.
Figure 2.4: The Hall effect

Figure 2.5: Clover leaf
In the case when one type of carrier is present, the mobility can be found from the conductivity and Hall effect, since $|\mathcal{R}_H| = B/N|q|$ and $|\mathcal{R}_H \sigma| = \mu$. The quantity $|\mathcal{R}_H \sigma|$ is generally written $\mu_H$ and called the Hall mobility to distinguish it from the drift mobility (114).

The sheet Hall Mobility $\mu_H = \frac{R_{HS}}{\sigma_s}$ ......... 2.6

$\mu_H$ is related to the conductivity mobility $\mu$ by the relationship

$$r = \frac{\mu_H}{\mu}$$ ......... 2.7

It follows, as previously stated, that

$$\mu = \frac{1}{n q \sigma}$$ ......... 2.8

where $n$ is the carrier concentration.

The sheet carrier concentration

$$n_s = \frac{r}{(q R_{HS})}$$ ......... 2.9

$r$ is assumed to be unity as the exact value is dependent on the scattering mechanisms and impurity concentration.

The activation efficiency is defined by $n_s / \text{Dose} \times 100\%$.

Van der Pauw (113) established the theory for Hall effect and specific resistivity measurements to be carried out on an arbitrary shaped flat sample if:-

1) The electrical contacts are located at the circumference of the sample.
2) The contacts are small compared with the size of the sample.
3) The sample is homogeneous in thickness.
4) The surface of the sample is singly connected (no isolated holes)
If four contacts are made, A, B, C and D as shown in figure (2.5), then the sheet resistivity, Hall coefficient, Hall mobility and carrier concentration may be calculated:

\[ s = \frac{\pi}{\ln 2} \frac{R_{AB,CD} + R_{BC,DA}}{2} f \]  \hspace{1cm} 2.10

\[ R_{AB,CD} \] is the potential difference between contacts C and D for unit current through A and B i.e. \( R_{AB,CD} = \frac{V_{CD}}{I_{AB}} \). \( f \) is a function dependent upon the electrical symmetry of the sample and is defined by:

\[ \frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} = f \cdot \text{arc\cosh} \left( \frac{\text{Exp} \left( \frac{\ln 2}{f} \right)}{2} \right) \]  \hspace{1cm} 2.11

For an electrically symmetric system

\[ R_{AB,CD} = R_{BC,DA} \] and \( f = 1 \)

The sheet Hall coefficient \( R_{HS} = \frac{\Delta R_{BD,AC}}{B} \) \hspace{1cm} 2.12

where \( B \) is the magnetic field and \( \Delta R_{BD,AC} \) is the difference between the values of \( R_{BD,AC} \) measured with and without the applied magnetic field.

To minimise errors in the clover-leaf shaped sample, the current was reversed as indicated below.
<table>
<thead>
<tr>
<th>Switch Position</th>
<th>Constant Current</th>
<th>Measured Voltage</th>
<th>Magnetic Field</th>
<th>Type of Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+ $I_{AB}$</td>
<td>$V_{CD}$</td>
<td>0</td>
<td>Resistivity</td>
</tr>
<tr>
<td>2</td>
<td>+ $I_{BC}$</td>
<td>$V_{AD}$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>+ $I_{BD}$</td>
<td>$V_{AC}$</td>
<td>0</td>
<td>Hall</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>+ B</td>
<td>&quot;</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>- B</td>
<td>&quot;</td>
</tr>
<tr>
<td>7</td>
<td>- $I_{AB}$</td>
<td>$V_{DC}$</td>
<td>0</td>
<td>Resistivity</td>
</tr>
<tr>
<td>8</td>
<td>- $I_{BC}$</td>
<td>$V_{DA}$</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>9</td>
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<td>$V_{CA}$</td>
<td>0</td>
<td>Hall</td>
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<tr>
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<td>&quot;</td>
<td>&quot;</td>
<td>+ B</td>
<td>&quot;</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>&quot;</td>
<td>- B</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

From these twelve readings the sheet values for the carrier concentration (Equations 2.9 & 2.12), mobility (Equations 2.6, 2.10 & 2.12) resistivity (Equation 2.10) and Hall coefficient (Equation 2.12) were calculated.

**Electrical Profiling by the Differential Hall Technique**

On completion of the twelve measurements, the sample was etched in a solution of concentrated sulphuric acid, hydrogen peroxide and deionized water in the volume ratios of 1:1:125 which produced an etch rate of about 300Å per minute. After making up the etch it was stirred for thirty minutes to ensure homogeneity. The sample contacts were protected from the etch by Apiezon black wax which was applied from a solution of wax dissolved in toluene. The clover leaf was immersed in the etchant between 30 and 120 seconds. After this the clover leaf was rinsed in three stages for a total time of 30 seconds. Electrical measurements were then repeated on the etched sample in de-ionised water. This method reduced any
temperature variation of the sample and eliminated the necessity to dry samples. Etching was discontinued when measurements became unstable.

The step height was measured after the final etch, using a Rank Taylor Hobson Talystep in order to calculate the etch rate.

The volume carrier or hole concentration (n or p) and mobility (\(\mu\)) were calculated from the values of \(R_{HS}\) and \(\rho_s\) obtained for each etch step and using the equation derived by Buehler (115)

Buehler assumed that the conducting layer may be divided into a series of layers of thickness \(d_i\). The mobility (\(\mu_i\)) and the carrier concentration (\(n_i\)) of the \(i^{th}\) layer are given by:

\[
q n_i \mu_i d_i = \frac{(R_{HS})_i}{\rho_s^2}_i - \frac{(R_{HS})_{i+1}}{\rho_s^2}_{i+1} \quad \ldots \ldots \quad 2.13
\]

\[
q n_i \mu_i d_i = \frac{1}{\rho_s}_i - \frac{1}{\rho_s}_{i+1} \quad \ldots \ldots \quad 2.14
\]

Hence \(\mu_i = \frac{\Delta (R_{HS}/\rho_s^2)_i}{\Delta (1/\rho_s)_i}\) \(\ldots \ldots \quad 2.15\)

\[
n_i = \frac{\Delta (1/\rho_s)_i}{qd_i u_i} \quad \ldots \ldots \quad 2.16
\]

**Hall measurement errors**

The Hall scattering factor (\(r\)) which is assumed to be unity may lead to errors of \(n_s\) of up to 15% at room temperature (116). Sample currents were maintained to within \(\pm 0.5\%\) on a Keithley current source. Substrate and surface current effects were no greater than about 1% of the total current through the layer. Only in the tail of the profile
where resistivities of up to $5 \times 10^4 \Omega/\square$ were measured was it possible for error to increase to $\pm 5\%$.

A magnetic field of $\pm 0.5T$ was used. The voltage drop across a water cooled resistor incorporated in series with the magnetic poles was kept within $\pm 0.5\%$. It is therefore assumed that the error in the magnetic field value was equal to this error.

Most voltage measurements were measured to $\pm 0.01mV$ except in unstable regions of the profile with resistivities greater than $5\times 10^3 \Omega/\square$. The voltage errors were greatest for the measurement corresponding to $\Delta R_{BC,AC}$ as this could correspond to the difference of two similar voltages with and without the magnetic field on. In the case of n-type layers this error was between $\pm 0.5 \times 5\%$ but for p-type layers, the error was between $\pm 15$ and $\pm 9.5\%$. Where possible the current was adjusted to give errors on all the other voltage readings of less than $0.5\%$ for both n- and p-type measurements.

Six to eight step height measurements were taken using a Rank-Taylor Hobson Talystep. The mean of these readings were taken to calculate the etch rate to within $\pm 5\%$. For laser annealed samples where the surface was rough in some cases, this could be as high as $\pm 15\%$.

**Uncertainties of Hall and resistivity measurements**

By partial differentiation of Equation 2.10 the uncertainty in sheet resistivity

$$\frac{\delta \rho}{\rho} = \frac{\delta R_{AB,CD}}{R_{AB,CD}} \quad \ldots \ldots \quad 2.17$$

$$= \pm 1.5\%$$
From equation 2.12, the error in the sheet Hall coefficient

\[ \frac{\delta R_{HS}}{R_{HS}} = \frac{\delta \Delta R_{ED,AC}}{\Delta R_{ED,AC}} + \frac{\delta B}{B} \]  

\[ = \pm 1\% \text{ to } 5.5\% \text{ (Se)} \]
\[ \pm 5.5\% \text{ to } 10\% \text{ (Zn)} \]

From equation 2.6 \( \mu_H = \frac{R_{HS}}{\sigma_s} \)

\[ \frac{\delta \mu}{\mu} = \frac{\delta R_{HS}}{R_{HS}} + \frac{\delta \sigma}{\sigma} \]  

\[ = \pm 2.5\% \text{ to } \pm 7\% \text{ (Se)} \]
\[ \pm 7\% \text{ to } \pm 11.5\% \text{ (Zn)} \]

From equation 2.9 \( n_s = \frac{r}{(\sigma R_{HS})} \)

\[ \therefore \frac{\delta n_s}{n_s} = \frac{\delta r}{r} + \frac{\delta R_{HS}}{R_{HS}} \]  

where \( \delta r/r \) is the uncertainty in the Hall scattering factor.

From equations 2.15, 2.16 and appendix 2.

\[ \frac{\delta \mu_i}{\mu_i} \approx 2\left(1/\sigma_s\right) \left(1 - \frac{(R_{HS}/\sigma_s)_{i+1}}{(R_{HS}/\sigma_s)_i}\right) + \left(\frac{R_{HS}i}{(\sigma_s)_i}\right) \left(1 - \frac{(R_{HS}/\sigma_s^2)_{i+1}}{(R_{HS}/\sigma_s^2)_i}\right) \]  

\[ \frac{\delta n_i}{n_i} \approx \frac{\delta d_i}{d_i} + \frac{\delta u_i}{u_i} \]  

In most cases the errors of the profiles are within \( \pm 8\% \) for \( \mu_i \) and \( \pm 13\% \) for \( n_i \), which does not include errors for the Hall scattering factor. However, it is possible for zinc implanted electrical profiles to have errors up to \( \pm 14\% \) for \( \mu_i \) and \( \pm 19\% \) for \( n_i \) in the tail region of the profile (see appendix 2).
2.5.2 Rutherford Backscattering Spectroscopy

Rutherford Backscattering Spectroscopy (RBS) in combination with channeling was used to monitor the ion implantation damage before and after annealing. A collimated 1.5 MeV He\(^+\) beam with a maximum current of 10nA was directed at a chamber containing the sample mounted on a three axis goniometer. This allows the sample to be moved with respect to the beam so that, for crystalline material the beam can be aligned in terms of crystallographic directions. After striking the target some of the beam is scattered and particles scattered within a particular solid angle are detected in a silicon surface barrier detector with an energy resolution of about 15 keV. The detector was mounted at 150° to the incident beam. (See Fig. 2.6) The pulses from the detector are amplified, analysed and stored. The height of a pulse depends on the energy of the particle striking the detector, so that separation of the pulses according to their height is equivalent to energy analysis of the scattered particles entering the detector. This analysis is done by means of a computer based 512 channel energy analyser which also stores the data.

The energy, \(E\), of a particle of mass \(M\), energy, \(E_0\), scattering from a particle of mass \(M_2\) is:

\[
E = k^2E_0
\]

when

\[
k = \frac{M_1\cos\theta + (M_2^2 - M_1^2 \sin^2\theta)^{1/2}}{M_1 + M_2}
\]

and \(\theta\) is the scattering angle.

Helium ions not scattered at the surface lose energy by inelastic processes as they pass through the lattice before colliding elastically with the target atoms at some depth below the surface. After collision they again lose energy inelastically as they leave the target on their passage to the detector. The observed energy of a backscattered particle
Figure 2.6: Trajectories of helium particles elastically scattered at the surface and at a depth $x$. 
from a depth $x$ in the sample (117) is given by

$$E_{\text{obs}} = k^2 \left( E - \int_0^{x / \cos \Theta_1} S^*(E) dE - \int_0^{x / \cos \Theta_2} S(E) dE \right)$$

$S^*(E)$ and $S(E)$ are the stopping powers of the incoming and outgoing beams and $\Theta_1$ and $\Theta_2$ are the angles between the incoming and outgoing beams and the surface normal respectively. $\Theta_b$ is the backscattered angle ($150^\circ$). $E_{\text{obs}}$ and $E$ are the observed energies of the backscattered and incident helium particles respectively.

Exposure of the GaAs to the helium beam in a random direction yields a random backscattering spectrum as all the target atoms act as scattering centres for the beam. However, exposure to a beam incident in a major crystallographic direction gives a channelled spectrum with up to 96% of the beam moving near to the atoms in the lattice rows. The ratio of the aligned yield to the random yield behind the back edge of a damage peak is defined as $X_{\text{min}}$. This method has been employed to measure the departures from crystallinity in as implanted and post ion implanted annealed GaAs.

2.5.3 Ellipsometry

The reflection of light by surfaces produces different polarization transformations depending on the surface properties. This effect was used to measure the complex refractive index of GaAs. This is a well used technique for measuring the refractive index and thickness of a thin film as the modified polarization carries this information. However in this case only the GaAs substrate properties were measured.

Monochromatic ($\lambda = 0.6328\mu\text{m}$) linearly polarized light was made to fall on to the GaAs surface to be investigated, with its direction of vibration at $45^\circ$ to the plane of incidence. The elliptically polarized
reflected light passes through a quarter-wave plate which was adjusted until the light emerging from it becomes linearly polarized; as revealed by its becoming completely extinguishable by a polarizer. Measurement of the angular setting of both the quarter-wave plate and the polarizer for the extinguish condition allow the orientation and ellipticity of the reflected light to be determined. This is all the information necessary to deduce the properties of the surface.

The ellipsometer used was that at the university and is similar to the one described by Anand and Momodu (118).

The complex refractive index $n^*$ may be expressed as:

$$n^* = n - ik$$

$n$, real refractive index
$k$, extinction coefficient.

The absorption coefficient is defined as:

$$= 4\pi k \lambda^{-1}$$

where $\lambda$ is the wavelength of the analysing light.
Chapter 3

RESULTS

3.1 Zn IMPLANTATION

3.1.1 Graphite Strip Heater

A dose of $1 \times 10^{15}$ Zn$^+$ cm$^{-2}$ was implanted into semi-insulating GaAs at 60, 150 and 300 keV and annealed with a graphite strip heater using Si$_3$N$_4$ or AlN as encapsulants. The average sheet electrical results are shown in Table 3.1 and the profiles are presented in figures 3.1, 3.2 and 3.3. The anneal times at temperature were chosen to achieve the maximum electrical activation at that temperature. Increasing the times results in further diffusion of the zinc but the electrical activity does not significantly change.

100% electrical activity was achieved after 900°C anneals and a dwell time of 25s using a Si$_3$N$_4$ encapsulant, (figs. 3.1 and 3.2) but profiles penetrated deeply into the material indicating that fast indiffusion of zinc had occurred. The peak hole concentration decreased with increasing energy. Very little diffusion was observed for the 800°C anneals. A lower degree of activation was measured for AlN encapsulated samples (fig. 3.3) compared with those capped with Si$_3$N$_4$. 100% activation was only approached after annealing at 1000°C using AlN, with peak hole concentrations of $4-5 \times 10^{19}$ cm$^{-3}$.

A few samples were dual implanted with 65 keV $^{75}$As$^+$ and 60 keV $^{66}$Zn$^+$ with doses of $5 \times 10^{14}$ cm$^{-2}$ and $1 \times 10^{15}$ cm$^{-2}$ for each ion and annealed at 900°C for 25s with a Si$_3$N$_4$ encapsulant (fig. 3.4). The dual implant limited the diffusion of zinc and peak hole concentrations of up to $5 \times 10^{19}$ cm$^{-3}$ with activities up to 100% were achieved compared with peak values of $2-3 \times 10^{19}$ cm$^{-3}$ for single ion implants (fig. 3.2).
<table>
<thead>
<tr>
<th>Material</th>
<th>S. I.</th>
<th>S. I. Cr. doped</th>
<th>S. I.</th>
<th>S. I. undoped</th>
</tr>
</thead>
<tbody>
<tr>
<td>76+6</td>
<td>1.0+6</td>
<td>1.0+6</td>
<td>1.0+6</td>
<td>1.0+6</td>
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<tr>
<td>76+4</td>
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<td>1.0+6</td>
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</tr>
</tbody>
</table>

Table 3.12: Sheet electrical properties for GSN results.
Figure 3.1: Electrical profiles of $1 \times 10^{15} \text{Zn}^+ \text{cm}^{-2}$ implanted at energies of 60, 150 and 300 keV after a $900^\circ \text{C}/25$ s GSH anneal using Si$_3$N$_4$ encapsulation.
Figure 3.2: Electrical profiles of $1 \times 10^{15} \text{Zn}^+ \text{cm}^{-2}$ implanted at an energy of 60 keV after a 900, 850 and 800°C GSH anneal using $\text{Si}_3\text{N}_4$ encapsulation.
Figure 3.3: Electrical profiles of $1 \times 10^{15}$ Zn$^+$ cm$^{-2}$ implants at an energy of 60 keV after a 1000, 900 and 850°C GSH anneal using AlN encapsulation.
Figure 3.4: Electrical profiles of dual implants of Zn$^+$ at 60 keV and As$^+$ at 65 keV after a 900°C/25s GSH anneal using Si$_3$N$_4$ encapsulation.
By plotting the reciprocal of the annealing temperature against the saturated sheet hole concentration, the activation energy was calculated (fig. 3.5) to be 0.85 ± 0.1 eV for both AlN and Si$_3$N$_4$ capped samples. The Si$_3$N$_4$ encapsulated samples annealed at 900°C were not used in this plot since a saturation of electrical properties was achieved at this temperature. This type of plot becomes invalid at high temperatures as the slope of the curve tends to zero. By projecting this line to a sheet hole concentration of $1 \times 10^{15}$ cm$^{-2}$ in figure 3.5, it is found that a minimum temperature of 875°C is required to fully activate a dose of $1 \times 10^{15}$ Zn$^+$, using a Si$_3$N$_4$ cap.

3.1.2 Electron beam

Anneals at a power density of 100 W cm$^{-2}$ carried out on uncapped GaAs implanted with 60 keV, $1 \times 10^{15}$ Zn$^+$ cm$^{-2}$ revealed that the accuracy of the anneal time had to be better than ± 0.1 s for a 1.3 s anneal or the surface would thermally convert, often to n-type conduction or the implant would not activate appreciably. In this narrow time/temperature window the reproducibility was very poor and so further anneals were accomplished using capped samples.

The electrical profiles after electron beam annealing (fig. 3.6) for implanted material (60 keV, $1 \times 10^{15}$ Zn$^+$ cm$^{-2}$) show that it is possible to obtain a high percentage electrical activity with a hole concentration of 7-8 $\times 10^{19}$ cm$^{-3}$ and a corresponding mobility of about 40 cm$^2$ V$^{-1}$ s$^{-1}$, without significant indiffusion. This was achieved by irradiating for a total time of 3 s at a power density of 50 and 60 W cm$^{-2}$ which correspond to a calculated peak temperature of about 1040°C and 1120°C respectively. As the power density is increased for the same irradiation time, significant profile broadening occurs, 70 W cm$^{-2}$ corresponding to a sample temperature of almost 1200°C.
The slope of the lines gives an activation energy of $0.85 \pm 0.1$ eV.
Figure 3.6: Electrical profiles of $1 \times 10^{15} \text{Zn}^+ \text{cm}^{-2}$ implanted at an energy of 60 keV after a 3\text{Si}_2\text{EBA} for power densities between 50 and 70 W cm$^{-2}$ using Si$_3$N$_4$ encapsulation.
Lower power densities can also be used to anneal successfully and examples of this are shown in figure 3.7. The 24 W cm\(^{-2}\)/15 s exposure corresponds to a maximum temperature of 870°C which is reached in about 7 s. The 28 W cm\(^{-2}\) exposure corresponds to a saturation temperature of 910°C which is obtained in about 6 s. For these two conditions of anneal there is a small amount of broadening of the profile. When the time at 870°C (24 W cm\(^{-2}\)) was increased to 30 s (including the rise time) significant profile broadening occurred.

3.1.3 Canless

60 keV and 150 keV implants at a dose of \(1 \times 10^{15} \, \text{Zn}^+ \, \text{cm}^{-2}\) and 150 keV implants at a dose of \(1 \times 10^{16} \, \text{Zn}^+ \, \text{cm}^{-2}\), were annealed at 850°C and 880°C for about 20 minutes in an AsH\(_3\) ambient. Electrical profiles with low activation (<16%) and limited diffusion were obtained (Table 3.2 and figs. 3.8, 3.9, 3.10). SIMS results indicate that more than 50% of the implanted dose was lost from the surface (fig. 3.11) for this annealing condition. A few samples had an additional 900°C anneal for 25 s with a Si\(_3\)N\(_4\) cap and subsequently mobilities of up to 20% greater were recorded but the electrical activity did not increase significantly.

3.1.4 Q switched Ruby Laser without a Diffuser

150 keV implants at a dose of \(1 \times 10^{15} \, \text{Zn}^+ \, \text{cm}^{-2}\) into n-type GaAs were laser irradiated without an encapsulant. The sheet electrical results as a function of energy density are presented in table 3.3 and fig. 3.12. These results indicate that the electrical activation has a maximum at 0.5 J cm\(^{-2}\) with a slight decrease at high energy densities and with a decrease in electrical activation also occurring between 0.18 and 0.3 J cm\(^{-2}\). Using multiple pulses at 0.18 J cm\(^{-2}\) there is a sudden transition in electrical activation using between five and seven shots. RBS and TEM
Figure 3.7: Electrical profiles of $1 \times 10^{15} \text{Zn}^+ \text{cm}^{-2}$ implanted at an energy of 60 keV after an EBA for power densities between 24 and 28 Wcm$^{-2}$ using Si$_3$N$_4$ encapsulation.
Table 7.21: Sheet electroless results after caps were annealed with an argon overpressure.

<table>
<thead>
<tr>
<th>Material</th>
<th>(cm⁻²) Pose</th>
<th>(cm⁻²) Energy</th>
<th>(cm⁻²) x 10⁻⁴</th>
<th>(cm⁻²) x 10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>3.5</td>
<td>60</td>
<td>1.26</td>
<td>1.0 x 10⁻⁴</td>
</tr>
<tr>
<td>925</td>
<td>3.5</td>
<td>60</td>
<td>1.25</td>
<td>1.0 x 10⁻⁴</td>
</tr>
<tr>
<td>950</td>
<td>3.5</td>
<td>60</td>
<td>1.20</td>
<td>1.0 x 10⁻⁴</td>
</tr>
<tr>
<td>980</td>
<td>3.5</td>
<td>60</td>
<td>1.20</td>
<td>1.0 x 10⁻⁴</td>
</tr>
<tr>
<td>1.1</td>
<td>3.5</td>
<td>60</td>
<td>1.20</td>
<td>1.0 x 10⁻⁴</td>
</tr>
</tbody>
</table>

Note: After an approximate 20 minute temperature cycle.
Figure 3.8: Electrical profiles of \(1 \times 10^{15} \text{Zn}^+ \text{cm}^{-2}\) implanted at an energy of 60 keV after a capless anneal with an \(\text{AsH}_3\) overpressure at 850 and 880 \(^{\circ}\text{C}\) with an approximate 20 minute temperature cycle.
Figure 3.9: Electrical profiles of $1 \times 10^{15} \text{Zn}^+ \text{cm}^{-2}$ implanted at an energy of 150 keV after a capless anneal with an AsH$_3$ overpressure at 850 and 880°C with an approximate 20 minute temperature cycle.
Figure 3.10: Electrical profiles of $1 \times 10^{16}$ Zn$^+$ cm$^{-2}$ implanted at an energy of 150 keV after a capless anneal with an AsH$_3$ overpressure at 850 and 880°C, with an approximate 20 minute temperature cycle.
Figure 3.11: SIMS results for $1 \times 10^{15} \text{Zn}^+ \text{cm}^{-2}$ implanted at 60 keV as implanted and annealed at 850°C in an AsH$_3$ ambient.
Figure 5.12: Sheet electrical results of $1 \times 10^{15}$ Zn/cm$^2$ implanted at an energy of 150 keV after laser irradiation with a Q switched ruby laser without a diffuser and uncapped.
<table>
<thead>
<tr>
<th>Material</th>
<th>Laser Energy J cm(^{-2})</th>
<th>R.B.S. X(_{\text{min}}) %</th>
<th>TEM observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>n type</td>
<td>0.18</td>
<td>4.2 ± 0.2</td>
<td>13 ± 2</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>2.6 ± 0.4</td>
<td>25 ± 3</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>4.7 ± 0.7</td>
<td>21 ± 3</td>
</tr>
<tr>
<td></td>
<td>0.83</td>
<td>2.9 ± 0.2</td>
<td>47 ± 9</td>
</tr>
<tr>
<td></td>
<td>1.38</td>
<td>1.5 ± 0.1</td>
<td>72 ± 9</td>
</tr>
<tr>
<td></td>
<td>2 x 0.18</td>
<td>3.0</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>3 x &quot;</td>
<td>2.7</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>5 x &quot;</td>
<td>2.9</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>7 x &quot;</td>
<td>6.4</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>10 x &quot;</td>
<td>6.3</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 3.3: Sheet electrical results of 1 x 10\(^{15}\) Zn\(^+\) cm\(^{-2}\) implanted at an energy of 150 keV after laser irradiation with a Q-switched ruby laser without a diffuser and uncapped.

<table>
<thead>
<tr>
<th>Material</th>
<th>Laser Energy J cm(^{-2})</th>
<th>TEM observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>n type</td>
<td>0</td>
<td>56.6 ± 2</td>
</tr>
<tr>
<td></td>
<td>0.18</td>
<td>16.4 ± 1</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>12.0 ± 1</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>6.7 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>10.2 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>0.84</td>
<td>7.9 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>1.40</td>
<td>9.4 ± 0.5</td>
</tr>
</tbody>
</table>

Table 3.4: RBS & TEM results of 1 x 10\(^{15}\) Zn\(^+\) cm\(^{-2}\) at an energy of 150 keV after laser irradiation with a Q-switched ruby laser without a diffuser and uncapped.
observations are shown in Table 3.4. The as implanted samples were amorphous with stacking faults being annealed out up to 0.3 J cm\(^{-2}\). At 0.5 J cm\(^{-2}\) \(\chi\text{ min}\) increased from 6.7\% to 10.2\% with the underlying surface becoming crystalline. Energy densities greater than 0.5 J cm\(^{-2}\) produce damage to the underlying surface. Ellipsometry measurements (Table 3.5) of the absorption coefficient agree with \(\chi\text{ min}\) obtained from RBS in that the surface properties improve up to 0.3 J cm\(^{-2}\) and then degrade at 0.5 J cm\(^{-2}\). For comparison, anneals using the GSH have been included to demonstrate how efficient the 900\(^\circ\)C/25s anneal is in producing crystalline GaAs with a \(\chi\text{ min}\) of 5 \(\pm\) 0.5\% and an absorption coefficient of 7.5 \(\times 10^4\) cm\(^{-1}\). This compares with a measured absorption coefficient of 6.0 \(\times 10^4\) cm\(^{-1}\) for virgin GaAs, 3.02 \(\times 10^5\) cm\(^{-1}\) for as implanted GaAs and 1.21 \(\times 10^5\) cm\(^{-1}\) for implanted and laser irradiated at 0.31 J cm\(^{-2}\) (Table 3.5). Figure 3.13 compares the as implanted \(\chi\text{ min}\) values as a function of laser energy density with unimplanted GaAs. \(\chi\text{ min}\) increases for unimplanted GaAs to a peak of about 10\% at 0.8 J cm\(^{-2}\). This is similar to the peak measured for implanted GaAs which occurred at a lower energy of 0.5 J cm\(^{-2}\). A few samples which were annealed in a vacuum did not have a Ga rich surface when analysed by RBS.

3.1.5 Q Switched Ruby Laser with a Diffuser

The results are shown in Table 3.6 and Fig. 3.14. The Hall measurements will be correct to within \(\pm 10\%\) but error bars were not indicated as these points were not repeated. The peak electrical activity occurs between 0.6 and 0.8 J cm\(^{-2}\); however, the highest value measured was 45\% at 0.84 J cm\(^{-2}\). Electrical activation decreased at higher energy densities. Mobilities rapidly increased with energy density to 26 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 0.61 J cm\(^{-2}\) and then remained approximately constant at higher energy densities.
Figure 5.1*5: RBS measurements on laser irradiated samples without a diffuser implanted with $1 \times 10^{15} \text{Zn}^+ \text{cm}^{-2}$ implanted at an energy of 150 keV and unimplanted GaAs.
<table>
<thead>
<tr>
<th>Energy of 195 Kev</th>
<th>Computed Index</th>
<th>Experimentally Determined Index</th>
<th>Type of Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.06 + 0.05</td>
<td>3.77 + 0.05</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.21 + 0.05</td>
<td>1.48 + 0.05</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.27 + 0.05</td>
<td>1.79 + 0.05</td>
<td>3.84 + 0.05</td>
<td>&quot;</td>
</tr>
<tr>
<td>2.05 + 0.05</td>
<td>2.67 + 0.05</td>
<td>3.64 + 0.05</td>
<td>6.34 Gr. removed</td>
</tr>
<tr>
<td>0.75 + 0.05</td>
<td>0.72 + 0.05</td>
<td>3.80 + 0.05</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.01 + 0.05</td>
<td>0.05 + 0.05</td>
<td>3.80 + 0.05</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

The laser irradiation of the ion implanted glass (1 x 10^5 cm^-2) was with a switched ruby laser without a diffuser and unsmoothed.
Table 3.6: Sheet electrical results of 1 x 10^{15} Zn^{+} cm^{-2} implanted at an energy of 150 keV after laser irradiation with a Q switched ruby laser with a diffuser and uncapped.
Figure 3.14: Sheet electrical results of $1 \times 10^{15}$ Zn$^+$ cm$^{-2}$ implanted at an energy of 150 keV after laser irradiation with a Q switched ruby laser with a diffuser and uncapped.
3.1.6 Q Switched Nd-glass Laser without a Diffuser

With a lower absorption coefficient for this longer wavelength, higher energy densities were necessary in order to obtain the required annealing temperature. Severe damage to the surface was produced with an energy density of 10 J cm\(^{-2}\) and the samples were of very high resistivity. At 6 J cm\(^{-2}\) the surface was beginning to deteriorate with the best electrical results at 5 J cm\(^{-2}\) as shown in Table 3.7.

3.2 SELENIUM IMPLANTATION

3.2.1 Graphite Strip Heater and capless Annealing

Doses of 5 \(\times 10^{12}\) Se\(^{++}\) cm\(^{-2}\) were implanted at an energy of 700 keV and encapsulated with Si\(_3\)N\(_4\) and compared with capless annealing in AsH\(_3\). Capped samples were annealed at 900°C for 25 s on a GSH and capless samples were annealed at 850, 880 and 895°C for approximately 20 minutes. Figure 3.15 shows the electron concentration and mobility profiles obtained. The electrical activity increased with temperature to 74% with mobilities of about 4000 cm\(^2\)V\(^{-1}\)s\(^{-1}\).

Doses of 1 \(\times 10^{14}\) Se\(^{+}\) cm\(^{-2}\) were implanted at an energy of 100-400 keV and annealed using Si\(_3\)N\(_4\) or AlN encapsulants with anneals (temperature/dwell times) of: 850°C/100 s, 900°C/25 s, 950°C/4 s and 1000°C/2 s. The time to reach 1000°C varied between 15 and 20 s. The sheet electrical results are given in Figure 3.16. Figure 3.17 shows electron concentration and mobility profiles of samples annealed at 1000°C with an AlN encapsulant. There was no noticeable difference in the electrical results of samples capped with AlN or Si\(_3\)N\(_4\) and annealed at 900°C or below. At temperatures greater than 900°C the Si\(_3\)N\(_4\) cap tended to fail and so AlN was used. The percentage electrical activity increased with annealing temperature and ion energy. Carrier concentrations of 5-6 \(\times 10^{18}\) cm\(^{-3}\) with activities of about 80% were recorded. An activation energy of
Table 3.7: Sheet electrical results of $1 \times 10^{15} \text{Zn}^+ \text{cm}^{-2}$ implanted at an energy of 150 keV after laser irradiation with a Q switched Nd-glass laser without a diffuser and uncapped.
Fig. 3.15: Electrical profiles of $5 \times 10^{12} \text{Se}^{++} \text{cm}^{-2}$ implanted at an energy of 700 keV annealed with and without caps.
Fig. 3.16: Sheet electrical results of $1 \times 10^{14}$ Se$^+$ cm$^{-2}$ implanted at an energy between 100 and 400 keV and annealed by a GSH.
Fig. 3.17: Electrical profiles of $1 \times 10^{14} \text{ Se}^+ \text{ cm}^{-2}$ implanted at an energy between 100 and 400 keV and annealed at $1000^\circ \text{C}/2\text{s}$ by a GSH
1.2 ± 0.1 eV was calculated for the attainment of electrical activity (Figure 3.18) by plotting ln (n_e) versus the reciprocal of the annealing temperature and measuring the slope of the line.

Doses of 1 x 10^{14} Se^+ cm^{-2} implanted at an energy of 300 keV were also annealed at 900, 850, 825 and 800°C for a range of annealing times. (Some of the results have been taken from Sealy et al (119)) These results are plotted in figure 3.19, demonstrating how the anneal time, to reach a saturated sheet value, decreases with increasing temperature.

RBS was done on GaAs implanted with 10^{13}-10^{15} Se^+ cm^{-2} at energies of 100 keV (Figure 3.20) and 300 keV (Figure 3.21) to demonstrate the build up of damage with ion dose. An amorphous layer whose thickness increased with increasing ion energy formed with doses of 5 x 10^{13} cm^{-2}. Estimates of the amorphous layer thickness and the maximum depth of damage by extending the back edge of the spectrum down to the spectrum for virgin material are shown in Table 3.8. After annealing at 1000°C all the X_{min} values were between 5 and 6%. In figures 3.20 and 3.21 damage peaks for 5 x 10^{13} Se^+ cm^{-2}, for implants at 100 keV and 300 keV occurred at about 300 Å and 850 Å respectively. The depth of the damage peaks are about 80% of the projected ranges which agrees with Gecim et al (120).
Figure 3.18: Sheet carrier concentrations of $1 \times 10^{14}$ Se$^+$ cm$^{-2}$ implanted at an energy between 100 and 400 keV after a 1000°C/2s, 950°C/4s, 900°C/25s and 850°C/100°C GSH anneal using AlN or Si$_3$N$_4$ encapsulation. The slope of the lines gives an activation of $1.2 \pm 0.1$ eV.
Figure 3.19: Sheet carrier concentration of $1 \times 10^{14} \text{Se}^+ \text{cm}^{-2}$ implanted at an energy of 300 keV and annealed between 800 and 1000°C for a range of time on a GSH, with theoretical curves from page 84.
Figure 3.20: RBS results for doses from $1 \times 10^{13}$ to $1 \times 10^{15}$ Se$^+$ cm$^{-2}$ implanted at an energy of 100 keV.
Figure 3.21: RBS results for doses from $1 \times 10^{13}$ to $1 \times 10^{15}$ Se$^+$ cm$^{-2}$ implanted at an energy of 300 keV
<table>
<thead>
<tr>
<th>Ion Energy (keV)</th>
<th>Dose (cm$^{-2}$)</th>
<th>Amorphous thickness (Å)</th>
<th>Maximum damage depth (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>$5 \times 10^{13}$</td>
<td>300 ± 200</td>
<td>1450</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{14}$</td>
<td>400 ± 200</td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td>$5 \times 10^{14}$</td>
<td>500 ± 200</td>
<td>1950</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{15}$</td>
<td>600 ± 200</td>
<td>2150</td>
</tr>
<tr>
<td>300</td>
<td>$5 \times 10^{13}$</td>
<td>0 to 300 (buried)</td>
<td>3600</td>
</tr>
<tr>
<td></td>
<td>$7 \times 10^{13}$</td>
<td>1100 ± 200</td>
<td>3750</td>
</tr>
<tr>
<td></td>
<td>$5 \times 10^{14}$</td>
<td>1700 ± 200</td>
<td>4600</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{15}$</td>
<td>1900 ± 200</td>
<td>4950</td>
</tr>
</tbody>
</table>

Table 3.8: Estimates of amorphous layer thickness and the maximum damage depth from RBS results.
3.3 UNIMPLANTED MATERIAL

3.3.1 Optimum Si₃N₄ Thickness

The resistivity of the as-received substrate material was $2 \times 10^9 \, \Omega \text{/square}$. The resistivity after the GSH anneal at 900°C for 25 s (at temperature) for a range of Si₃N₄ encapsulant thicknesses is shown in Figure 3.22. A rate of rise in temperature of 70°C s⁻¹ was used. Sheet resistivities greater than $1 \times 10^8 \, \Omega \text{/square}$ are maintained for encapsulant thicknesses of 700-1200 Å. Using a slower rate of rise of 30°C s⁻¹ the Si₃N₄ layer can be increased to 1800 Å and still provide adequate protection for the GaAs. The dominant failure mechanism of the Si₃N₄ was due to the enlargement of pin holes during the anneal. In extreme cases, particularly with a very thick layer, cracks appeared linking together the enlarged pin holes.

3.3.2 Electron Beam

EBA was carried out on unimplanted material without an encapsulant. The e-beam power densities for particular times which just produce surface blemishes, observed by optical microscopy, are shown in Figure 3.23. For points greater than 7 Wcm⁻² on and to the right of the line, gallium precipitates (121) (Fig. 3.24) were observed on the surface using SEM. At 7 Wcm⁻² precipitates were not observed after 460 s which is on the line in figure 3.23. However precipitates were observed of 0.07um diameter after 560s. This is due to the sample holder heating up and allowing the sample temperature to rise to approximately 570°C. At temperatures below 570°C precipitates have not been seen. The sudden change in the gradient of the curve takes place at about 640°C for uncapped material.
Figure 3.22: Thermal conversion of S.I. GaAs after a 900°C/25s graphite strip anneal with varying thicknesses of Si₃N₄ encapsulant.
**Figure 5.23:** Maximum electron beam power density before surface damage occurs for uncapped and capped GaAs.
Figure 3.24: Gallium precipitates observed by SEK after EBA of unimplanted GaAs at power densities and times when they were first observed. a) 7Wcm$^{-2}$/560s, b) 10Wcm$^{-2}$/30s, c) 12Wcm$^{-2}$/18s, d) 32Wcm$^{-2}$/5s.
Included in figure 3.23 are the conditions when the $\text{Si}_3\text{N}_4$ encapsulant fails, taken from Shahid et al (67). These experiments showed that the $\text{Si}_3\text{N}_4$ encapsulant could withstand an anneal cycle to about $1200^\circ\text{C}$, providing the time was short (3 s). However, it was observed that longer times caused many pinholes to form in the $\text{Si}_3\text{N}_4$ and it eventually failed completely.
4.1 ZINC IMPLANTS

4.1.1 Model for the Electrical Activation and Diffusion of Zinc

The activation of zinc is enhanced in areas where damage is being annealed out (122). Even annealing at 650°C will produce a high hole concentration in the region of the damage profile (123). This suggests that gallium vacancies are readily generated by ion-implanted damage. This effect is enhanced by the non-stoichiometric distribution of gallium and arsenic in the implanted region (124). With interstitial zinc reacting with gallium vacancies to form shallow acceptors (125,126) the dominant defect may be interstitial gallium (127) from the generation of Frenkel defects. It is clear from Table 3.1 that the type of encapsulant used (AlN or Si₃N₄) makes a significant difference to the electrical activation. This is thought to be due to the difference in the thermal expansion coefficient between GaAs (128) and Si₃N₄ (129) or GaAs and AlN (130). High lattice bending is associated with an increase in dislocation density (131). It is therefore possible that the strain between the encapsulant and the GaAs substrate may be allowing the growth of dislocations and point defects to occur which relieves the strain by the generation of interstitial gallium and dislocations. This process may therefore increase the gallium vacancy concentration, causing the electrical activity to increase for the higher strained material.

High concentrations of zinc (>2 x 10¹⁹ cm⁻³) are unable to diffuse significantly or fully activate at temperatures less than about 850°C due to the zinc complexing with defects in the implanted region (92,132). At about 850°C these complexes dissociate allowing the implanted Zn to
diffuse interstitially. There will be a tendency for low concentrations of zinc not associated with complexes to diffuse into the bulk material for temperatures less than $850^\circ C$. Anneal times longer than 25 s at $900^\circ C$ do not make a significant difference to the shape of the electrical profile (93). Tuck et al (133) have demonstrated that with a $700^\circ C$ 15 minute zinc diffusion, a 15 minute post diffusion anneal up to $900^\circ C$ with an arsenic overpressure and the zinc vapour source removed, resulted in little further movement of the profile. It is probable that once the zinc atoms have been activated on a gallium lattice they do not diffuse appreciably. This emphasises the problem that drive-in zinc diffusion methods without the zinc source require longer times at temperature than discussed in this thesis. However, for ion implanted GaAs there is significant diffusion in the early stages of the anneal if the zinc concentration is greater than about $2 \times 10^{19} \text{ cm}^{-3}$ and the anneal temperature is $850^\circ C$ or above. Consequently the $1000^\circ C$ anneal using AlN (fig. 3.3) will diffuse to a similarly deep profile compared to the $900^\circ C$ anneal using $\text{Si}_3\text{N}_4$ (100) (fig. 3.2). There are still high diffusion rates using AlN as there are less gallium vacancies compared with the $\text{Si}_3\text{N}_4$ case, to retard the diffusion and hence a lower electrical activity occurs with AlN compared with $\text{Si}_3\text{N}_4$.

Following the model developed by Hurle (134), it is possible to establish a number of reactions for the formation of defects in GaAs which will influence the incorporation of zinc. The predominant disorder is proposed to be the Frenkel defect on the arsenic sublattice:

$$\text{As}_{\text{As}} + V_1 \rightleftharpoons \text{As}_1 + V_{\text{As}}$$

In addition arsenic may be incorporated directly from an arsenic ambient which is accomplished via the reaction

$$\frac{1}{2}\text{As}_2 (g) + V_1 \rightleftharpoons \text{As}_1$$
It is proposed that Frenkel defects can form on the gallium sublattice, hence:

\[ \text{Ga}_{Ga} + V_i \rightleftharpoons \text{Ga}_i + V_{Ga} \quad \ldots \quad 4.3 \]

and the number of defects (vacancies) on the two sublattices are related via the Schottky reaction:

\[ V_{Ga} + V_{As} \rightleftharpoons 0 \quad \ldots \quad \ldots \quad 4.4 \]

In equations 4.1 to 4.4, the subscripts refer to positions in the lattice. Thus \( V_i \) and \( V_{Ga} \) correspond to vacant interstitial and vacant gallium sites respectively, whilst \( \text{As}_i \) and \( \text{Ga}_i \) correspond to arsenic and gallium which occupy interstitial sites.

The mass action equations corresponding to equation 4.1 to 4.4 are reproduced in equations 4.5 to 4.8 respectively in which the square brackets denote concentrations:

\[
\begin{align*}
\left[ \text{As}_i \right] & \quad \left[ V_{As} \right] = K_{fa} \quad \ldots \quad 4.5 \\
\left[ \text{As}_i \right] & \quad \left[ \text{As}_2i \right] = K_{As_2} \quad \ldots \quad 4.6 \\
\left[ \text{Ga}_i \right] & \quad \left[ V_{Ga} \right] = K_{fg} \quad \ldots \quad 4.7 \\
\left[ V_{Ga} \right] & \quad \left[ V_{As} \right] = K_{s} \quad \ldots \quad 4.8
\end{align*}
\]

Let us consider first the condition in which the arsenic pressure is allowed to increase. From equations 4.5 and 4.6, \( \left[ \text{As}_i \right] \) increases and hence \( \left[ V_{As} \right] \) decreases with increasing arsenic pressure. If \( \left[ V_{As} \right] \) decreases, then from equation 4.8 \( \left[ V_{Ga} \right] \) will increase. Conversely, a decrease in arsenic pressure will reduce the number of \( \left[ V_{Ga} \right] \). If we now consider the addition of zinc atoms to GaAs, then these will occupy either gallium vacancies or interstitial positions and so we would expect a reaction of the following type to occur:
Thus we would expect zinc to occupy interstitial sites only if there were insufficient gallium vacancies present. In ion implanted material, large concentrations of vacancies and interstitials form and so prior to annealing there are plenty of available gallium vacancies for the zinc atoms to occupy. Depending on the annealing conditions, that is, whether anneals are capless in an arsine atmosphere or in a furnace with a cap, then the number of gallium vacancies available is likely to vary. Hence, the percentage electrical activity and the amount of profile broadening (diffusion) will also depend on the annealing conditions. The diffusion coefficient of zinc decreases with increasing arsenic pressure in the ambient (135) due to the increase in gallium vacancies. It is unlikely that arsenic diffuses from the surface via vacancies on its own sublattice to the implanted zinc as this mechanism has a low diffusion coefficient (136). Therefore the arsenic ambient probably effects the zinc profile via indiffusing gallium vacancies or out diffusing defects.

4.1.2 Graphite Strip Heater, Electron Beam and Capless Annealing

For a dose of $1 \times 10^{15}$ Zn+ cm$^{-2}$ it is not until a critical temperature of about 850°C is reached (fig. 3.2), for capped samples, that significant diffusion takes place. The sudden change in diffusion is unlikely to be due to the interstitial diffusion constant (137) changing rapidly with temperature but more likely to be due to a change in defect concentration indicated by the proposed model for diffusion of zinc and its electrical activation.
The use of AlN is effecting the activation of the implant compared with Si$_3$N$_4$ (figs 3.2 and 3.3 Table 3.1) and this may be partially due to the strain at the encapsulant-GaAs interface effecting the release of zinc from damage complexes. The strain will drive interstitial type defects into the bulk material and vacancies or vacancy related defects to the surface to achieve a lower chemical potential in the implanted region (138). The change in the distribution of gallium vacancies (97) will effect the diffusion and activation of the zinc. With anneals above about 850°C using a Si$_3$N$_4$ encapsulant, more zinc is released from damage complexes compared with the case when an AlN encapsulant is used (figs 3.2 and 3.3). This will initially produce a very sharp profile with a large proportion of the zinc occupying gallium vacancies in the first few seconds of the anneal (fig. 3.6). As the anneal continues, a further increase in the activation occurs by the indiffusion of zinc from the regions where the concentration is high until an equilibrium peak concentration of about $2 \times 10^{19}$ cm$^{-3}$ is reached. For the zinc to diffuse so readily with concentrations greater than $2 \times 10^{19}$ cm$^{-3}$ once it has been activated, may be suggesting that arsenic vacancies generated by the ion implantation damage (132,138) are influencing the activated zinc on gallium lattice sites to move onto interstitial sites.

With anneals above about 850°C using an AlN encapsulant, less zinc is released from damage complexes compared with when a Si$_3$N$_4$ encapsulant is used. In addition the proposed zinc model predicts the presence of a lower concentration of gallium vacancies due to the lower strain at the AlN/GaAs interface compared with the Si$_3$N$_4$/GaAs interface. Consequently with a lower concentration of gallium vacancies to retard the diffusion using an AlN encapsulant, the zinc readily diffuses at a lower concentration than in the Si$_3$N$_4$ case. However with doses lower
than $1 \times 10^{15}$ Zn$^+$ cm$^{-2}$ the gallium vacancies will have a greater retarding influence and may dominate when the strain due to the encapsulant is low. Kasahara et al. (139) found a large difference in zinc diffusion for a range of encapsulants with different strain properties. Equally there may be differences at higher doses (140) where the damage will extend deeper into the bulk material. It is clear that the effect of strain on the diffusion of zinc cannot be discussed without considering the consequences of the strain effects on implantation damage and the formation of gallium vacancies. The electrical activation energy (141), $0.85 \pm 0.1$ eV for both AlN and Si$_3$N$_4$ encapsulants indicates that the electrical activation mechanism is the same in both cases.

Dual implantation of zinc and arsenic allows the composition to be varied in a controlled way in the implanted layer (142). The implantation of arsenic produces gallium vacancies which retards the diffusion of interstitial zinc (97) giving rise to a sharper, peaked profile (fig. 3.4). With capless annealing the diffusion of zinc is retarded even more than for the dual implants. However, with capless anneals about 50% of the dose is lost presumably by outdiffusion and evaporation (fig. 3.11) which will also reduce the in-diffusion of zinc due to the smaller number of zinc atoms available. In addition to strain effecting the diffusion, the arsenic-rich surface may be reacting with the out-diffusing zinc and forming Zn$_2$As$_2$ (143). In the case of dual implants (Zn + As) there is not enough arsenic to compensate for all of the zinc. Increasing the temperature from 850°C to 880°C increases the electrical activity but the effect is suppressed by additional zinc being lost from the surface.

EBA has the capacity to reach temperatures greater than 850°C in a shorter time than the GSH. The high temperature allows zinc-damage complexes to anneal out to achieve a high percentage electrical activity
Due to the short 3 s anneal time the substitutional-interstitial diffusion of zinc is limited and hole concentrations of $7-8 \times 10^{19} \text{ cm}^{-3}$ are produced. EBA of capless unimplanted GaAs has shown that gallium precipitates form above about $570^\circ \text{C}$ which is significantly below the congruent sublimation temperature of $657^\circ \text{C}$ for Langmuir evaporation conditions (40). This may be due to very rapid localised heating as the power density of the beam is considerably higher than the averaged power density across the scanned area. This effect may influence the surface temperature momentarily as the e-beam passes over the surface and its energy is absorbed in a small volume. By the time the beam has returned (30ms) the heat has been dissipated into the bulk material. Consequently the bulk temperature of the GaAs is uniform provided there are no heat sinks.

4.1.3 Q switched Ruby laser without a Diffuser

The zinc implantation produces a surface amorphous layer, with a narrow band of fine damage immediately below it. The laser melts the surface to a depth determined by the laser energy density. If the melt-front at its greatest depth lies in the amorphous layer, the regrowth consists of polycrystalline material. If the melt-front reaches the fine damage band, the regrowth consists of single-crystal material which contains dislocations and stacking faults threading up to the surface from the damage band. If the melt-front goes below the fine damage band, the regrowth consists of single-crystal material which is free from such defects. This general behaviour has been described previously by others, e.g. Sadana et al (144), who performed similar TEM studies of Si and GaAs that had been implanted and pulse laser annealed. However, this work (145) shows that as the melt-front goes still deeper, the regrowth again consists of single-crystal material, but local areas contain large numbers of
dislocation tangles. Hence there is a definite energy density range, with upper and lower limits, for which the recrystallized layer is virtually free from defects (table 3.4).

The reason why these dislocation tangles form in GaAs at the higher laser energy densities is because an additional process occurs. When the surface layers of unencapsulated GaAs slices are melted by laser annealing, arsenic is rapidly lost from the surface because of its high vapour pressure and this leads to the formation of a gallium-rich surface when irradiated in the presence of air. Once this surface decomposition has occurred, losses of gallium and the implanted dopant occur in addition to the continuing arsenic loss. RBS showed that samples irradiated in a vacuum did not have a gallium rich surface. This was a difficult experiment to carry out so the results are not conclusive. However if correct, there may be the possibility of gallium and arsenic evaporating equally from the melted surface unless gallium oxides or nitrides form which stabilise the gallium.

Electrical activity was measured without an anneal, due probably to the residual damage. However because of the extremely low mobilities, the measurements were thought to be unreliable. At 0.2 J cm$^{-2}$ the mobility was increased and a stable sheet hole concentration was measured (see fig. 3.12). At 0.3 J cm$^{-2}$, RBS and TEM (Table 3.4) show that the damage has been significantly reduced; consequently the mobility increased but the conduction from the residual damage decreased. With increasing energy density the zinc was activated but, due to surface evaporation (35) the electrical activation of zinc is reduced at energy densities above 0.5 J cm$^{-2}$. This is a lower energy density than with the diffuser. The reason for this will be described in section 4.1.4. 0.5 J cm$^{-2}$ represents the energy density which produced the best electrical results but decomposition occurred as shown by RBS (Table 3.4) and ellipsometry
However, beneath the surface layer TEM micrographs (Table 3.4) have shown the presence of crystalline material. For unimplanted material the RBS results showed that the damage peak induced by the laser, shifted to higher energies. This may be explained from the ellipsometry results which show that the absorption coefficient for implanted GaAs is higher than that for unimplanted. Sell et al (146) reported a value of $4.5 \times 10^4$ cm$^{-1}$ for the absorption coefficient of crystalline GaAs which is similar to the value $6 \times 10^4$ cm$^{-1}$ in Table 3.5.

Another indication that the change in the absorption coefficient was significant was that multiple pulses had an effect on the implant at $0.18$ J cm$^{-2}$ (Table 3.3). With the absorption coefficient decreasing, each pulse penetrates deeper into the damaged layer.

4.1.4 Q Switched Ruby Laser with a diffuser

The laser irradiation had a very different effect on the surface when the diffuser was used as it does not allow high intensity spikes through the amorphous layer. For example, at $0.2$ J cm$^{-2}$ without the diffuser TEM reveals that part of the melt front penetrated (in the form of spikes) through the amorphous layer. However, by using the diffuser the high intensity spikes were considerably reduced and, therefore, at $0.2$ J cm$^{-2}$ the amorphous layer was not penetrated producing a higher resistivity than samples without the diffuser. The first signs of recrystallisation without a diffuser was at $0.3$ J cm$^{-2}$ but with the diffuser it was $0.6$ J cm$^{-2}$. The laser energy density scale in the two cases is displaced by approximately a factor of two in energy density (27). This is due to the energy distribution within the laser beam being significantly modified by the diffuser. The energy values given refer to average values for the whole beam area, while the specimens were annealed in the central area of the beam. The energy densities without
the diffuser should thus be multiplied by two to make a comparison with samples which have been irradiated with a diffuser in place. Above 0.8 J cm\(^{-2}\), with the diffuser, the electrical properties degrade far quicker than without the diffuser.

One additional effect which was observed without the diffuser was the presence of periodic bands of dense dislocation arrays with a spacing the same as the wavelength of the laser (0.69µm). This effect has been observed previously by other investigators, eg Leamy et al (147) and Hill (148), in silicon which had been laser annealed without a diffuser. Hill showed that the use of a diffuser eliminated other periodic features which had various spacings in the range 2-7µm. This was the dominant periodic feature observed in this work, and occurred on a wide scale in the approximate laser energy density range of 0.5 and 0.8 J cm\(^{-2}\).

4.1.5 Q Switched Nd-glass Laser without a Diffuser

These results (Table 3.6) were an improvement on the ruby laser. The longer wavelength penetrates deeper into the bulk material as the wavelength is outside the absorption edge for GaAs. Consequently higher energy densities than the ruby laser were required to anneal samples in the solid phase. The surface quality was better than that observed after ruby laser annealing. Deterioration of the surface took place at energy densities of 6 J cm\(^{-2}\) and disintegration at 10 J cm\(^{-2}\).

4.2 Selenium Implants

4.2.1 Electrical Activation Model for Selenium

This section discusses a model for the incorporation of implanted selenium in GaAs based on the results of transient annealing experiments.
A transmission electron microscopy study (17) has shown that, following an anneal at 500 to 600°C, all of the implanted selenium is in the form of precipitates. Following an anneal at 800°C to 900°C, only about 12% of the Se was estimated to be in the form of precipitates (149). This suggests that the lack of electrical activity in ion implanted GaAs may be due to the formation of complexes between vacancies and dopant atoms rather than the formation of precipitates. The presence of a Se$^{V}_{Ga}$ complex has been put forward by a number of research groups to explain the low electrical activity (150-152) and will also be used in this new model for the electrical activation of selenium implanted GaAs.

The selenium/gallium vacancy pair is thought to be a neutral centre (153-156). Selenium is unlikely to diffuse interstitially but diffuse via a vacancy on the gallium sublattice (157). After ion implantation it is reasonable to assume that most of the selenium atoms are on interstitial sites for room temperature implants (158,159). As suggested in section 4.1.1, the damage resulting from ion implantation is rich in gallium vacancies. A large increase in the concentration of selenium/gallium vacancy complexes is therefore expected in the early stages of the anneal. It is therefore assumed for the model that at the beginning of the anneal, all the implanted selenium is in the form of complexes. It is also assumed that the selenium complex defect diffuses until it combines with a gallium interstitial which neutralises it leaving the selenium on an arsenic site in which it behaves as a simple donor.

The implanted selenium for the purpose of this model is assumed to be distributed uniformly in the form of complexes within a layer of thickness corresponding to that of the as-implanted profile. Let $N$ be the number of selenium complexes available to diffuse to sinks, the sinks being gallium interstitials. The number of selenium complexes
which find a gallium interstitial sink per unit time is proportional to
the number of selenium complexes \( N(t) \) present at time, \( t \), that is:

\[
\frac{dN(t)}{dt} = -KN(t) \quad \text{..... 4.11}
\]

where \( K \) is the rate constant. This equation assumes that the sink
concentration remains constant. Equation 4.11 can be integrated to
give:

\[
N(t) = N_0 \text{Exp}(-Kt) \quad \text{..... 4.12}
\]

where \( N_0 \) is the initial concentration of selenium complexes, that is
the dose. \( K^{-1} \) may be considered as the average time that the selenium
complex diffuses and dissociates over an average distance, \( s \).
Therefore \( K = D s^{-2} \), where \( D \) is the diffusion coefficient of selenium
complexes in GaAs. Thus:

\[
K = K'D = K'D_0 \text{Exp}\left(\frac{-eE_d}{kT}\right) \quad \text{..... 4.13}
\]

where \( K' \) is the constant, \( s^{-2}, D_0 \) is a pre-exponential factor, \( e \)
the electronic charge, \( k \) Boltzmann's constant, \( T \) the absolute temperature
and \( E_d \) the activation energy of diffusion of selenium complexes in GaAs.
Combining equations (4.12) and (4.13) gives:

\[
N(t) = N_0 \text{Exp}\left(-K'D_0 t \text{Exp}\left(\frac{-eE_d}{kT}\right)\right) \quad \text{..... 4.14}
\]

The parameter measured is the sheet electron concentration \( n_t \) as
a function of annealing time and temperature up to \( 900^\circ\text{C} \) (see fig. 3.19).
Thus \( N(t) = (N_o - n_t) \) which can be written as a fractional change with
time, that is, \( (1-n_t/N_o) \) or \( (1-a_t) \) where \( a_t \) represents the electrical
activity as a function of time. Thus equation 4.14 may be written as:

\[
1-a_t = \text{Exp}\left(-K'D_0 t \text{Exp}\left(\frac{-eE_d}{kT}\right)\right) \quad \text{..... 4.15}
\]

which describes how the fraction of inactive selenium complexes \( (1-a_t) \)
varies with annealing time and annealing temperature. It is necessary
to write equation 4.15 in such a way as to aid the interpretation of experimental results for a particular anneal temperature in figure 3.19:

$$\ln(1-a_t)^{-1} = k'D_0 t \exp\left(\frac{-E_d}{kT}\right) \tag{4.16}$$

By plotting $\ln(1-a_t)^{-1}$ against $t$ for a particular temperature, the slope of the line $k'D_0 \exp\left(\frac{-E_d}{kT}\right)$ is calculated in Figure 4.1. $E_d$ is determined by plotting $\ln(k'D_0 \exp\left(\frac{-E_d}{kT}\right))$ against $1/T$. The slope will be $-E_d/k$ and the intercept is $\ln k'D_0$ (Figure 4.2). It is interesting to note that as the rate of change of electrical activation is

$$\frac{da_t}{dt} = k'D_0 (1-a_t) \exp\left(\frac{-E_d}{kT}\right)$$

and as the change in $a_t$ is small and $a_t \ll 1$ then

$$\frac{da_t}{dt} \approx k'D_0 \exp\left(\frac{-E_d}{kT}\right)$$

which gives a linear increase in $a_t$. Then $\frac{da_t}{dt} \approx k'D_0 \exp\left(\frac{-E_d}{kT}\right)$ the value of $E_d$ is $4.4 \pm 0.3$ eV and $\ln k'D_0$ is $39.2 \pm 3$. By taking $D_0 = 3 \times 10^3$ cm$^{-2}$ (15) the average diffusion length is between 1 and 13 interatomic spacings. This calculated energy of diffusion is close to a previously measured value of 4.16 eV by Goldstein for the diffusion of selenium in GaAs (15). Thus it is suggested that Goldstein observed the diffusion of complexes rather than single selenium atoms.

Figure 4.1 is demonstrating that there is already some electrical activation at $t = 0$. This is due to the significant rise time to temperature when electrical activation takes place. This, however, will not affect the calculations as the slopes of the lines are used in figure 4.1 and not the intercept. The lag time of the sample behind the graphite strip does have an important bearing on the errors of the results as samples may not have reached the recorded temperature for quoted times. No allowance for lag time was made in the results since its magnitude has not been measured accurately and it may vary with temperature. Until much shorter rise times can be achieved and also an accurate value of the lag time measured, the time dependence of the electrical activity at $900^\circ$C and
Figure 4.1: $\ln(1/(1-a_T))^{-1}$ against time (t) for a particular anneal temperature. The slope of the line $\Delta \ln(1/(1-a_T))/\Delta t$ is $K'D_0 \exp(-E_d/(kT))$. 
Figure 4.2: The determination of the activation energy of diffusion (the slope) and $\ln R'D_0$ (the intercept) by plotting $\Delta \ln(1/(1-a_t))/\Delta t$ against the reciprocal anneal temperature.
above will remain uncertain.

By using the straight line parts of figure 4.1, it is possible to construct the full lines shown in figure 3.19 in the regions where the activity varies with time. The saturation values in figure 3.18 were obtained at 850°C and above by experiment and below 850°C by plotting \( \ln a_t \) versus the reciprocal of the annealing temperature (fig. 3.19) and reading off the appropriate values at 825°C and 800°C. The activation energy for this process is \( 1.2 \pm 0.1 \) eV.
4.2.2 Graphite Strip Heater and Capless Annealing

The electrical activation of the implanted Se\(^+\) increases with time during an anneal until it saturates (fig. 3.19). The saturation value for the sheet carrier concentration and the time to reach this value varies with temperature. The times chosen for the G.S.H anneals were the minimum times required to reach this saturation value. However, an annealing time of 20 minutes was chosen for capless anneals to assure that the samples reached temperature under furnace conditions. Capless annealing was limited to less than 900°C as the loss of Ga is appreciable above this temperature.

The 700 keV implant with doses of \(5 \times 10^{12} \text{ Se}^{++} \text{ cm}^{-2}\) (Fig. 3.15) required temperatures greater than 850°C to obtain high electrical activities in contrast to lighter ions such as Si\(^+\) (54) which are fully activated at about 850°C. RBS results indicate that there is good crystalline material present after annealing for both GSH and capless annealing.

Electrical activation for \(1 \times 10^{14} \text{ Se}^{+} \text{ cm}^{-2}\) implants decreases with decreasing ion energy (Fig. 3.16). This is in agreement with Gamo et al (34) who reported high temperature anneals were required to activate selenium in the surface region. This is also shown in Fig. 3.17 using 1000°C anneals where the carrier concentration reached \(1-2 \times 10^{18} \text{ cm}^{-3}\) for the 100 keV implant and \(5-6 \times 10^{18} \text{ cm}^{-3}\) for the 400 keV implant. An AlN encapsulant was necessary for anneals above 900°C and is probably successful because it has a thermal expansion coefficient of \(6.4 \times 10^{-6} \text{ K}^{-1}\) at 1000°C and \(4.1 \times 10^{-6} \text{ K}^{-1}\) at 200°C which is closer to that of GaAs than the expansion coefficient of \(\text{Si}_{3}N_{4}\). Samples annealed at 1000°C had a \(X_{\text{min}}\) value between 5 and 6% which is close to the value for good crystalline material. The frequently observed reduction in carrier concentration near the surface for 100 keV and 200 keV implants (Fig. 3.17) suggests that
there is damage still present close to the LSS ranges which was not
detected by RBS.

The activation energy of 1.2 ± 0.1 eV (Fig. 3.18) was the same
within experimental error for all the energies used. When other work
(55, 44) is considered, it seems likely to a first order approximation
that the activation energy is the same for the temperature range 600°C
to 1140°C. This indicates that the same mechanism for activating
selenium prevails throughout this temperature range and this is suggested
to be splitting up of selenium-gallium vacancy complexes (150-152).

The 1 x 10¹⁴ Se⁺ cm⁻² results (Fig. 3.16) do not completely agree
with the work of Lidow et al (33) who did not observe a continued
increase in activation with temperature for all their implanted selenium
doses. However there is agreement with Bhattacharya et al (160) who have
investigated 1 x 10¹⁴ Se⁺ cm⁻² at 120 kV with 15 minute anneals between
850°C and 950°C with a Si_N₄ encapsulant. Both papers show electrical
profiles with high concentrations at the surface decreasing to flat
broad profiles which is in contrast to the results of this work (Fig. 3.17).
However, Inada et al (161, 162) who implanted 5 x 10¹³ Se⁺ cm⁻² at an
energy of 100 keV followed by annealing at 900°C for 15 minutes have
produced very similar results.

The RBS results of figures 3.20 and 3.21 show that a minimum dose
of 5 x 10¹³ cm⁻² is required to create amorphous material. Higher doses
extend the width of the amorphous layer. This is primarily independent
of ion energy due to the atomic concentration of selenium decreasing with
increasing energy but this is compensated by the fact that, the number of
displaced atoms per incident ion increases. The ion energy dictates the
position of this initial break down of crystallinity. It is interesting
to note that the estimated maximum damage depth coincides with the tail
of the electrical profiles (compare table 3.7 and figure 3.17). This suggests that activity occurs only in damaged regions of the crystal.

4.3 **UNIMPLANTED MATERIAL**

4.3.1 **Optimum Si$_3$N$_4$ Thickness**

The thickness limit of the Si$_3$N$_4$ encapsulant for a 900°C anneal is in agreement with SEM observations made by Inada et al (163). The difference in the thermal expansion coefficient of Si$_3$N$_4$ (4.0 x 10$^{-6}$K$^{-1}$ at 1000°C, 2.8 x 10$^{-6}$K$^{-1}$ at 200°C) (129) and GaAs (6.9 x 10$^{-6}$K$^{-1}$ at 200°C (128) produces large strains across the Si$_3$N$_4$/GaAs interface which are released when cracks are formed. The second observable failure mechanism was the enlargement of pin holes if the sample was at temperatures above 900°C for too long a time. By comparing the electron beam with the graphite heater results it appears that strain on the Si$_3$N$_4$/GaAs interface does not significantly increase once the temperature rise rate is of the order of 70°C s$^{-1}$ which suggests that a strain release mechanism may be taking place at around 900°C. With Si$_3$N$_4$ layers less than 800 Å thick it is speculated that defects in the Si$_3$N$_4$ layer penetrate through the layer whereas thicker layers cover up such defects.

4.3.2 **Electron Beam**

The calculated temperature time curves in Figure 4.3 all have the same surface effect on uncoated GaAs. In their present form it is difficult to characterise the curves by a precise time at which the samples were at a particular temperature, especially with the high power densities. An equivalent temperature/time step function for each curve is required in order to obtain further information about the curves.
This is not possible without information on the activation energy of the process which is demonstrated in Appendix 3. To overcome this problem a simpler approach is necessary: The area $A$, under the time-temperature curve between the peak temperature and $50^\circ C$ below the peak temperature ($T_{Pk}$) may be calculated, shown in figure 4.4. The time above this lower temperature ($T_{Pk} - 50$) is defined as the equivalent time ($t_E$) of the temperature/time curves. The equivalent temperature ($T_E$) is defined as:

$$T_E = T_{Pk} - 50 + \frac{A}{t_E} \quad \ldots \ldots \quad 4.17$$

Using equation 4.17 the temperature time curves in figure 4.4 may be changed to temperature time step functions. These values are plotted in figure 4.5 showing three regions; below $635^\circ C$, $635^\circ C$ to $930^\circ C$ and above $930^\circ C$. The sudden effect of GaAs being sublimed readily from the surface above $635 \pm 10^\circ C$ produced a sharp change in slope in figure 4.5. The second change from regions II to III at $930 \pm 30^\circ C$ may be a diffusion process in GaAs supplying arsenic from the bulk to the surface, first postulated by Arthur (164). This conclusion has been supported by studies with GaAs layers prepared by molecular beam epitaxy (165,166).

Gallium rich surfaces were prepared by annealing the samples above $530^\circ C$. During cooling to below $500^\circ C$ the surfaces converted to As-rich ones but heating to above $530^\circ C$ restored the Ga-rich structure again. This cycle could only be repeated a few times indicating that one substrate contained a limited supply of arsenic. It is probable that at $930^\circ C$ under conditions very different from MBE with the arsenic-rich GaAs used, the arsenic begins to out-diffuse from the bulk material and, therefore, starts to compensate for the As loss at the surface. It is also interesting to note that the anti-site defect $\text{As}_{Ga}$ is possibly stable up to $900^\circ C$ (167).
Figure 4.5: Electron beam temperature - time curves just before surface damage occurs for uncapped GaAs. Beam power densities are indicated in W cm$^{-2}$. 
This is probably one reason why a limited amount of capless annealing (without \( \text{AsH}_3 \)) at high temperatures and short times (\( \approx 1s \)) may be carried out. This effect may also be attributed to a strain release mechanism between the GaAs and \( \text{Si}_3\text{N}_4 \) interface due to the rapid change of topography. This would allow the \( \text{Si}_3\text{N}_4 \) to reach higher temperatures than 950°C as long as the excess As is out-diffusing from the bulk. This may account for the high temperatures obtainable using a \( \text{Si}_3\text{N}_4 \) encapsulant for an electron beam anneal with short times (\( \approx 3s \)).
Figure 4.4: The definition for the equivalent temperature:

\[ T_E = T_1 + A_1/t_1 \]

where \( A_1 \) is the shaded area and \( T_1 = T_{pk} - 50 \)
Figure 4.5: Calculated temperature/time dependence of the surface effect on uncapped GaAs using electron beam irradiation.
Chapter 5

CONCLUSIONS

5.1 Zinc Implants

Temperatures greater than 875°C are required to achieve 100% activation using a Si$_{3/4}$N$_{4}$ encapsulant and for doses up to 1x10$^{15}$ cm$^{-2}$. An Arrhenius plot was used to obtain this critical temperature. At anneal temperatures of 850°C and above there is a significant amount of diffusion which takes place for an atomic concentration of greater than 2x10$^{19}$ cm$^{-2}$. This is generally for doses greater than 1x10$^{14}$ cm$^{-2}$. The activation energy from the Arrhenius plot was 0.85eV, significantly lower than for selenium implants. Recent results, using modified annealing apparatus is indicating that this value may be lower still.

The diffusion of zinc at temperatures of 850°C and above was not very controllable with the GSH due to its relatively long rise time to temperature. The use of reactively evaporated AlN produces lower electrical activities than for Si$_{3/4}$N$_{4}$ encapsulants after annealing on the GSH. It was argued in the discussion of chapter 4 that this may be due to the difference in the expansion coefficient between the encapsulant and the GaAs. It is not at all clear how the strain on the GaAs during an anneal cycle varies with temperature, temperature ramp rates, encapsulant composition and surface quality of the substrate. If in addition to these unknowns the activation energy of zinc is lower than measured, then lower temperatures in the anneal cycle will have a greater influence than originally thought as demonstrated in appendix 3. Therefore another effect may be the deposition temperature of Si$_{3/4}$N$_{4}$ between 635 and 650°C, even though it was for short times. The lower electrical activation of zinc from using AlN could be compensated by the AlN withstanding higher anneal temperatures than Si$_{3/4}$N$_{4}$ thereby obtaining similar activation. Broad electrical profiles were observed for both encapsulants. There is a thickness limit for Si$_{3/4}$N$_{4}$ encapsulants which is dependent upon the peak anneal temperature, the rise time and the time at temperature. The Si$_{3/4}$N$_{4}$ will generally fail at 950°C but, for short times using EBA, it can withstand much higher temperatures.
Diffusion was limited by using an electron beam to anneal at high temperatures and short times which produced hole concentrations up to $8 \times 10^{19} \text{cm}^{-3}$. Furnace anneals with an $\text{AsH}_3$ over-pressure gave low percentage electrical activities but did limit the diffusion of zinc. However out-diffusion of zinc did occur, and zinc was lost from the surface.

Laser anneals gave poor mobilities by introducing damage into the surface or by not fully annealing out damage in the solid phase. Due to the change in refractive index as the damage is annealed out, multiple pulses at low energies from the Q switched ruby laser were shown to activate the zinc. This method may produce better results using the Nd-glass laser under conditions such that the GaAs is close to its melting point and crystal growth is in the solid phase.

A model was developed for the electrical activation of zinc. Vacancies and zinc complexes determine the electrical activation and diffusion of the implanted zinc profile during an anneal cycle. At anneal temperatures below $350^\circ\text{C}$ there is limited diffusion. However, due to the interstitial diffusion mechanism of zinc it is suspected that there will be a tendency for low concentrations of zinc (less than $1 \times 10^{17} \text{cm}^{-3}$) to diffuse into the GaAs. At anneal temperatures of $350^\circ\text{C}$ and above the zinc readily diffuses from the implanted surface layer. This mechanism may be associated with the break up of complexes and the releasing of zinc interstitials. However, once a zinc interstitial moves onto a gallium vacancy and at the same time the atomic concentration is less than $2 \times 10^{19} \text{cm}^{-3}$, then there is only a small probability of it diffusing further. Consequently there is a large diffusion effect of purely interstitial zinc which is eventually substituted for by an interstitial-substitutional diffusion mechanism. By adjusting the gallium vacancy concentration, this diffusion effect may be modified as with co-implantation of zinc and arsenic or annealing with an arsine ambient.
5.2 Selenium Implants

Annealing times at temperature of the order of seconds have removed radiation damage and activated selenium ions implanted into GaAs at room temperature. Carrier concentrations of $5-6 \times 10^{18} \text{cm}^{-3}$ have been achieved following an anneal at 1000°C with an AlN encapsulant. The encapsulant Si$_{3}N_{4}$ gave similar results to AlN for anneal temperatures of 900°C and less, unlike the zinc results. In addition low doses have been activated which are suitable for the channel regions of FETs. For the fabrication of selenium implanted integrated circuits high energy ion accelerators and high temperature transient annealing techniques are required.

A simple model for the electrical activation of selenium implanted into GaAs has been developed which is consistent with published data and involves the annihilation of (Se-\text{V}_{\text{Ga}}) complexes by gallium interstitials. By studying the temporal evolution of electrical activity, an energy which may be associated with or is the diffusion energy of selenium in GaAs was measured to be 4.4eV. The high value suggests that it is a vacancy related diffusion mechanism. In the discussion of the model, it was assumed that the electrical activation of the selenium took place at the same time as the break up of the complex. It is quite possible that the substitutional selenium on an arsenic site dissociates itself from the gallium vacancy without the requirement for interstitial gallium. Thus forming momentary an unstable double vacancy, $V_{\text{As}} - V_{\text{Ga}}$. The precise process is not clear at this stage. The electrical activation of selenium at equilibrium was measured to be 1.2eV. This is a relatively low value but it is assumed to be related to the splitting up of the complex and the activation of the selenium on an arsenic vacancy. It is possible that this energy may be the difference in energy of a number of inter-related processes.
5.3 Future Work

The temporal evolution of electrical activity of zinc should be fully studied to obtain the associated diffusion energy associated with the process. It will also be important to identify if there are two separate annealing processes; one for temperatures 600 to 800°C and a second for 850 to 1000°C. With improved time and temperature measurements to the GSH it should be possible to monitor the temperature-time cycles accurately for both zinc and selenium. At high temperatures it may be necessary to use an equivalent temperature-time profile as shown in appendix 3. This will be possible as the electrical activation energies of zinc and selenium are known. Other dopants for GaAs should be investigated to establish their associated diffusion and electrical activation energies. From this work it may be possible to formulate a precise model of the electrical activation of zinc and selenium which can predict the relative energies associated with the process.

Future work should also include experiments on the temporal evolution of implanted crystalline damage and surface effects of unimplanted GaAs. Very little work has been carried out on this subject. Without a better understanding of the unimplanted substrate itself, the models to predict what is happening to implanted GaAs will be limited.

The deterioration of the Ni–Au–Ge contact to n-type GaAs, is related to the penetration and spreading of Au, which decreases the density of low-resistance Ni2GeAs areas (168). Thus, to attain an ohmic contact with better reliability in the future, particularly at high temperatures, it is important to investigate non-alloyed contacts (169). This may be obtained by using high doses of selenium to form carrier concentrations of the order $1 \times 10^{19} \text{cm}^{-3}$.

A parameter which is useful in predicting the ohmic characteristics of a metal–semiconductor interface is the tunnelling parameter...
$E_\text{oo} (170)$ defined by

$$E_\text{oo} = \left(\frac{e^2 \hbar}{n/m^* \varepsilon}\right)^{\frac{1}{2}}$$

where $e$ is the electronic charge, $\hbar$ is the Planck constant, $m^*$ is the effective mass, $\varepsilon$ is the dielectric constant, and $n$ is the donor concentration. For $E_\text{oo}/kT \ll 1$, the contact will behave as a Schottky barrier while for $E_\text{oo}/kT \gg 1$ the contact will exhibit Ohmic characteristics due to tunnelling. For carrier concentrations of about $2 \times 10^{18}$ cm$^{-2}$ when $E_\text{oo}/kT \approx 1$ there are mixed transport properties at the interface due to thermionically induced field emission. For doping concentrations much less than $2 \times 10^{18}$ cm$^{-3}$ the contact will exhibit Schottky barrier characteristics while for $n \gg 2 \times 10^{18}$ cm$^{-3}$ ($n \geq 1 \times 10^{19}$ cm$^{-3}$) the contact should be ohmic.

Refractory metallizations for ohmic contacts generally use Ge doping for the GaAs to form the $n^+$ contact layer. However these types of contacts require an anneal temperature between 500 and 750°C (171). The contact resistance has been shown not to increase appreciably up to 190 hours at 350°C compared with that using AuGeNi which changed two orders of magnitude at this temperature and time (172). This high temperature anneal cycle may be eliminated by using implanted dopants instead of Ge to form the $n^+$ layers. Thus obtaining high carrier concentrations greater than $1 \times 10^{19}$ cm$^{-3}$ at the surface of III-V compounds is very important for the next generation of devices. Hence selenium ion implantation will play an important role in this area of work. It is important to establish this technology on three inch wafers and at the same time use selenium implants for a range of devices. This requires a number of improvements in key areas; ion accelerators, encapsulation and annealing.
There is an ever increasing demand for buried active layers. Selenium, due to its mass, requires MeV energies for suitable implant depths. Conventional DC accelerators can only produce low beam currents at these energies which is not suitable for high dose implants. A second approach which has the potential for higher beam currents at MeV energies is the linear r.f. accelerator (173).

Encapsulation over large areas for high temperature anneals is a major problem. The deposition of AlN by CVD methods has been established in recent years (174). However plasma enhanced CVD is a new field. The advantage is the lower deposition temperature and that insitu surface preparation before the encapsulant is plasma deposited may be carried out on wafers.

Rapid thermal annealing has a very important role to play in establishing high carrier concentrations as well as in other areas (80). This method of annealing is still very much in the research stage.

The advantage of zinc over other p-type dopants is the ability to obtain high hole concentrations. However to make this dopant acceptable in today's small geometry devices even faster anneal cycles are required than are necessary for selenium. Therefore further improvements to annealing techniques for wafers are required.
References


APPENDIX: 1

Temperature-Time calculations for EBA

All materials reflect part of the radiant energy incident upon them and emit less radiant energy than a blackbody radiator at the same temperature. The radiant flux emitted per unit area, \( M_R \), of a blackbody radiator is given by the Stefan-Boltzmann equation:

\[
M_R = \sigma T^4
\]

where \( \sigma \) is the Stefan-Boltzmann constant.

This can be applied to real surfaces by using the emittance as a proportionality factor. The emittance of a real surface is given by:

\[
M_R = \varepsilon(2\Omega, T) (T^4 - T_0^4)
\]

where \( \varepsilon(2\Omega, T) \) is the hemispherical total emittance of the specimen at temperature \( T \) and background temperature of \( T_0 \).

A fraction of the sample area \( (A_{th}) \) was in thermal contact with the sample holder. The thermal flux \( (M_c) \) conducted away from the sample is given by:

\[
M_c = A_{th} K_L (T - T_0)/d
\]

where \( K_L \) is the thermal conductivity and \( d \) is the sample thickness.

The flux absorbed by the sample from the electron beam is:

\[
M_E = kP
\]

where \( P \) is the beam power per unit area and \( k \) is the fraction of electrons which are not backscattered. It follows that:
The temperature change rate \[ \frac{dT}{dt} = \frac{M_E - M_R - M_C}{dC_p/\rho} \]

where \( C_p \) is the specific heat and \( \rho \) is the density of the GaAs.

The equation used in the computer programme was

\[ \frac{dC_p}{\rho} \frac{dT}{dt} = kP - 6C^\circ (T^4 - T_0^4) - A_{Th} K_L (T - T_0)/\delta \]

\( T \) Temperature (K)
\( T_0 \) Temperature of sample holder (K)
\( t \) Time (s).
\( P \) Beam power (Wcm\(^{-2}\))
\( \sigma \) Stefan - Boltzmann constant
\( 5.67 \times 10^{-12} \text{ Wcm}^{-2} \text{ K}^{-4} \)
\( \varepsilon \) Emissivity
\( -1.67 \times 10^{-6} T^2 + 5.05 \times 10^{-3} T - 1.82 \)
\( C_p \) Specific heat
\( 8.1 \times 10^{-5} T + 0.302 (\text{Jg}^{-1} \text{ K}^{-1}) \) (175)
\( K_L \) Thermal conductivity
\( 302 \times T^{-1.137} (\text{Wcm}^{-1} \text{ K}^{-1}) \) (176)
\( d \) 0.039 cm, sample thickness
\( \delta \) 5.3 gcm\(^{-3}\) density
\( k \) 0.89, fraction of absorbed electrons
\( A_{Th} \) 1/540, Fraction of area in thermal contact.
\( T_0 \) 0.8 \((T - 294) \times \exp(-560/ (t + 223)) + 294 \)

\( A_{Th}, \varepsilon \) and \( T_0 \) were used to calibrate the programme with experimental results.

With a change of 1°C from \( T \) to \( T + 1 \) the time interval for this change is:
\[ \Delta t = \frac{dC_p}{k^P - \varepsilon \sigma (T^4 - T_0^4) - A_{th} K_L (T - T_0)/d} \]

In the programme the temperature was stepped in 1°C intervals with \( \Delta t \) added to the existing time for each temperature step.
Hall Measurement Errors for Electric Profiles

The volume carrier or hole concentration (n or p) and mobility (\( \mu \)) are calculated from the values of \( R_{HS} \) and \( \sigma_s \) obtained for each etch step and using the equation derived by Buehler (115).

Buehler assumed that the conducting layer may be divided into a series of layers of thickness \( d_i \). The mobility \( \mu_i \) and the carrier concentration \( n_i \) of the \( i \)th layer are given by:

\[
\mu_i = \frac{(R_{HS}/\sigma_s^2) - (R_{HS}/\sigma_s^2)_{i+1}}{(1/\sigma_s)_i - (1/\sigma_s)_{i+1}}
\]

\[
n_i = \frac{(1/\sigma_s)_i - (1/\sigma_s)_{i+1}}{q d_i \mu_i}
\]

Taking the natural log of equation 1 and substituting \( \sigma_s \) for \( 1/\sigma_s \) gives:

\[
\ln u_i = \ln (R_{HS} \sigma_s^{-2})_i - (R_{HS} \sigma_s^{-2})_{i+1} - \ln (\sigma_s)_i - (\sigma_s)_{i+1}
\]

Taking the partial differential of equation 3 with respect to \( \mu_i \) gives:

\[
\frac{\delta \ln u_i}{\delta \mu_i} = 1
\]

\[
= \frac{2 (R_{HS} \sigma_s^{-2})_i \delta (\sigma_s)_i / \delta u_i + (\sigma_s^2)_i \delta (R_{HS})_i / \delta u_i}{(R_{HS} \sigma_s^{-2})_i - (R_{HS} \sigma_s^{-2})_{i+1}} - 2 (R_{HS} \sigma_s^{-2})_{i+1} \delta (\sigma_s)_{i+1} / \delta u_i - (\sigma_s^2)_{i+1} \delta (R_{HS})_{i+1} / \delta u_i
\]

\[
= \frac{\delta (\sigma_s)_i / \delta \mu_i - \delta (\sigma_s)_{i+1} / \delta \mu_i}{(\sigma_s)_i - (\sigma_s)_{i+1}}
\]
Multiplying both sides by $\delta R_i$ and $1/(R_{HS} \sigma_s^2 i)/1/(R_{HS} \sigma_s^2 i)$ gives:

$$\frac{\delta R_i}{R_i} = \frac{2 \delta (\sigma_s^2 i)/(\sigma_s^2 i) + \delta (R_{HS} i)/(R_{HS} i) - 2(R_{HS} \sigma_s^2 i + 1)(\sigma_s^2 i)}{(1-(R_{HS} \sigma_s^2 i + 1)/(R_{HS} \sigma_s^2 i)}$$

$$- \delta (\sigma_s^2 i + 1)/(R_{HS} \sigma_s^2 i)$$

$$\frac{(\sigma_s^2 i) - (\sigma_s^2 i+1)}{(\sigma_s^2 i) - (\sigma_s^2 i+1)}$$

It would be correct to assume the worse case where $\delta (\sigma_s^2 i+1) = -\delta (\sigma_s^2 i)$ and $\delta (R_{HS} i + 1) = -\delta (R_{HS} i)$. However, by proceeding with this approach, gives an error of over 100% for the main part of the zinc electrical profiles. Due to the consistency of the results, this is not the case. It is therefore assumed that errors take the form $\delta (\sigma_s^2 i+1) = \delta (\sigma_s^2 i)$ and $\delta (R_{HS} i + 1) = \delta (R_{HS} i)$ indicating that the sign of the error from measurement $i$ to $i+1$ does not vary causing a doubling of the error if the sum or difference is taken.

This is effectively suggesting that:

$$\frac{\delta ((\sigma_s^2 i) - (\sigma_s^2 i+1))}{((\sigma_s^2 i) - (\sigma_s^2 i+1))} = 0$$

This is not the case, but it is small at less than $1\%$, and therefore it is reasonable to proceed with this approximation.

Therefore:

$$\delta (\sigma_s^2 i) = \delta (\sigma_s^2 i+1) \text{ and } \delta (R_{HS} i) = \delta (R_{HS} i+1)$$

$$\frac{\delta u_i}{u_i} = 2 \frac{\delta (\sigma_s^2 i)}{(\sigma_s^2 i)} \frac{(1 - \frac{(R_{HS} \sigma_s^2 i+1)}{(R_{HS} \sigma_s^2 i)})}{(\frac{1 - \frac{(\sigma_s^2 i)}{(R_{HS} \sigma_s^2 i)})}{(\frac{1 - \frac{(\sigma_s^2 i+1)}{(R_{HS} \sigma_s^2 i)})}} \frac{1 - \frac{(\sigma_s^2 i)}{(R_{HS} \sigma_s^2 i)})}{(\frac{1 - \frac{(\sigma_s^2 i+1)}{(R_{HS} \sigma_s^2 i)})}}$$

$$\cdots 6$$
To derive the error equation for \( n_i \), the natural log of equation 2 is taken and \( 1/\sigma \) substituted for \( \sigma_i \):

\[
\ln n_i = \ln \left( \left( \sigma_i \right)_i - \left( \sigma_i \right)_{i+1} \right) - \ln q - \ln d_i - \ln \mu_i \quad \ldots \quad 7
\]

Taking the partial differential of equation 7 with respect to \( n_i \) gives:

\[
\frac{\delta \ln n_i}{\delta n_i} = \frac{1}{n_i} - \frac{\delta (\sigma_i)_i/\delta n_i - \delta (\sigma_i)_{i+1}/\delta n_i}{(\sigma_i)_i - (\sigma_i)_{i+1}} - \frac{\delta d_i/\delta n_i - \delta \mu_i/\delta n_i}{d_i \mu_i} \quad \ldots \quad 8
\]

Assuming \( \delta (\sigma_i)_i = \delta (\sigma_i)_{i+1} \) it follows:

\[
\frac{\delta n_i}{n_i} = -\frac{\delta d_i}{d_i} - \frac{\delta \mu_i}{\mu_i} \quad \ldots \quad 9
\]

It should be noted that the errors for \( \mu_i \) and \( n_i \) are of opposite sign i.e. if a \( n_i \) value is too high due to an error \( \delta n_i/n_i \) then the corresponding \( \mu_i \) value will be lower than it should be.

\( (R_{HS} \sigma_i)_{i+1}/(R_{HS} \sigma_i)_i \) varied between 0.8 and 0.9 in most cases throughout the majority of the profiles for Zn and Se. So a value of 0.85 is taken for the error calculations. \( (\sigma_i)_{i+1}/(\sigma_i)_i \) was of the order of 0.8 but could drop to 0.55 in the tail of the electrical profile for Zn and Se. \( \delta (\sigma_i)_i/(\sigma_i)_i \) is taken to be \( \pm 1.5\% \). However, the real distinction between the errors for Zn and Se is in the value \( \delta (R_{HS})_i/(R_{HS})_i \), which could be maintained to \( \pm 1\% \) for Se and \( \pm 5.5\% \) for Zn. As the tail of the electrical profile was reached these values could be of the order \( \pm 5.5\% \) and \( \pm 10\% \) for Se and Zn respectively. Substituting these values into equation 6 and 9 gives the following results:

| \( \delta \mu_i/\mu_i \) for Se implanted profiles | \( \pm 3\% \), in tail \( \pm 8\% \) |
| " Zn " " " | \( \pm 8\% \), " \( \pm 14\% \) |
| \( \delta n_i/n_i \) " Se " " | \( \pm 8\% \), " \( \pm 13\% \) |
| " Zn " " | \( \pm 13\% \), " \( \pm 19\% \) |
APPENDIX 3

Equivalent Temperature-Time Profiles

The ramp-up and ramp-down sections of a temperature cycle are not vertical and the plateau temperature may not be constant. In long furnace anneals these effects tend to have little influence on diffusion effects and average out over the anneal cycle. In rapid thermal annealing, these effects must be taken into account.

The equivalent anneal cycle must have the same diffusion length \( (s) \) as the original anneal cycle.

\[
\begin{align*}
\text{peak temperature} & = T_{pk} \\
\text{equivalent temperature} & = T_E \\
\text{time} & = t
\end{align*}
\]

If the time of the anneal cycle is the same as the anneal time \((t)\) at the equivalent temperature, then it is possible to calculate the average of the exponential in the diffusion equation over the anneal cycle. Hence:

\[
s = \sqrt{Dt}
\]

\[
s^2 = D_o t \exp\left(\frac{-sE_d}{kT}\right)
\]

\[
D_o t \exp\left(\frac{-sE_d}{kT_E}\right) = D_o \int_0^t \exp\left(\frac{-sE_d}{kT}\right) dt
\]

\[
T_E = \left(-\frac{k}{E_d}\right) \ln\left(1 + \int_0^t \exp\left(\frac{-sE_d}{kT}\right) dt\right)^{-1}
\]

In some cases it is necessary to have an anneal time \((t_E)\) associated with the peak temperature of the anneal:—
If the temperature rise and fall rates are the same and linear between 1000 and 1300K then the variation of $t_E$ as a function of $E_d$ is shown in graph A.

$$t \exp\left(\frac{-eE_d}{kT_E}\right) = t_E \exp\left(\frac{-eE_d}{kT_{pk}}\right)$$

$$t_E = t \exp\left(\frac{eE_d}{k} \left(\frac{1}{T_{pk}} - \frac{1}{T_E}\right)\right)$$

where

$$\frac{1}{T_E} = \frac{k}{eE_d} \ln\left(\frac{1}{t} \int_0^t \exp\left(\frac{-eE_d}{kT}\right) \, dt\right)$$
Graph A: Variation of the equivalent time as a function of activation energy of diffusion for an anneal cycle between 1000 and 1300K.

Temperatures < 1000K taken into account.