

THE OBSERVATION OF DEFECTS IN GaAs
AND GaP

Thesis submitted for the degree of
Doctor of Philosophy

by

Brian David Chase

July 1970

Department of Metallurgy,
Imperial College of
Science and Technology,
University of London.

Abstract.

Defects in GaAs laser diodes and in GaP red electroluminescent lamps have been examined using a range of different techniques.

GaAs diodes were examined using the scanning electron microscope (SEM). Impurity segregation effects were observed in Te doped material using both charge collection and cathodoluminescence techniques. Slices cut from single crystal melt grown GaAs ingots have been examined using a Borrmann Anomalous Transmission X-ray camera specially constructed for the purpose. Precipitates and inclusions present in a Zn diffused surface have been studied using electron probe microanalysis and optical techniques.

Pulled GaP and epitaxial layers grown by both the vapour phase and liquid phase techniques have been examined using transmission electron microscopy. The defect content of liquid epitaxial layers was found to be very low by comparison with material grown by the other methods. Analyses have been made of stacking fault and dislocation complexes in these materials. An electrochemical technique for preparing thin specimens of GaP for electron microscopy has been developed. In some cases this resulted in the formation of extensive networks of corrosion tunnels within the specimens. GaP diodes have also been examined in the SEM. The spatial separation between the electrical p-n junction as measured by the charge collection technique and the junction detected in cathodoluminescence has been found to correlate with device efficiency. The influence on efficiency of minority carrier diffusion lengths (measured using the SEM) and parameters derived from the I-V characteristics of diodes has also been investigated.

	<u>CONTENTS</u>	page no.
Abstract		2
Chapter 1. <u>Introduction</u>		7
Chapter 2. <u>Review of Literature</u>		10
2.1 Recombination		10
2.1.1 Excitation		10
2.1.2 Radiative Processes		12
2.1.3 Non Radiative Processes		13
2.1.4 Recombination at a p-n Junction		15
2.2 Radiative Recombination and Absorption in GaAs.		18
2.2.1 Band Structure of GaAs		18
2.2.2 Absorption in GaAs		18
2.2.3 Cathodoluminescence in GaAs		20
2.2.4 Electroluminescence in GaAs		22
2.2.5 Laser Action		22
2.2.6 Fabrication of GaAs lasers		25
2.2.7 Threshold Current		26
2.2.8 Operating Characteristics		26
2.3 Radiative Recombination in GaP		28
2.3.1 Bound Exciton Transitions at Neutral Donors and Acceptors.		29
2.3.2 Bound Excitons at Isoelectronic Impurities		29
2.3.3 Absorption in GaP		31
2.3.4 GaP Electroluminescent Diodes		31
2.4 Material Properties of GaAs and GaP		35
2.4.1 Crystal Structure		35
2.4.2 Dislocations in the Sphalerite Structure		36
2.4.3 Misfit Dislocations		39
2.4.4 Growth of GaAs		40
2.4.5 Growth of GaP		43

2.5	The Behaviour of Impurities in GaAs and GaP	45
2.5.1	Zinc Diffusion in GaAs	45
2.5.2	The Behaviour of Donors in GaAs	46
2.5.3	Impurities in GaP	47
2.5.4	Phase Changes	48
2.6	The Observation of Defects	49
2.6.1	Etching	50
2.6.2	Infra-red and Visible Light Transmission	50
2.6.3	X-ray Topography of Single Crystals	51
2.6.4	Scanning Electron Microscopy	55
2.6.5	Transmission Electron Microscopy	59
Chapter 3.	<u>Experimental</u>	62
3.1	Preparation of GaAs	62
3.2	Preparation of GaP	63
3.3	Etching and Polishing	64
3.4	X-ray Topography	64
3.4.1	Construction of the camera	64
3.4.2	Operation	67
3.4.3	X-ray geometry in the camera	68
3.4.4	Resolution	70
3.5	Scanning Electron Beam Techniques	71
3.5.1	The Display of Surface Detail	71
3.5.2	The Charge Collection Mode	73
3.5.3	The Cathodoluminescent Mode	74
3.5.4	Additional Features	77
3.5.5	The mounting of Specimens	78
3.6	Transmission Electron Microscopy	80
3.6.1	The Thinning Apparatus	80
3.6.2	The Thinning Process	82
3.6.3	Mounting Specimens for Thinning	84

Chapter 4. <u>Experimental Results</u>	87
4.1 X-ray Topography of GaAs	87
4.1.1 Diffraction Vectors	87
4.1.2 White Radiation	89
4.1.3 Topographs	92
4.2 Inclusion in Zn Diffused GaAs	94
4.3 The Examination of GaAs Laser Diodes in the Electron Probe.	97
4.3.1 Charge Collection	97
4.3.2 Te Doped Material	102
4.3.3 Comparison of Charge Collection and Cathodoluminescence Micrographs	107
4.4 Scanning Electron Microscopy of GaP	108
4.4.1 The Examination of Pulled Material in the Electron Probe.	108
4.4.2 The Examination of GaP Diodes	110
4.4.3 Line Scan Observations	114
4.4.4 I-V Characteristics of GaP Diodes	118
4.5 Transmission Electron Microscopy of GaP	119
4.5.1 GaP Grown by Vapour Phase Epitaxy	119
4.5.2 Pulled Material	136
4.5.3 GaP Grown by Liquid Phase Epitaxy	140
4.5.4 Electrochemical Polishing	142
Chapter 5. <u>Discussion of Results</u>	154
5.1 X-ray Topography	154
5.2 Inclusions in Zn diffused GaAs	157
5.3 Scanning Electron Microscopy	163
5.3.1 Charge Collection in GaAs Laser Diodes	163
5.3.2 Charge Collection in GaP Diodes	168
5.3.3 The Detection of Cathodoluminescence	170
5.3.4 Cathodoluminescence in Te Doped GaAs	172

5.3.5	Cathodoluminescence in GaP	175
5.4	Transmission Electron Microscopy of GaP	182
5.4.1	Thinning	182
5.4.2	Defects in Vapour Phase Grown GaP	185
5.4.3	Defects in Pulled and Liquid Epitaxial GaP	187
5.4.4	Electrochemical Polishing of GaP	191
Chapter 6. Summary and Conclusions.		194
List of References		198
Acknowledgements		204

CHAPTER 1.

Introduction

The development of III-V compounds has proceeded rapidly since the discovery of their semiconducting properties first predicted by Welker (1952). In particular great interest has been shown in those compounds which exhibit radiative recombination and foremost among these are GaAs and GaP. The radiative properties of these two compounds are however fundamentally different. GaAs is a direct band gap semiconductor which exhibits highly efficient band to band radiative recombination in the infra-red ($\sim 9000 \text{ \AA}$) at room temperature. GaAs electroluminescent devices are thus suitable for use as sources of infra-red but by far the most important development has been the GaAs laser. The development of the GaAs laser and the theory behind its operation are reviewed in chapter 2.

A coherent laser beam at optical wavelengths is, in principle, capable of being modulated at extremely high frequencies and therefore of carrying large quantities of information. In the atmosphere, absorption and scattering would limit the use to relatively short range communication links. However, it seems likely that this range will be extended by using low-loss fibre optic systems currently under development to couple to GaAs lasers with intermediate GaAs lasers as amplifiers. GaAs lasers have been used to carry communications in outer space where their small size and weight compared to other types of laser is an advantage. They are also used by the U.S. Army as rangefinders accurate over distances up to one mile and are also used as low level altimeters in aircraft.

GaP, unlike GaAs, has an indirect band gap and this means that direct band-to-band transitions have a very low probability. Thus GaP by itself cannot be used to make lasers. However, by combining it

with GaAs in the form $\text{GaAs}_x\text{P}_{1-x}$ the band structure is such that lasers can be produced emitting visible radiation with a wavelength near $6000 \text{ \AA}$ (Holonyak and Bevacqua 1962). In GaP itself useful visible radiation in the red and green portions of the spectrum can be produced by recombination via impurity levels and exciton states within the band gap. These recombination processes and the development of GaP lamps are described in chapter 2. The useful life of a GaP electroluminescent diode is potentially much greater than that of conventional tungsten lamps and gas discharge tubes. This makes it particularly suitable for applications where a high reliability factor is required. Indicator lights in aircraft present a typical example where failure could have serious consequences. Another use would be in the lighting of push button telephone dials where periodic replacement of conventional lights is uneconomical.

The fundamentals of GaAs and GaP device operation are now well understood and current research is concentrated on increasing the electroluminescent quantum efficiency and on increasing the device yield (i.e. the percentage of devices with acceptable performance). Essentially this is a materials problem and many improvements in purification and fabrication techniques have been made. However, crystal defects and precipitates are generally still present and can have deleterious effects on the efficiency and spatial distribution of radiation from both lamps and lasers. The object of the present research was to develop a set of observation techniques to determine the precise nature of these defects and their relation to device performance.

Initially the project was concerned solely with GaAs lasers. These were examined in a specially adapted electron probe microanalyser using a number of different operational modes and a report on this work has already been published (Holt and Chase 1968). In addition

to this, defects in diffused and undiffused slices were examined using optical and X-ray techniques. Concurrently with this however, interest in GaP lamps was boosted by a report of devices with external quantum efficiencies approaching 2% (Logan et al 1967). Research at S.E.R.L. Baldock (the sponsors of this project) was turned to GaP and consequently the emphasis of this research was also changed.

Little was known about the defect structures to be found in GaP and in particular no systematic investigation had been made using the transmission electron microscope. In the present work a variety of diode materials grown by different methods and with different dopants were examined using this instrument. In addition, scanning electron microscope techniques similar to those used for GaAs were employed to examine GaP diodes for gross defects and other features closely related to device performance.

CHAPTER 2

THEORY AND REVIEW.

2.1. Recombination.

One of the objects of this research was the correlation of defects with variations in luminescent efficiency. In this section the general aspects of recombination processes will be discussed.

2.1.1. Excitation.

The production of light from a semiconductor occurs only as a result of initial stimulation. This may result from an incident beam of light (photoluminescence) or of electrons (cathodoluminescence) or by the application of an electric field (electroluminescence). An incoming pulse of energy has a statistical chance of exciting an electron from a lower to a higher energy state in the band structure so forming an electron hole pair or of exciting the electron into an excited state of an impurity.

Donor and acceptor impurities present in a semiconductor may be ionised to give up electrons and holes respectively. These impurities are then characterised by levels in the band structure separated from the respective conduction or valence band by the ionisation energy. For low dopant concentration of one type at low (extrinsic) temperatures the Fermi level is situated between the impurity level and its respective band. As the doping is increased the Fermi level can move into the band, at which point the material is said to be degenerate. Also the impurity level splits according to the Pauli Exclusion Principle and eventually merges with the band causing band broadening and a reduction of the energy gap. In compensated material both electrons and holes are produced by the ionisation of impurities. In this case band broadening will occur at high enough doping levels and the position of the Fermi level will be dependent on the majority carrier density.

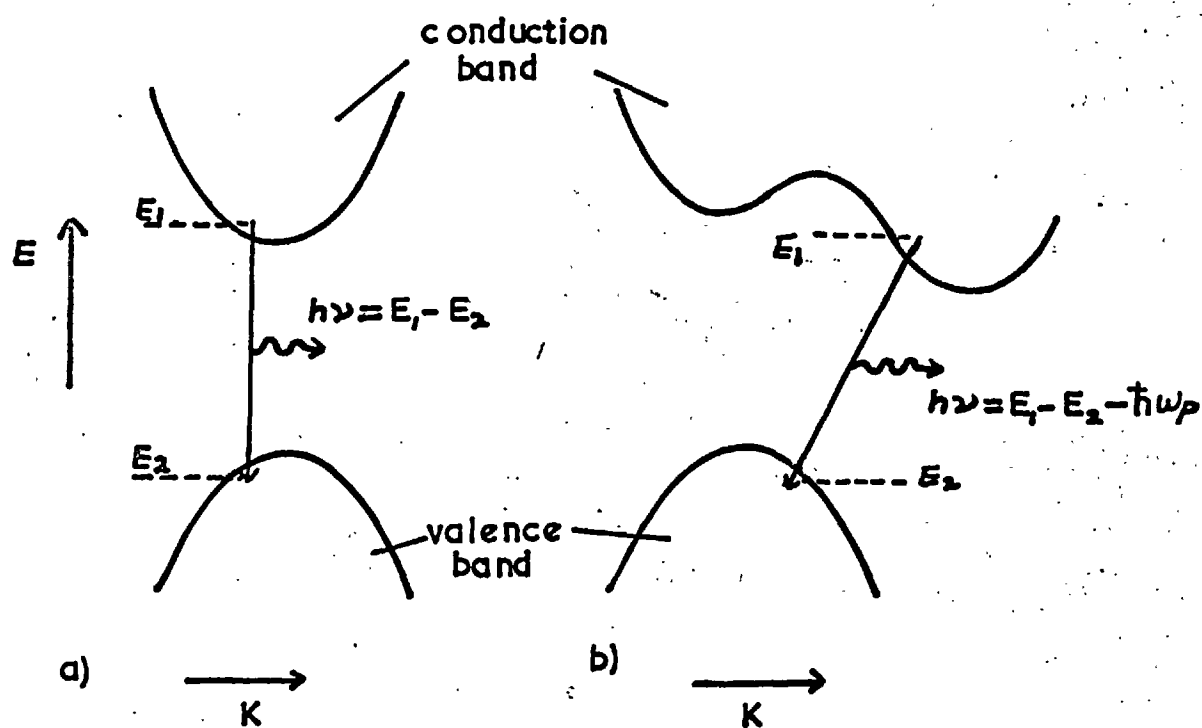


Figure 2.1 Energy-momentum diagram illustrating the differences in band to band recombination in direct and indirect gap semiconductors.
 a) direct transitions with no phonon participation.
 b) Indirect transitions requiring phonon participation to conserve momentum.

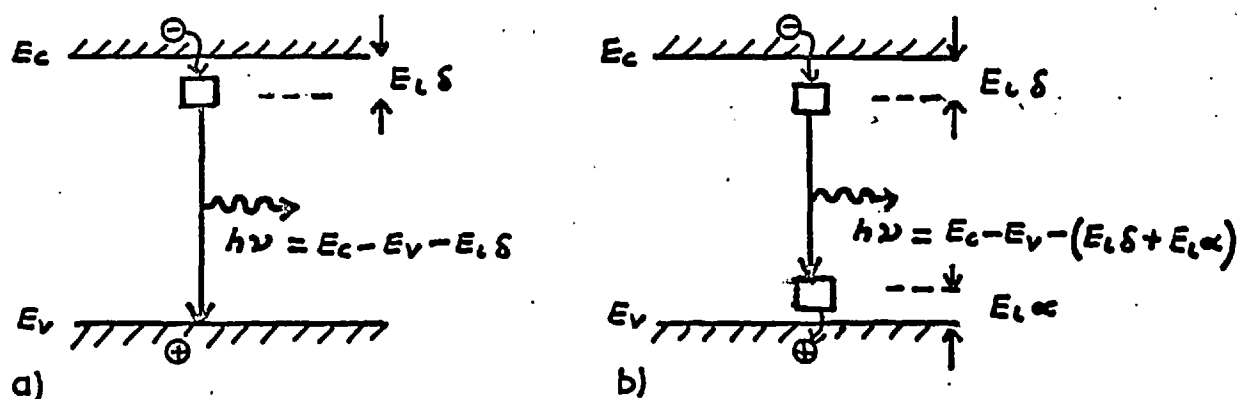


Figure 2.2 Energy band diagrams illustrating radiative recombination process a) recombination via an impurity state or recombination centre. b) a donor-acceptor pair transition.

2.1.2. Radiative Processes.

Recombination of an electron hole pair may occur radiatively with the production of a photon, non radiatively with the production of thermal energy or by a combination of both. The simplest case to consider is the direct recombination of an electron and hole by collision. This is illustrated by the energy momentum diagram in Figure 2.1. Here the momentum of the electron is given by $\hbar \mathbf{k}$ where $\mathbf{k}$ is the wave vector of the electron. The figure shows a section of the three dimensional energy diagram taken along one principal symmetry axis of the crystal. Semiconductors are classified as direct or indirect gap according to whether or not the absolute minimum of the conduction band occurs at the same wave vector as the absolute maximum of the valence band. Figure 2.1a illustrates recombination in a direct gap material such as GaAs while Figure 2.1b refers to an indirect gap material such as GaP. In the case of the direct gap material both energy and momentum are conserved in recombination and the photon energy is given by:-

$$h\nu = E_1 - E_2.$$

In the indirect gap material momentum must be conserved in recombination by phonon participation:-

$$h\nu = E_1 - E_2 - \hbar\omega_p$$

Where $\hbar\omega_p$ is the energy involved in the production of the phonon.

Due to this phonon participation the radiative lifetime is relatively long (about 10^{-5} sec) and this effectively gives the other non-radiative processes time to operate thus reducing the quantum efficiency of the emission (Burns & Nathan 1964)

Radiative recombination may also occur via an impurity state or recombination centre (Figure 2.2a). In this case a free carrier diffuses or drifts till it encounters an impurity centre which can receive it. It then falls into this vacant state and the energy due to the momentum change is dissipated as heat. The trapped electron

is stationary and this statistically increases the probability of recombination with a hole. Once this has occurred the impurity centre is free to take part in a repetition of the process. Similarly the trapping of a hole at an acceptor followed by recombination with an electron may occur.

Because an electron and a hole have an attractive coulombic interaction, they together may form stable bound states called exciton states. These states are loosely bound to atoms and several atoms can be enclosed by the orbits of the electrons within the states. The energy of these associated electron - hole pairs may be transferred through a crystal by means of diffusion and the energy stored in an exciton can be given up in various ways both radiative and non radiative.

2.1.3. Non radiative Processes.

Three main processes can occur leading to non radiative recombination. Decay leading to the emission of a series of phonons can occur if a ladder of exciton states exists between the conduction and valence bands. It is also possible in this case that large radius orbits of impurity atoms may supplement the exciton states.

Auger processes involving the transfer of recombination energy to a passing free electron can occur. The energised electron can then decay by emitting a succession of phonons. Surface recombination is another important process. In this case the recombination properties are influenced by the excess of free states within the forbidden energy gap which are associated with a surface. The recombination process is similar in nature to that occurring in the bulk material but the transitions are mostly non radiative.

The relative probabilities of the various forms of recombination have been calculated by Hall (1959) for Ge and for a similar material with a direct gap. The diagram (Figure 2.3) indicates that in direct

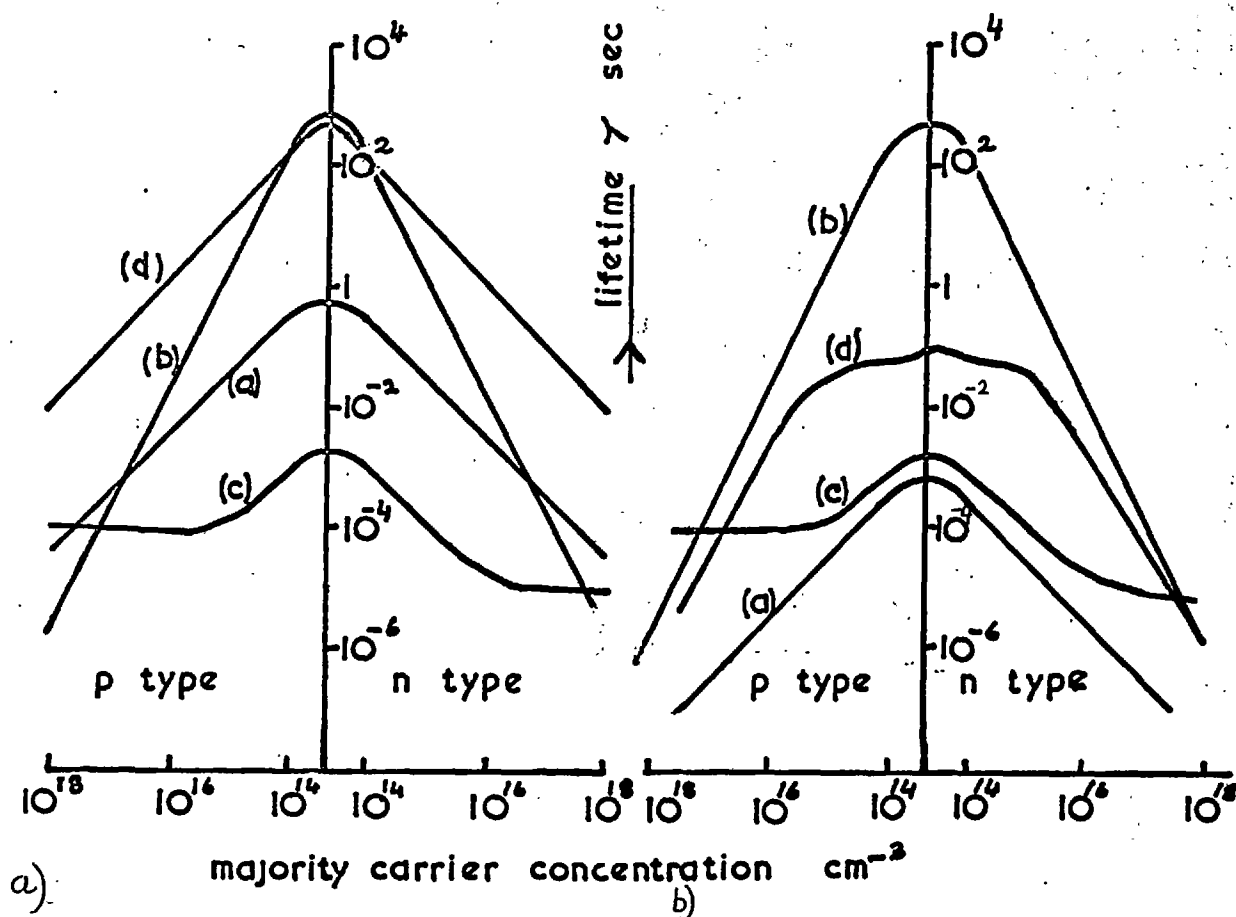


Figure 2.3 a) Lifetimes predicted for recombination processes in Ge at 300°K.
 b) Similar data for a direct gap material resembling Ge at 300°K.
 The processes considered are a) radiative, b) intrinsic Auger
 c) Multiphonon via impurities and d) extrinsic Auger (via
 impurities).

gap materials, radiative recombination is likely to be the dominant process, provided the concentration of recombination centres is as small as in Ge. For similar indirect gap materials, radiative recombination is less favourable than multiphonon recombination. The Auger process is very temperature dependent so for greatest radiative efficiency the temperature must be as low as possible. The relative probabilities of recombination processes in GaAs have also been calculated (Kyser and Wittry 1966).

2.1.4. Recombination at a p - n junction.

Figure 2.4a shows an energy diagram of a p - n junction with degenerate doping on both sides at zero applied voltage. The Fermi levels on either side are at the same energy and there is no net current flow. If a forward bias is applied to raise the potential of the n side relative to the p side then electrons can more easily diffuse over the top of the barrier from n to p where they can recombine with holes in the valence band (Figure 2.4b). It is also easier for holes to diffuse to the n side where they recombine with electrons. A p - n junction can be also reversed biased as shown in Figure 2.4c. If the junction is sufficiently narrow, current flow then occurs by tunnelling and subsequent avalanche breakdown. The net result is to inject high energy majority carriers into each side of the junction. These majority carriers have energies greatly exceeding the equilibrium energy and decay can occur to the thermal mean by a relaxation process. The spectra produced by such a mechanism are very different in nature to those produced by minority carrier effects in the case of forward biasing and are highly dependent on the position of the absorption edge.

Forward biasing is the more usual method for exciting radiative recombination. With low band gap semi-conductors, recombination of the carriers ~~generally occurs~~ some distance away from the depletion layer,

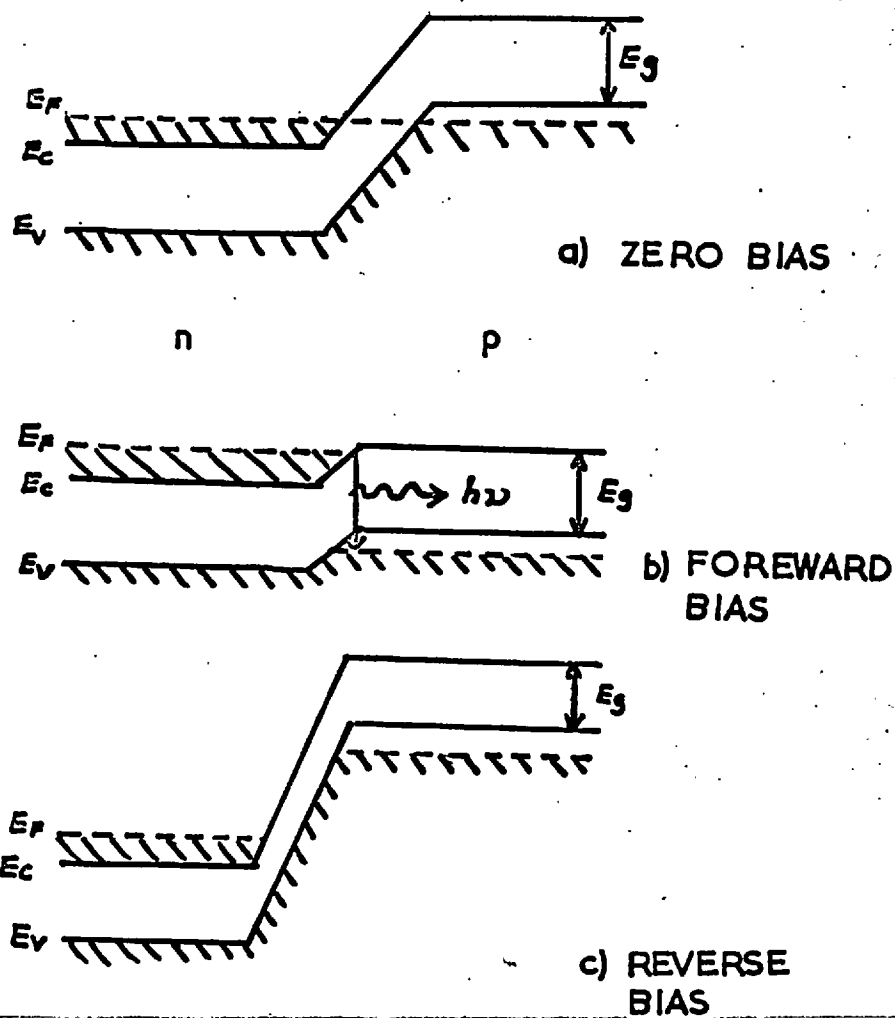


Figure 2.4 Energy diagram of a p-n junction for varying bias conditions.

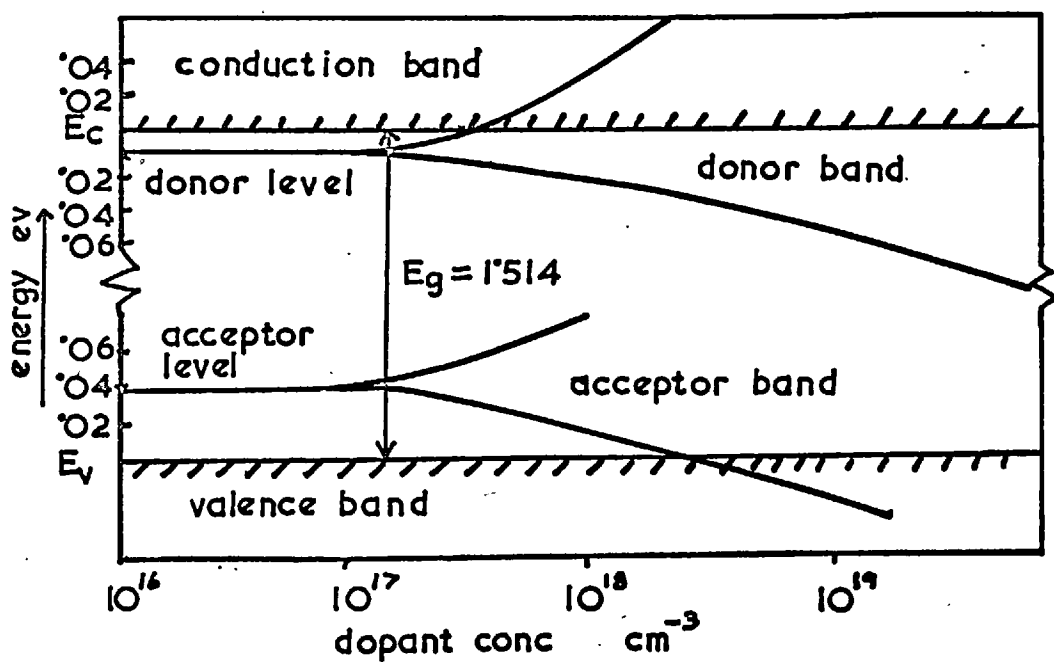


Figure 2.5 Schematic representation of energy bands in Te doped GaAs (after Lucovsky 1964).

but, with high band gaps, recombination can occur in the space charge layer itself. This has been treated theoretically by Sah, Noyce and Shockley (1957) who derived expressions to describe the electrical characteristics of diodes in which carrier recombination within the space charge region was important. They showed that the simple p - n junction theory (Shockley 1949) does not apply and that the I - V characteristics are best described by an expression of the form:-

$$I = I_0 \exp eV / \beta kT$$

where e is the electronic charge and β is a constant. For diodes with recombination occurring as a result of diffusion outside the space charge region $\beta = 1$. Whereas for diodes with space charge recombination predominating $\beta = 2$.

When excess carriers are present the distribution of electrons among the conduction band states can be represented by a function:-

$$f_c(E) = (1 + \exp (E - E_n)/kT)^{-1}$$

E_n is called the quasi fermi level for electrons. A similar quasi fermi level E_p exists for holes in the valence band. Using this expression the probabilities of absorption or emission of a quantum of radiation can be calculated. The condition for emission to exceed absorption, and hence for amplification by stimulated emission to be possible, is expressed for a direct gap material as:-

$$E_n - E_p > h\nu$$

Where $h\nu$ is the energy of the emitted radiation. For a GaAs laser the quasi fermi levels can be related to the current density across the junction and so the threshold current for laser action can be derived. A number of treatments of this problem have been reviewed by Thornton (1967 Chapter 13).

Keyes (1963) pointed out that a condition is imposed on the doping levels in p - n junctions necessary for laser action. Since $E_n - E_p$

cannot be greater than the built in voltage, it follows that the built in voltage must be greater than $h\nu$. This means that in practice both the n and p type material must be degenerate so that the quasi fermi level separation is greater than the band gap as required. The high doping levels needed to insure this, mean that defects and the associated segregation and migration of impurities are more common in lasers than in less heavily doped diodes and thus more likely to disrupt the uniformity of the material.

2.2. Radiative Recombination and Absorption in GaAs.

2.2.1. Band Structure of GaAs.

Extensive research has been carried out into the emission and absorption spectra of GaAs. As a result important information on the band structure has been obtained. The band structure as a function of doping for $k = 0$ is shown in Figure 2.5.

In lightly doped GaAs crystals, sharp spectral lines observed in luminescence and absorption can be ascribed to accepted transitions involving excitons and donor acceptor pairs. In heavily doped crystals, broad impurity band transitions occur. Due to the large Bohr radii of the impurity atoms, mutual interactions occur at low donor and acceptor concentrations, 8×10^{16} atoms/cm³ for donors (Broom et al 1958), resulting in the formation of impurity bands. At modest impurity concentrations (5×10^{17} atoms/cm³ for donors) the impurity bands broaden and merge with the conduction or valence bands. Due to the low effective masses in GaAs, particularly in the conduction band, the density of states is small and the material becomes degenerate at relatively low free carrier concentrations.

2.2.2. Absorption in GaAs.

Absorption in GaAs is highly dependent on doping. For intrinsic

GaAs the absorption and spontaneous emission spectra can be calculated. Here the absorption coefficient varies as the square root of the difference between the photon energy and the energy gap. This results from the variations in the density of states with energy (Elliott 1957). Sturge (1962) showed that the measured absorption edge agreed with the theory of Elliott only when an allowance was made for free exciton interactions.

At high doping levels the theory becomes more complex. When the impurity levels merge with the conduction or valence bands and the levels broaden, the result is an apparent shrinkage of the band gap and this tends to shift the absorption edge to lower energies. However, a compensating shift to higher energies - the Burstein shift - also occurs as the material becomes degenerate (Burstein 1954) due to the filling of states in one of the bands. In contrast to this, radiative recombination has a different form to the absorption because it is energetically favourable for carriers well below the Fermi level to be used. Thus the luminescence due to degenerate and non degenerate bands is similar. However band broadening and gap shrinkage act to shift both the absorption edge and the recombination peak to lower energies.

The behaviour of the absorption edge in GaAs as a function of doping has been investigated experimentally. Hill (1964) using dopants Te, Se, Zn and Cd studied the absorption edge at 77°K and 300°K. At 77°K with low donor concentration a rough fit with the Burstein shift was observed, but at higher doping levels and at room temperature the gap shrinkage predominated.

Turner and Reese (1964) investigated laser type GaAs and found Burstein shift agreement in both n-type and heavily doped p-type material. Absorption data with the Burstein shift predominant has also been

presented by Kudman and Vieland (1963) and Braunstein et al (1963).

2.2.3. Cathodoluminescence in GaAs.

Cathodoluminescence in GaAs was first studied in 1964. In general, electron beams of energy less than 100 keV were used to avoid radiation damage and the principal objective was to pump GaAs lasers to threshold. Using low energy 15 keV electrons, Cusano (1964) examined the emission spectra as a function of doping. He found that the broad emission peak at 1.3 eV which showed sublinear dependence on current density could be swamped at moderate doping by using a sufficiently high excitation density. He presented data on peak position, half width and efficiency variations with doping, Figure 2.6. The curves had similar shapes at 77° and 300°K. The lower efficiency at 300°K when the doping level was less than 5×10^{18} atoms/cm³ was attributed to the decrease in populated donors through which minority holes recombine. A reduction in efficiency was observed at doping levels near 10^{19} atoms/cm³ at either temperature. He attributed this to non radiative recombination at defects associated with the precipitation of impurities.

Wittry and Kyser (1964) used a small plane grating monochromator to examine the radiation emitted by GaAs in an electron probe microanalyser. Their results however were negative as they failed to resolve any spectral peaks characteristic of impurities.

Casey and Kaiser (1967) examined GaAs with Te doping between 0.2×10^{18} and 8×10^{18} atoms cm⁻³. From measurements of the spectral half widths they were able to determine the free electron concentration to within 15% at 5×10^{17} atoms cm⁻³ and 7% at 5×10^{18} atoms cm⁻³. Below 5×10^{17} atoms cm⁻³ the spectral shape remained constant.

Electron probe microanalysers and scanning electron microscopes can also be used to build up a cathodoluminescent map of a specimen.

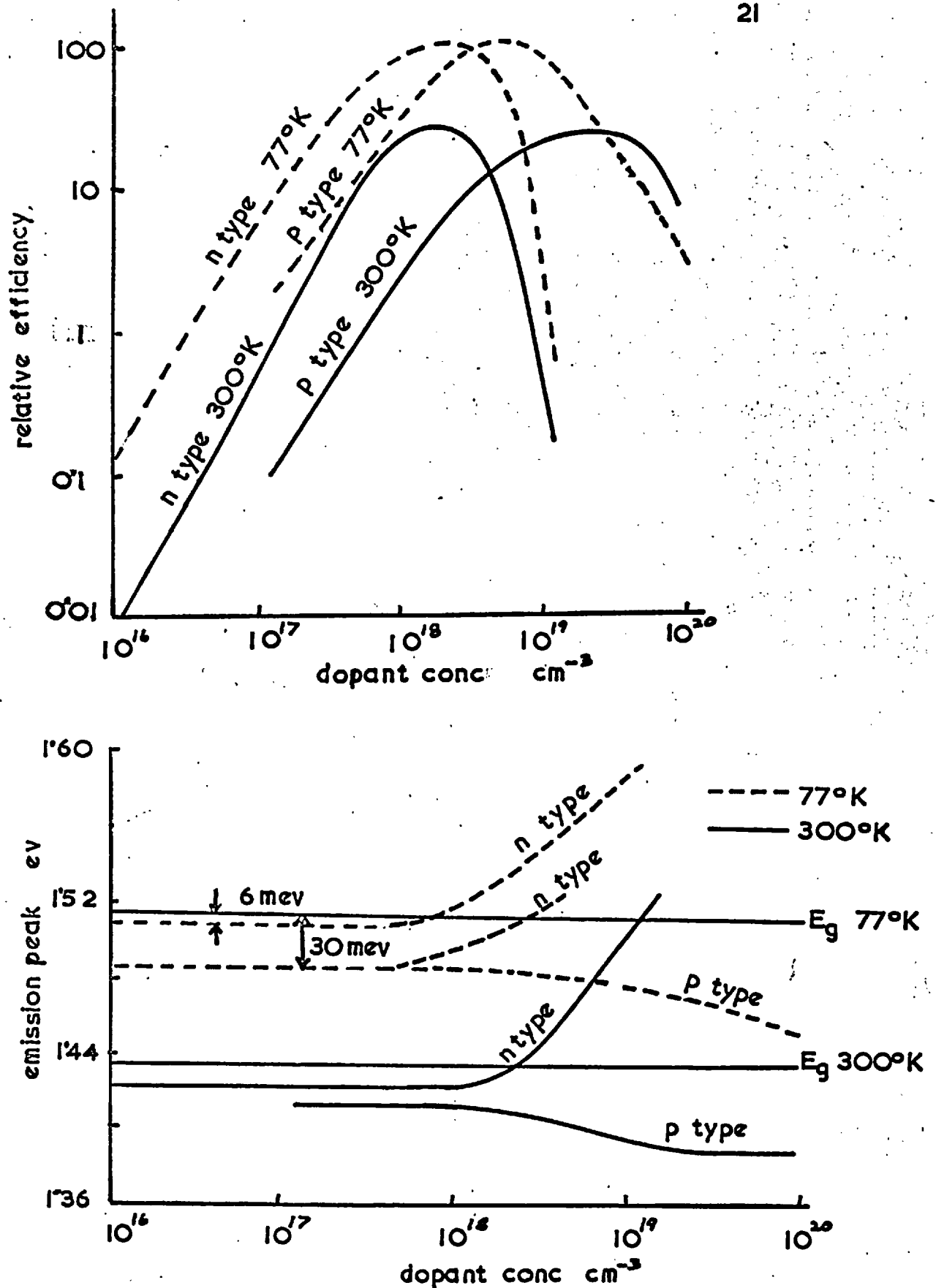


Figure 2.6 a) Dependence of relative efficiency of GaAs band edge emission on doping for 77°K and 300°K (After Cusano 1964).
 b) Dependence of position of the spectral peak of GaAs band edge emission on doping for 77°K and 300°K (after Cusano 1964).

This technique will be discussed in Section 2.5.4.

2.2.4. Electroluminescence in GaAs.

In general, electroluminescent spectra are similar to those observed in photoluminescence and cathodoluminescence. Minor differences arise however due to the variations in compensation across the junction and the non-equilibrium state induced by biasing. Recombination may also occur as a result of tunnelling, in which case the spectral distribution varies considerably with bias.

It has been established that in heavily doped materials the radiative recombination occurs on the p side of the junction (Lasher and Stern 1964, Hall 1963). Also the electroluminescent peak was found at about the same wavelength as that from similarly doped material in photoluminescence. Lasher and Stern explained this theoretically using a band filling model. On both sides of the junction, donors form an impurity band which merges with the conduction band. Injection of electrons from the n side can be achieved by a process of tunnelling at constant energy between states in the impurity band. On the p side recombination then occurs probably via a hole trapped on an acceptor which may be smeared into an impurity band.

The main aspects of electroluminescence in GaAs have been treated in reviews by Gershenzon (1966) Burns and Nathan (1964) and also by Thornton (1967).

2.2.5. Laser Action.

Laser action can only take place in materials with a suitable band structure. In a laser with four levels (Figure 2.7) electrons are initially excited from the ground state to level 3. From here they decay to level 2 with the emission of photons or phonons. In level 2 the lifetime must be long enough to enable a population

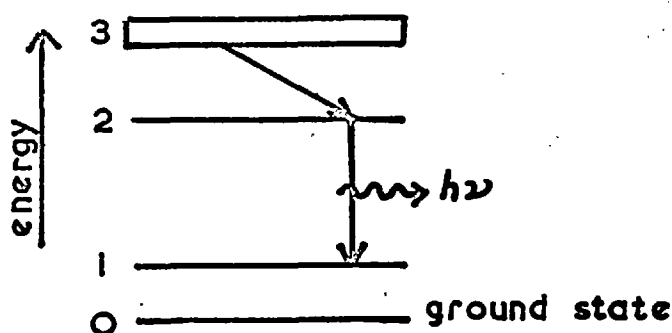


Figure 2.7 A one dimensional diagram illustrating the energy levels in a four level laser.

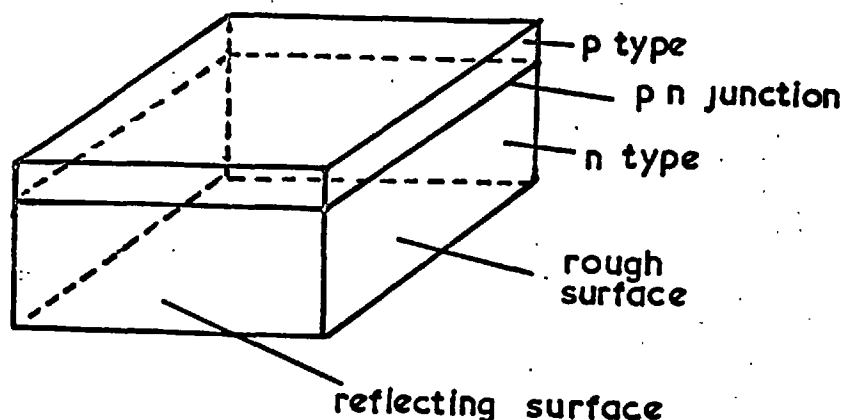


Figure 2.8 The construction of the reflecting (Fabry Perot) cavity of a GaAs laser diode.

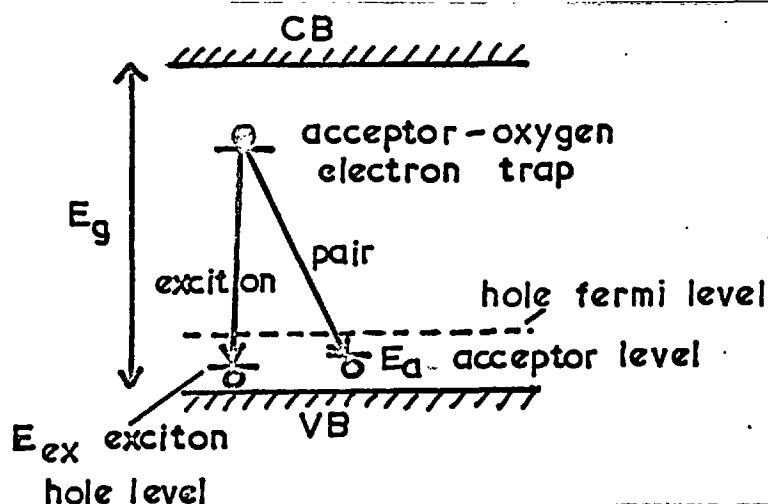


Figure 2.9 The suggested recombination mechanism in Zn-O or Zn-O doped GaP (Cuthbert et al 1968). Electrons are trapped at Cd-O or Zn-O complexes. These -ve charged complexes (E_{ex}) can then attract a hole and recombination can occur giving rise to the bound exciton band. Alternatively the trapped electrons can recombine with holes at distant acceptor atoms. At room temperature the emission is almost all excitonic.

inversion to be established. The rate of pumping must be adequate to maintain this inversion so that there are more filled states in level 2 than level 1. Level 1 in a three level laser is the same as Level 0, the ground state.

Electrons in level 2 initially decay at random to level 1 with the emission of photons. These photons however can stimulate other electrons in level 2 to fall to level 1 with the emission of other photons identical in phase, direction and energy to the originals. To enable a continuous supply of coherent radiation to be produced, the lasing material is enclosed in a cavity with accurately parallel reflecting surfaces at either end. Eventually a photon will be produced which moves in a direction perpendicular to the mirror faces. If the cavity length is equal to an integral number of half wavelengths a state of resonance will result. If on average each photon produced stimulates at least one more photon before leaving the system, and the pumping rate is sufficient to overcome absorption, laser action will commence. The laser beam emerges through the reflecting surfaces and this means that the reflection coefficient of at least one of the surfaces must be less than unity.

The pumping of a conventional gas or solid state laser is achieved by external electromagnetic stimulation. In contrast, the semiconductor laser can be excited simply by passing a current across a p - n junction. Following results from recombination radiation in Si, Haynes (1960) showed that states near the top of the valence band would correspond to level 1 and states near the bottom of the conduction band to level 2. Level 3, less precisely defined, would correspond to states at a higher level in the conduction band.

Observations of stimulated emission in forward biased GaAs were first reported in the latter half of 1962 by Nathan et al (1962),

Hall et al (1962), Quist et al (1962) and Broom et al (1963). The diodes were operated at 77°K using short current pulses. In 1963 stimulated emission in GaAs was reported at room temperature (Burns and Nathan 1963). Progress in the field has proceeded rapidly with considerable effort going into improving the materials and the fabrication techniques to get better performance and higher device yields.

2.2.6. Fabrication of GaAs Lasers.

The p - n junction in a GaAs laser can be conveniently formed by the diffusion of Zn into an n-type substrate with donor concentration in the range 10^{17} to $6 \times 10^{18} \text{ cm}^{-3}$. Typically the Zn concentration rises rapidly away from the junction to about 10^{20} cm^{-3} in a distance of 5μ and then slowly increases to about $2 \times 10^{20} \text{ cm}^{-3}$ at surface. The junction depth varies with diffusion time and temperature between 2 and 100μ . For optimum efficiency it is essential that the p - n junction should be flat. Defects in the substrate crystal can give rise to a non planar diffusion front (Pilkahn & Rupprecht 1964) and are thus detrimental to device performance. The preferred method of diode formation is now by liquid epitaxy which avoids this problem and is found to give diodes with lower threshold current densities (Pilkahn & Rupprecht 1967).

The reflecting ends of the resonant cavity are made perpendicular to the junction by cleaving or polishing. If the original slice is of $\{100\}$ orientation the $\{110\}$ cleavage planes can be used. The other pair of sides perpendicular to the junction are given a rough finish to eliminate feedback. The construction of a diode is illustrated in Figure 2.8. Ohmic contacts are made to the n and p sides of the junction by alloying. These contacts are made massive to act as efficient heat sinks (see also section 3.1).

2.2.7. Threshold Current.

The crystal parameters which control the threshold current density have received close attention. Dousmanis et al (1964) found the threshold current to be a factor of three lower in solution regrown laser junctions than in diffused diodes. This was probably due to a reduction in defect concentration by virtue of the lower growth temperature. Photoluminescence experiments of Williams and Blacknall (1967) indicated a reduction in deep level transitions in solution grown GaAs compared to melt grown material. It is thus probable that large concentrations of lattice defects exist in melt grown material which largely dominate the recombination process. It is possible that these defects are in the form of vacancies or associated complexes as described in Section 2.5.2.

Carlson (1967) found that the threshold for diffused diodes could be reduced by up to 40% by annealing at 900°C with an As overpressure. The physical effect of the anneal was to shift the junction deeper by 6μ and to reduce the Zn concentration near the junction. Etching studies showed the density of diffusion induced dislocations to be much reduced. Carlson suggested that traps initially clustered at the dislocations may not move with the junction during the annealing process. Later work (Hill & Holt 1968, Kressel et al 1969) indicates that non-uniform doping in the form of growth striations and precipitation is more important than dislocations as an influence on device performance.

2.2.8. Operating Characteristics.

Below threshold the majority of the light is internally reflected and absorbed in the inactive regions of the diode. Even above threshold external quantum efficiencies are less than 50% and a good deal of energy is dissipated non-radiatively. Efficient cooling is

essential and is normally achieved by placing the laser in contact with a large metal heat sink cooled by a cryogenic liquid bath. In order to prevent frosting of the mirror surfaces the laser must be kept under vacuum. By pulsing the supply current it is possible to obtain very high current values yet keep the overall power consumption to a minimum.

The emission spectrum of a GaAs laser is of a multimode nature corresponding to the resonant cavity (Burns & Nathan 1964). For typical laser lengths these modes are separated by $1 - 2\lambda^0$. Also of interest is the spatial distribution of the emitted radiation at the mirror faces. The stimulated emission as with electroluminescence originates on the p side of the junction. In most cases however, the distribution along the junction is not uniform but is concentrated in small areas. At threshold only one of these spots usually appears. As the current is increased this spot broadens and further spots appear until the entire junction is illuminated. Broom et al (1963) found that the patterns were similar when viewed from either end of the laser. This indicated that the spots were actually filaments of light passing right through the diode perpendicular to the mirror faces. This filamentary behaviour is still not fully understood. Abrahams and Buicocchi (1965), using a dislocation etch they had developed, found reasonable correlation between filaments and certain dislocations which gave rise to large etch pits on the $\{110\}$ mirror faces. By polishing down to the junction from the p side and etching they found the dislocations concerned were heavily decorated and part of a regular misfit array. They suggested that the decorating species might be Zn by reason of its high diffusivity.

Hill and Holt (1968), examined diffused laser diodes containing growth striations lying normal to the mirror faces and which intersected the junction at roughly 60^0 . Filamentary action was observed

at positions corresponding to regions in the striations with low infrared absorption coefficient. Subsequent etching of the junction plane showed up both the stria and a misfit dislocation network. In diodes grown by liquid epitaxy Kressel et al (1969), using similar methods to Hill & Holt, found that a low dislocation density was not a sufficient condition for satisfactory laser performance. They found that considerable degradation in laser performance resulted from non-uniform impurity distributions either in the form of growth striations or precipitation.

Jönscher and Boyle (1966) found that the far field pattern indicated some degree of coherence between filaments probably due to optical coupling effects in the junction plane. They associated the formation of filaments with changes in the free carrier concentration due to current density fluctuations. Such changes could alter the refractive index locally and stimulate filament formation by acting as a waveguide to prevent the filament spreading.

The field of semiconductor lasers has been reviewed by Burns & Nathan (1964) Nathan (1966) and more recently by Thornton (1967).

2.3. Radiative Recombination in GaP.

The band gap of GaP is 2.2 eV at room temperature. It is this that makes GaP such an important material as it allows the emission of light in the visible portion of the spectrum. The band gap is indirect with the conduction band minimum along the $\langle 100 \rangle$ k axis and the valence band maximum at the centre of the axis. This makes radiative recombination in GaP much less efficient than in a direct gap material such as GaAs. However, the best efficiencies obtained with GaP ($\sim 3\%$) are still high compared with other materials which produce visible electroluminescence. Intrinsic band to band transitions have not been identified in the low temperature luminescence of

any of the indirect gap III - V compounds. They may however, make a small ~~small~~ contribution to the room temperature luminescence recorded from some GaP diodes with exceptionally high efficiency for near band gap transitions (Dean et al 1967). The principal recombination mechanisms involve impurities and will be discussed individually.

2.3.1. Bound Exciton Transitions at Neutral Donors and Acceptors.

As discovered in Si (Haynes 1960) no - phonon recombinations of excitons bound to impurity centres are possible since momentum can be conserved through coupling to the impurity. In sulphur doped GaP, comparison with absorption spectra shows that at 4.2°K the strong line near 2.31 eV, the 'C' line, is due to no - phonon transitions (Thomas et al 1963). Such transitions also result in a spectrum of lines to lower energies. S, Te and Se all form neutral donor complexes at the phosphorus site in GaP. Comparison of the spectra from material with these different dopants shows that the positions of the low energy lines vary according to the donor ionisation energy. No corresponding spectra have been reported for excitons bound to neutral acceptors.

2.3.2. Bound Excitons at Isoelectronic Impurities.

In GaP doped with Nitrogen an absorption emission line, the 'A' line, is observed close to the energy gap. This and associated spectral peaks have been shown to arise from excitons bound at Nitrogen impurities which are isoelectronic substituents for Phosphorus (Thomas and Hopfield 1966).

Morgan et al (1968) examined spectra from Cd doped GaP. They reported a sharp no - phonon line associated with Cd - O impurities. They showed that this, the strong red luminescence previously attributed to recombination between distant donor acceptor pairs, arose from nearest neighbour Cd - O complexes. The Cd - O complex is

effectively an isoelectronic substituent and the binding of the exciton to this defect is similar to that for Nitrogen substituents. Studies of Zn - O doped material showed similar complexes with single interior (atomic) separation but the spectra were broadened by a strong vibrational mode.

Cuthbert et al (1968) studied the luminescence from Zn - O and Cd - O doped GaP. Their suggested energy diagram for the process is reproduced in Figure 2.9. After trapping an electron, the Zn - O complex becomes charged and may attract and trap a hole. Electron and hole decay then gives rise to the bound exciton band. At low temperatures an additional band is present. This, a long lived pair band occurs if the charged exciton fails to trap a hole. Then the electron eventually recombines with a hole on a distant acceptor giving rise to this lower energy band. The overlap of the bands has a blurring effect and normal sharp spectral lines are absent. Similar observations were previously reported by Henry et al (1968). At room temperature the bound exciton decay predominates and can be explained by the assumption of a thermal equilibrium distribution of holes among hole states.

From absorption measurements Cuthbert et al found that the concentration of Zn - O complexes increased as the Zn concentration was increased past the optimum for luminescent efficiency. They suggested that concentration quenching probably by Auger recombination offset any increase in efficiency.

In compensated material at low temperatures, Thomas et al (1964) found evidence of donor-acceptor pair recombination. This they suggested was due to the ionised donors and acceptors having large capture cross sections for excess electrons and holes. Another suggested mechanism was that at low temperature the transition energy for interimpurity recombination is very large compared to the typical

phonon energy so the radiative transition probability is dominant.

To summarise, it appears that luminescence in GaP due to recombination between remote donor - acceptor pairs is not efficient at room temperature in the green, red or infra red, and the red room temperature luminescence in Zn - O ~~and~~ doped GaP is predominantly due to recombination at nearest neighbour Zn - O complexes which has a relatively short lifetime.

2.3.3. Absorption in GaP.

The optical absorption of pure GaP was examined in detail by Dean et al (1966). They showed that the corresponding transitions were of the allowed indirect type involving the creation of free excitons and electron hole pairs. Absorption associated with four different phonon energies was resolved. These findings were confirmed by Lorenz et al (1968) whose results are reproduced in Figure 2.10.

2.3.4. GaP Electroluminescent Diodes.

The first GaP electroluminescent diodes to be made were formed by the diffusion of Zn into a n-type vapour grown substrate (Grimmeiss et al 1961). More recently, both in-diffusion and out-diffusion of Zn have been used to form p - n junctions in solution grown substrates. (Gershenson et al 1966). For in-diffusion the substrates were doped with Te and O and for out diffusion with Zn, Te and O. Out-diffusion occurred concurrently with the alloying of the contacts. The crystal was heated up to 600°C for a few minutes and Zn diffused out from the ($\overline{111}$) face into the contact. The out-diffused diodes were found to have graded junctions and a quantum efficiency around 1.3×10^{-4} at room temperature. Of the in-diffused diodes the most efficient ($\sim 10^{-4}$), had abrupt junctions and were formed using the lowest diffusion temperature and times. Gershenson et al also used an

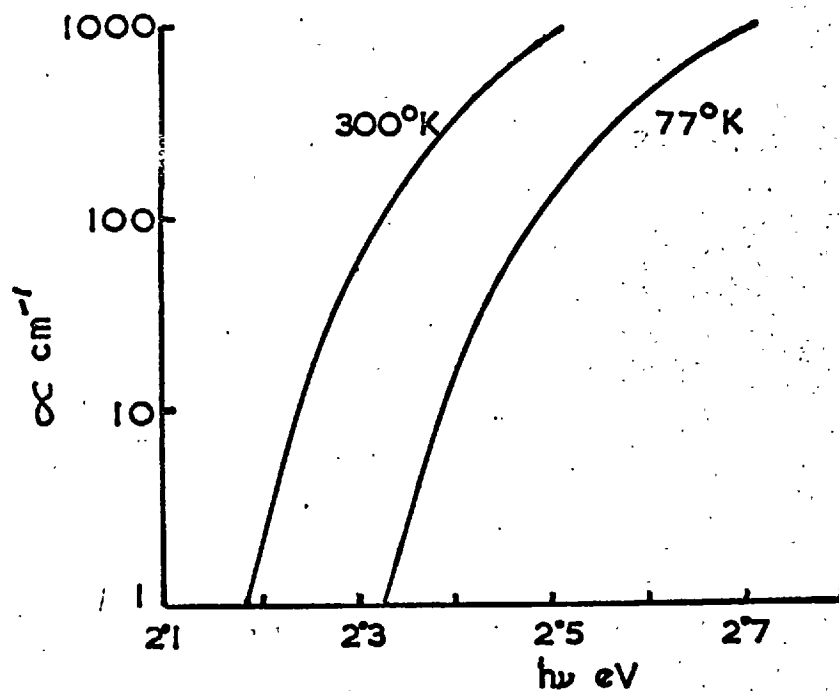


Figure 2.10 The absorption edge of intrinsic GaP at 77°K and 300°K. (After Lorenz et al 1968).

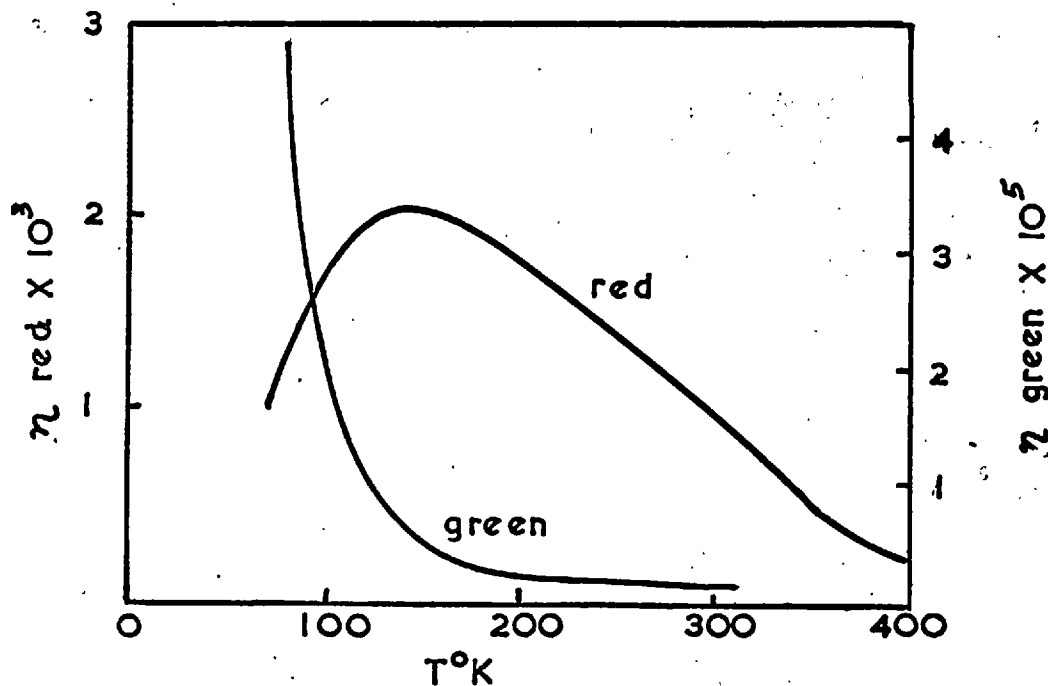


Figure 2.11 The temperature dependence of external quantum efficiency η_{ex} for red and green emitting diodes (After Lorenz and Pilkuhn 1966).

optical microscope to examine the spatial distribution of red and green electroluminescence emerging from the cleaved faces of some of the more efficient diodes. They found that the red electroluminescence arose from a diffusion current to Zn-O recombination centres on the p side of the junction. The point of maximum intensity of the red emission moved further into the p side as the current was increased, whereas the green emission peak remained stationary at the centre of the junction.

Epstein (1969) found that Zn diffused junctions produced in S doped substrates were all graded. The best efficiencies were obtained from those diodes with the highest junction gradients.

Lorenz and Pilkuhn (1966) described a method of making GaP diodes using liquid phase epitaxy. The substrates were solution grown platelets which were double-doped with Zn and Ga_2O_3 . The junctions were formed using liquid phase epitaxy (Nelson 1963) to grow a Te doped layer. Some specimens contained Ga inclusions but this could be avoided by close temperature control and by growing the layer only on the B or $(\overline{111})$ P face of the substrate. The value of β in the expression $I = I_0 \exp ev / \beta kT$ varied between 1.5 and 1.8 at room temperature in these diodes. At high temperatures the values of β decreased towards unity indicating that the diffusion current was becoming dominant. Capacitance measurements showed the junctions to be linearly graded. External quantum efficiencies found in these diodes were typically 0.3 to 0.5% at room temperature. Measurements were made of the efficiencies of red and green emission at various temperatures. The results reproduced in Figure 2.11 show that the green emission was dominant at low temperatures but that the red emission took over above 100°K.

Logan et al (1967) found that the external quantum efficiency of diodes grown by liquid phase epitaxy on solution grown substrates

could be increased as much as an order of magnitude by annealing. The heat treatment was effective in a variety of environments. This suggested that the improvement in efficiency was caused by processes such as precipitation or stoichiometric adjustments rather than the diffusion of an impurity. The junctions after annealing were found to be abrupt with β of the order 1.3. The maximum quantum efficiency of these diodes was very high $\sim 2\%$ at 25°C .

Shih et al (1968) constructed diodes using liquid epitaxy to deposit a Zn - O doped layer on to Te doped substrates. They found that the doping level of the substrate had a considerable effect on the grading of the junction. When Nd - Na, the free carrier concentration in the substrate, was high ($> 6 \times 10^{17} \text{ cm}^{-3}$) the as grown junctions were found to be graded. When the diodes were annealed at $600 - 700^\circ\text{C}$ the junctions became more abrupt and the external quantum efficiency was nearly doubled. After a further heat treatment at 900°C the junctions became graded again and the external quantum efficiency decreased. For substrates with Nd - Na $< 10^{17} \text{ cm}^{-3}$ the 'as grown' junctions were abrupt and remained so after heat treatment at either temperature. In the most efficient diodes, β had a value near unity. This supports the view that the red emission is enhanced when electrons thermally diffuse across the junction to the Zn - O recombination centres on the p side. (Gershenson et al 1966).

Kressel and Ladany (1968) determined the optimum doping level for substrates. The highest external quantum efficiency $\sim 0.5\%$ was observed when Nd - Na $\sim 2 \times 10^{17} \text{ cm}^{-3}$. They explained the increase in efficiency with doping up to this level by enhanced injection into the p region. At large Te concentrations $> 6 \times 10^{17} \text{ cm}^{-3}$ competing loss mechanisms become important. The junctions were found to be intermediate between graded and abrupt and capacitance measurements

indicated the presence of an intrinsic region. At high doping levels the free electron concentration in the n layer failed to follow the Te concentration in the melt. They suggested that complexes involving Te or precipitates such as Ga_2Te_3 might be present.

Ladany (1969) studied the external quantum efficiency of red emitting diodes as a function of doping in the p layer. The diodes were grown by successive growth of n and p layers by liquid phase epitaxy onto a solution grown n-type substrate. Diodes with efficiencies up to 1.4% resulted from optimisation of the Zn and O additions to the p melt but efficiencies of up to 3.4% could be obtained if the p melts were compensated by the addition of Te. The internal absorption in compensated diodes was found to be relatively high; consequently the external quantum efficiency could be considerably increased by immersing the diode in a liquid of high refractive index, such as glycol phthalate with $n = 1.57$, to reduce optical mismatch.

Gooch (1969) found, that in a range of liquid epitaxial and diffused red emitting diodes, that the electroluminescent output saturated at the same emission density irrespective of diode efficiency. A tentative explanation was that efficient injection of carriers into the p side of the junction gave rise to efficient diodes. This injection increases with current so that all diodes eventually reach a fundamental output limit but the more efficient diodes reach this at a lower current density than the less efficient ones.

2.4. Material Properties of GaAs and GaP.

2.4.1. Crystal Structure.

GaAs, GaP and the majority of the III-V compounds have the zinc-blende or sphalerite structure. This structure is typical of the tetrahedral phase of compounds with an average of four valence electrons per atom. It can be considered as being composed of two interpenetrating FCC lattices of the same orientation but displaced from each other

by a vector $a\langle\frac{111}{244}\rangle$, where a is the lattice parameter. One sublattice is composed entirely of a different type of atom to the other. In GaAs for example one sub lattice is entirely Ga and the other entirely As.

The sphalerite structure has no centre of symmetry and therefore exhibits polarity effects in certain crystallographic directions. The $\{111\}$ planes contain atoms of one type only with adjacent planes containing atoms of the opposite type. A $\{111\}$ surface can be formed by a separation along the plane AB illustrated in figure 2.12. This involves the breaking of one bond per atom whereas a separation along CD would involve three bonds per atom. Thus a GaAs slice with parallel $\{111\}$ surfaces can be expected to have one surface containing only Ga atoms and the other containing only As atoms. The former is denoted as an A or $\{111\}$ surface and the latter as a B or $\{\bar{1}\bar{1}\bar{1}\}$ surface. The observed polarity effects in III-V compounds are reviewed by Barber and Heasell (1965). They discuss in detail the various chemical and mechanical properties of the two surface types.

2.4.2. Dislocations in the Sphalerite Structure.

Haasen (1957) pointed out the existence of two types of edge dislocation in the sphalerite structure resulting from the polarity effects in the $\langle 111 \rangle$ directions. The row of atoms having uncompleted bonds and occurring along the edge of the extra half plane can be either of group III or of group V. This concept was further discussed by Venables and Broudy (1958). Using the method of Hornstra (1958), Holt (1962) described the atomic arrangement present at the cores of dislocations in the sphalerite structure. The various types of dislocation are summarised in table 2.1. Holt also extended a notation of Venables and Broudy to apply to dislocations in different materials. Dislocations where atoms on the edge of the

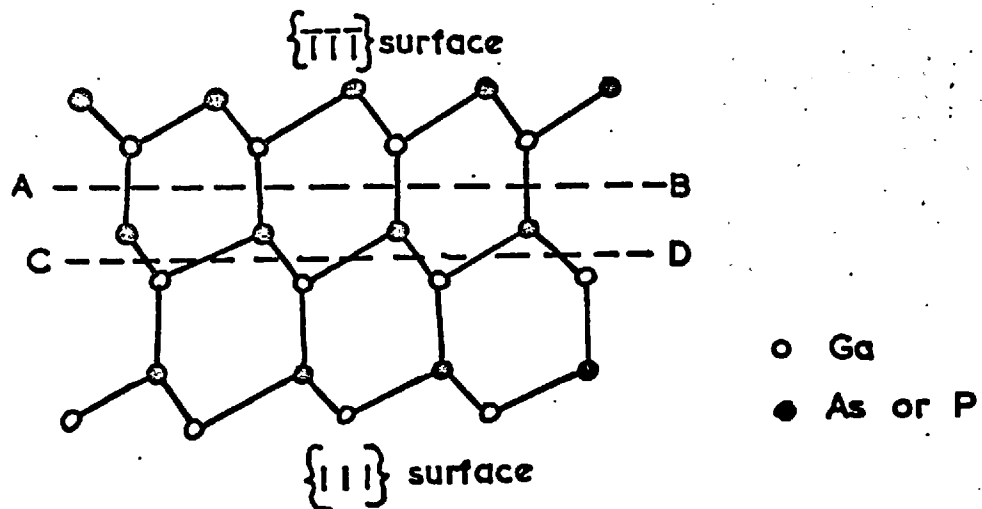


Figure 2.12 Plan view of the $(1\bar{1}0)$ plane of the sphalerite structure. Separation of the $\{111\}$ planes will occur along A-B as this involves breaking only one bond per atom as opposed to three bonds per atom for a separation along C-D. As a result the $\{111\}$ type faces will consist entirely of As or P atoms and the $\{1\bar{1}\bar{1}\}$ type faces entirely of Ga atoms.

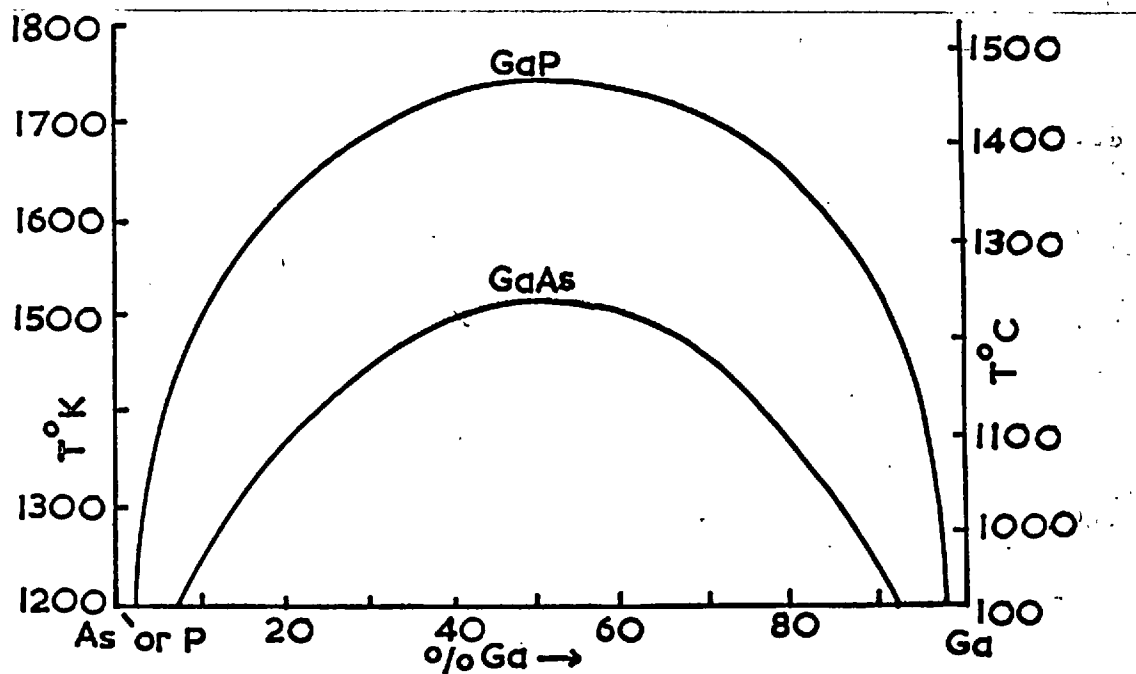


Figure 2.13 The liquidus curves of GaAs and GaP in the region of the melting point (After Thurmond 1965).

Dislocation	Burgers Vector $\underline{b}$	line $\underline{a}$	Glide Plane
Screw	$\frac{1}{2}\underline{a}\langle 110 \rangle$	$\langle 110 \rangle$	—
60°	$\frac{1}{2}\underline{a}\langle 110 \rangle$	$\langle 110 \rangle$	$\{111\}$
30°	$\frac{1}{2}\underline{a}\langle 110 \rangle$	$\langle 112 \rangle$	$\{111\}$
Edge	$\frac{1}{2}\underline{a}\langle 110 \rangle$	$\langle 110 \rangle$	$\{100\}$

Table 2.1 Types of dislocation in the sphalerite structure (Holt 1962).

extra half plane were of type III were termed α dislocations and those with type V atoms, β dislocations. Dislocations in the sphalerite structure may have localised donor or acceptor states associated with them. The mechanisms involved are more complex than those implied by the simple dangling bond model and Holt (1960) pointed out that the change in band structure introduced by the effective addition or removal of an electron at a dangling bond must not be neglected; the effect must be shared by all the remaining bonds and the induced states depend on the position of the fermi level. Heine (1966) described a one dimensional model in which a small amount of free volume representing the core of a dislocation is inserted into a ring of atomic potentials. The electrical effects of dislocations could be explained by the decrease in atom density at the core giving rise to a localised state in the band structure. The effects of these dislocation induced states on the electrical properties of In Sb were studied by Gatos et al (1961), by Bell et al (1966) and by Bell and Willoughby (1970). In each case plastic bending was used to introduce dislocations of known sign. Electrical measurements by Bell et al indicated that both In and Sb dislocations act as acceptor states in n-type material and that In dislocations act as acceptor states in p-type material. Bell & Willoughby extended these results and presented ^a theoretical analysis which gave reasonable agreement with experiment. They concluded that the In-dislocation level lay near the centre of the band gap while the Sb-level lay near the valence band.

There are no reports in the literature of any properties of the emission spectra of GaAs or GaP being attributed to dislocation induced levels. However, in Ge Gippius and Vavilov (1963), (1965), found that their radiative recombination spectra could be explained by assuming transitions involving energy levels within the band gap due

to dislocations. An analysis of carrier recombination at dislocations in Ge has been made by Figielski (1964). His theory, which deals mainly with recombination involving the temporary trapping of holes at a charged dislocation, was found to give good agreement with experiment.

2.4.3. Misfit Dislocations.

Arrays of misfit dislocations may be set up when there is a change in lattice parameter across a coherent interface. Such a change in lattice parameter is particularly characteristic of a heterojunction where different materials are involved. However, even across a conventional p-n junction, a lattice mismatch can result from the steep concentration gradient of wrong sized impurity atoms. A small mismatch can be accommodated elastically but if the resulting stress exceeds the plastic yield stress of the material, plastic flow, with the introduction of misfit dislocations, will occur. The geometry of misfit dislocations in the diamond and sphalerite structures has been described by Holt (1966). He also reviews experimental evidence relating to their formation and observation in various materials.

Misfit arrays were observed in Zn diffused GaAs by Abrahams and Buicchi (1966) using an etching technique. With the aid of X-ray topography Schwuttko and Rupprecht (1966) examined diffusion induced networks in GaAs. The observed contrast was consistent with the features observed being Lomer-Cottrell sessile dislocations. However, the measurements did not exclude the possibility that another high density network of similar or different dislocations was present.

In phosphorus diffused Si misfit dislocation arrays have been observed by electron microscopy (Washburn et al 1964) and by X-ray topography (Schwuttko and Queisser 1962). The dislocation density observed in the electron microscope was of the order 10^8 lines cm^{-2} or even larger while the dislocation density observed by X-ray

topography was 10^6 lines cm^{-2} or less.

Transmission electron microscopy was used by Abrahams et al (1969) to examine dislocations in heterojunctions formed by vapour phase growth of $\text{GaAs}_{1-x}\text{Px}$ on GaAs substrates. They found not only a set of misfit dislocations lying in the plane of growth but also a set of inclined dislocations which propagated through the growing crystal. It was found that these inclined dislocations would propagate through an ungraded region grown onto a graded heterojunction. A dislocation model was suggested which described the observed dislocation morphology. Stringfellow and Greene (1969) used X-ray topography and etching techniques to examine similar material. Their results and conclusions agreed with those of Abrahams et al.

2.4.4. Growth of GaAs.

Single crystal GaAs can be grown from the melt by a variety of standard techniques. Horizontal Bridgman, gradient freeze, floating zone melting and Czochralski pulling methods have all been used. Certain modifications have been necessary to ensure the presence of an arsenic overpressure of 0.9 atmos to prevent dissociation.

In the Bridgman method a quartz boat containing Ga is placed at one end of a quartz tube. Excess As is placed at the other end of the tube which is then evacuated and sealed. The tube is placed in a furnace which has a region at 1240°C and a region at 605°C with a uniform temperature gradient in between. The Ga is placed in the hot part of the furnace and the As in the cool part. The As vapourises and is absorbed by the Ga. The Ga is allowed to absorb a stoichiometric amount of As and then the tube is moved slowly (about 2 cm/hour) down the temperature gradient so that its contents gradually freeze. A very even rate of freezing is required to minimise segregation effects. The gradient freeze method achieves this more effectively

by reducing the power input to the furnace and moving the temperature gradient relative to the melt.

The main problem with the above methods is to avoid contamination of the crystal with silica from the tube and boat. The floating zone method overcomes this problem by avoiding the use of a crucible. A rod of polycrystalline GaAs is clamped vertically and a narrow molten zone is passed down it many times. The material grows as a large single crystal and zone refining results in purification of the upper part of the rod.

The Czochralski technique is often used for growing single crystal GaAs. A seed crystal is dipped into a GaAs melt and slowly withdrawn. A rotation imposed on the seed crystal is found to improve the quality of the final material. Gas-tight movable lead throughs must be used and in the Liquid Encapsulation (LE) technique (Bass and Oliver 1966) arsenic loss is minimised by covering the melt surface with a layer of molten boric oxide. Often however, this technique gives rise to impurity striations which have a periodicity associated with the rotation. This effect is particularly noticeable when highly doped material suitable for lasers is being grown. Striations have also been observed in materials grown by a Czochralski technique not involving rotation. In InSb Morizane et al (1966) obtained a direct correlation between such striations and temperature fluctuations at the growth interface. Similar striations were observed in material produced by boat growing and zone melting techniques by Muller and Wilhelm (1964) and Cole and Winegard (1965). They found that these striations could also be correlated with time dependent fluctuations of the temperature. Hurle (1966) showed that temperature fluctuations observed in a Ga melt in a horizontal boat were due to a progressive thermal wave propagated down the temperature gradient. The wavelength of the oscillations was related directly to the length of the boat.

Chedzey and Hurle (1966) reported that the same phenomena occurred in the molten zone technique. They found that the fluctuations could be suppressed by the application of a steady magnetic field which gave rise to eddy current damping of the fluid oscillations. The temperature fluctuations observed by Morizane et al, Muller and Wilhelm, and by Cole and Winegard can be explained by the above mechanism. The temperature fluctuations lead to variations in the growth rate at the crystal face and consequently modify the effective impurity segregation coefficient. Thus bands of varying impurity concentration are produced in the crystal. In GaAs, impurity striations have been observed by a number of workers but no study has been made during growth. Ziegler and Henkel (1965) used infra red transmission to examine striations in Czochralski grown GaAs and studied their effect on laser action. Meiran (1965) examined striations in Czochralski pulled GaAs using electron microscopy. With $N_{Te} > 2 \times 10^{18}$ Te atoms cm^{-3} , precipitates were observed, the density of which varied across the striations. Also in Te doped GaAs Wittry (1966) observed bands of varying Te concentration using the X-ray fluorescence and cathodoluminescence modes of an electron probe microanalyser. Casey (1967) examined striations in similar material using cathodoluminescence.

Single crystals of GaAs can also be grown from solution or from the vapour phase. By growing III - V compounds from a solution using the group III element as a solvent both the growth temperature and the dissociation pressure of the group V element are much reduced. Panish et al (1966) found that solution grown GaAs exhibited none of the deep level transitions in photoluminescence observed in crystals grown from the melt. This they attributed to the lower defect concentration introduced at the lower growing temperature.

2.4.5. Growth of GaP.

At the melting point of GaP (1465°C) the vapour pressure of phosphorus is 35 atmos and this creates considerable problems in growing GaP from the melt. These problems can be overcome however, using the liquid encapsulation process as described by Bass and Oliver (1968). The apparatus involved is similar to that used for GaAs (section 2.4.4.) but the high pressures involved make the use of a closed circuit T.V. monitor and remote control obligatory. More usually alternative lower temperature techniques are employed. Spontaneous crystallisation or solution growth provides a simple method of growing GaP platelets (Wolff et al 1954). In this technique a solution of GaP in Ga is cooled from around 1150°C to room temperature and small platelets of GaP are produced in the melt. Suitable dopants can be added to the GaP and such platelets used as substrates for the formation of p-n junctions either by Zn diffusion (Logan et al 1967) or by liquid or vapour phase epitaxy. Plaskett et al (1967) described a technique where a zone of liquid Ga saturated with GaP was passed upward through a GaP ingot. This method had the advantages of low temperature and resulted in minimum contamination from the container materials.

The technique of liquid phase epitaxy as described by Nelson (1963) is widely used in the formation of GaP diodes. Two forms of this technique are the tipping and vertical dip methods. The tipping method was described in detail by Lorenz and Pilkuhn (1966). The substrates used were grown from solution by spontaneous crystallisation. The substrate was held down in one end of a quartz or graphite boat with a quartz pin. In the other end of the boat a Ga - GaP mixture was placed and the appropriate dopant added. The boat was then enclosed in a quartz tube and heated to $\sim 1140^{\circ}\text{C}$ over about 45 minutes.

The boat was then tipped so that the saturated solution of GaP covered the substrate. The temperature was reduced to 700°C over 40 minutes and then the furnace shut off completely. Once at room temperature the epitaxially overgrown substrate could be removed and isolated from the remaining Ga by boiling in a solution of 50% HCl. The vertical dip method is similar except that the substrate crystal is inserted into the solution from above. The solution is initially held at a temperature between 1110 and 1140°C in an atmosphere of argon or forming gas. In both these techniques some degree of melt back of the substrate is employed to remove surface damage prior to growth. It is essential for the substrate to be GaP rather than GaAs or other materials which would dissolve preferentially in the liquid Ga. Substrates must therefore be prepared by alternative methods.

Vapour phase epitaxy has also been used to grow GaP. Both open and closed tube methods have been successfully employed and a variety of agents used as carriers. Perhaps most widely used is the open tube system in which Ga and PCl_3 are used as the source material and hydrogen used as the carrier. A typical system of this type is described by Taylor et al (1968) who grew layers on both the $\text{A}(\overline{111})$ and $\text{B}(\overline{111})$ faces of GaAs and GaP substrates. They found that a pronounced orientation effect existed in the layers whereby films grown on $\text{B}(\overline{111})$ faces were low resistivity and n-type while those grown on $\text{A}(\overline{111})$ faces were high resistivity and p-type. Also films grown on $\text{A}(\overline{111})$ faces tended to be smooth with occasional triangular or hexagonal pits whereas films grown on $\text{B}(\overline{111})$ faces were completely covered with hexagonal hillocks. It has not proved possible to dope vapour grown material with Zn and O so only undoped or n-type material is prepared in this way. Saul (1968) showed that the quality of vapour phase grown material is affected by thermal mismatch between a GaAs substrate and the GaP overgrowth. Much better quality material can

be obtained by homo-epitaxy using a GaP substrate.

A detailed review of methods of growth applied to the III - V compounds has been presented by Willardson and Goering (1962). Bailey (1967) reviews more recent developments of the general techniques.

2.5. The Behaviour of Impurities in GaAs and GaP.

Impurities are essential to the formation of a p-n junction but irregular distribution and precipitation can have a deleterious effect on device performance.

2.5.1. Zinc diffusion in GaAs.

Using radioactive tracer methods Goldstein (1961) and Cunnell and Gooch (1960) found that Zn diffuses into GaAs more rapidly than is predicted by Fick's Law. There is a sharp fall off in Zn concentration near the diffusion front and consequently a well defined p-n junction. For this reason Zn is almost universally used as an acceptor for the preparation of diffused p-n junctions in GaAs. Longini (1963) proposed a mechanism which could account for this anomalous diffusion. The Zn could diffuse interstitially and hence have a large diffusion coefficient combined with a smaller coefficient for substitutional diffusion in the Ga sub-lattice. Weisberg and Blank (1963) made a detailed study of this mechanism and found good theoretical agreement with the experimental data of Goldstein, and Cunnell and Gooch.

Chang and Pearson (1964) made further additions to the theory. They showed that interstitial Zn atoms would act as doubly charged donors whereas substitutional Zn atoms are either neutral or act as singly ionised donors. Casey and Panish (1968) used phase diagram and solubility data to optimise a Zn diffusion source. They found that a source containing 5, 50, 45 atomic percent Ga, As, Zn, provided a significant improvement in the reproducibility and planarity of the Zn diffusion compared with using a source of elemental Zn.

2.5.2. The Behaviour of Donors in GaAs.

Of the common donors, Te and Se are group VI elements whereas Si is group IV. It has been observed that at high doping levels the donor concentration diverges from the free electron concentration indicating that donors are present in an unionised form. Vieland and Kudman (1963) investigated this phenomenon in bulk Se doped GaAs. They showed that at concentrations in excess of $4 \times 10^{17} \text{ cm}^{-3}$ some of the Se enters the lattice as an optically active complex $V_{\text{Ga}} + \text{Se}_3$ (V_{Ga} denotes a Ga vacancy). This gives rise to a deep level 0.9 eV below the conduction band and leads to appreciable absorption near 1.5 eV. They suggested that this model was generally applicable to the doping of III - V compounds with group VI elements. Schottky (1966) further developed the theory and showed that the results depend on the binding energy of the complex and formation enthalpy of vacancies.

Electron microscope studies by Abrahams et al (1967) revealed considerable precipitation in GaAs highly doped with Se. Evidence obtained from moiré fringe patterns indicated that the precipitates might be $\text{Ga}_2 \text{Se}_3$ particles which could account for the presence of Se in an unionized form. Kressel et al (1968) made a study of Te and Se doped GaAs grown by liquid phase epitaxy. In photoluminescence they observed a broad emission band centred at 1.2 eV and which increased in intensity relative to the band gap radiation with increasing dopant concentration in the 10^{18} cm^{-3} range. They suggested that the recombination centres responsible for this band were neutral $V_{\text{Ga}} + 3\text{Te}$ complexes of the type described by Vieland and Kudman. In very highly Te doped material precipitates were observed using the transmission electron microscope. These were identified by diffraction pattern analysis as $\text{Ga}_2 \text{Te}_3$. It was suggested that non radiative recombination via these precipitates could account for the observed decrease in radiative efficiency when the dopant concentration

is increased beyond $2-3 \times 10^{18} \text{ cm}^{-3}$.

Iizuka (1968 a) investigated highly Te doped GaAs with a free carrier concentration of $6.4 \times 10^{18} \text{ cm}^{-3}$. Large inclusions outcropping at the surface were visible to the naked eye after mechanical polishing. X-ray microanalysis of the inclusions showed the presence of Te and Ga, and the absence of As. This led him to suggest that Te atoms were substituted on As sites. The formation of such large inclusions was attributed to constitutional supercooling in the melt during crystal growth. Dislocations present round each inclusion were interpreted as resulting from the difference in thermal expansion coefficients between the inclusion and the matrix. Iizuka (1968 b) used X-ray anomalous transmission (see section 2.6.3.) and etching (section 2.6.1.) to examine inhomogeneities in Te doped melt grown GaAs crystals with carrier concentrations greater than $1.6 \times 10^{18} \text{ cm}^{-3}$. Micro-precipitates were revealed both by the etch and in the X-ray topographs. In the vicinity of dislocations both techniques indicated localised precipitate free regions about 30 to 150 μ m in diameter. Similar impurity segregation and depletion effects at dislocations have been examined using the cathodoluminescence mode of the scanning electron microscope. This work by Wittry and Kyser (1964), Casey (1967) and by Shaw and Thornton (1968) will be described in section 2.6.4.

2.5.3. Impurities in GaP.

Trumbore et al (1965) investigated the solubility and electrical behaviour of Zn, Se, S and Te in GaP crystals grown from solution. The solid solubilities of the donor impurities were found to vary linearly with the melt concentrations at lower doping levels and with the square root of the melt concentration at higher doping levels. For Zn, the solid solubility varied only as the square root of the melt

concentration. This is consistent with the idea of a singly ionised acceptor dissolving in an extrinsic semiconductor. The excess donor and acceptor concentrations were significantly lower than the impurity concentrations at the high doping levels. Quenching experiments indicated Zn precipitation in samples with a Zn concentration of $1.5 \times 10^{19} \text{ cm}^{-3}$. Such Zn precipitation had previously been reported by Gershenson and Mikulyak (1964). In n-type material however, Trumbore et al found little evidence for precipitation of impurity atoms. Thus it was assumed that the electrically active impurities were present as part of a neutral complex such as that described by Vieland and Kudman (1963) for donors in GaAs (see section 2.5.2.)

Foster et al (1966) used a radiochemical technique to determine the effective segregation coefficients, K_{eff} , of Zn, Se and Te in GaP grown from a 10% solution in Ga. For Zn, K_{eff} was low, between 0.04 and 0.08, but for Se and Te the value was 6.3 and 2.6 respectively. They also reported that their solution grown crystals exhibited a dendritic morphology.

2.5.4. Phase Changes.

GaAs and GaP are both congruently melting compounds, i.e. they melt and freeze at a fixed temperature with no compositional change between the solid and liquid phases. It is, however, necessary for the equilibrium vapour pressure of the volatile component, As or P, to be maintained or else decomposition will occur. The Ga - As and Ga - P phase diagrams have been investigated by Thurmond (1965) and the liquidus curves of these two systems are reproduced in figure 2.13. Both GaAs and GaP have finite existence regions, i.e. there is a limited composition range over which they exist as compounds. Small variations in stoichiometry are thus possible and will result in variations in the concentration of vacancies and other point defects.

A theoretical discussion of this problem is given by Albers and Haas (1969).

The doping of GaAs and GaP for device purposes is seldom much above 3×10^{18} atoms cm^{-3} and hence rather too small to be represented meaningfully on a phase diagram. Precipitation of impurity atoms does occur even at these concentrations (see section 2.5.2.) and the ternary phase diagram can be useful for determination of the precipitating species. Panish (1966 a) describes the ternary phase diagram for the Ga - As - Zn system. As and Zn form two congruently melting compounds Zn_3As_2 and ZnAs_2 but the phase diagram consists principally of two primary phase fields resulting from the precipitation of GaAs and Zn_3As_2 , respectively. This phase diagram has been used (Casey and Panish 1968) to determine the ideal composition of a source for Zn diffusion (see section 2.5.1.). This composition must be within the region of the phase diagram in which GaAs is stable otherwise surface decomposition will occur. For Ga - P - Zn (Panish 1966 b) the phase diagram is similar. The main feature is the extensive phase field of Zn_3P_2 which exists over part of the GaP - Zn pseudobinary.

In both the Ga - As - Te (Panish 1967 a) and the Ga - P - Te systems (Panish 1967 b), Ga and Te form two congruently ~~melting~~ melting compounds GaTe and Ga_2Te_3 . The solid solubility of these compounds and also of Te in GaAs and GaP is very small and hence precipitation is likely at low doping levels.

2.6. The Observation of Defects.

Defects in semiconductors can vary from macroscopic to sub-microscopic and the techniques available for their observation are individually restricted to certain ranges of magnification. For complete examination of a specimen several different methods of

observation must be employed. These methods will be discussed individually.

2.6.1. Etching.

In etching atoms are removed preferentially from regions of the specimen surface strained by dislocations, impurities or vacancies. The reliability of the technique was revealed by Dash (1956) who showed that etch pits in Si had a one to one correspondence with decorated dislocations seen by infra-red transmission.

In the sphalerite structure the etching characteristics are different for the A and B type $\{111\}$ surfaces. This was demonstrated for GaAs by White and Roth (1959) who used a HCl , HNO_3 , H_2O solution in the ratio 2 : 1 : 2. They found etch pits were produced only on the A or Ga $\cdot$ $(\bar{1}\bar{1}\bar{1})$ surface. In general the B surface of a III - V compound is more reactive than the A surface. However, in the presence of certain inhibitors or oxidising agents the reactivity of the B surface can be reduced to that of the A surface. Certain inhibitors can also cause the B surface to show dislocation etch pits. Using this principle Abrahams and Buiocchi (1965) developed the AB etchant which produced etch pits at dislocations on any low index plane in GaAs. This consisted of CrO_3 , HF , AgNO_3 , H_2O in the amounts 1 gm, 1cc, 8 mg, 2cc; CrO_3 acting as an oxidising agent and AgNO_3 as an inhibitor. This etchant has also been applied successfully to $\text{GaAs}_{1-x}\text{P}_x$ materials by Stringfellow and Greene (1969). A number of dislocation etches for GaP have been described by Saul (1968).

2.6.2. Infra-red and Visible Light Transmission.

The homogeneity of GaAs and GaP can be examined by viewing transmitted light of photon energy less than the band gap. For GaAs, wavelengths greater than $9000 \text{ \AA}^0$ are transmitted at room temperature.

Observations must be made using either an image converter or infra-red sensitive film. The absorption coefficient of GaAs is highly dependent on impurity concentration at near - band gap energies so that small variations can be detected in transmission. Ziegler and Henkel (1965) found that growth striations in GaAs could be made visible if the specimen orientation was correct.

Dash (1957) showed that dislocations in Si could be made visible in infra-red transmission by means of copper decoration. In Si, copper diffuses interstitially and precipitates substitutionally along edge dislocations. Black and Jungbluth (1967 b) using infra-red transmission found precipitates and decorated dislocations in Zn doped GaAs. They correlated their transmission patterns with etch patterns and found convincing evidence for precipitation of Zn on dislocations.

GaP transmits a considerable portion of the visible spectrum. Zn decoration of dislocations in GaP was examined by Gershenzon and Mikulyak (1962) using optical means. Under the microscope they were able to resolve individual dislocations. Their results indicated that screw dislocations did not become decorated but that grain boundaries, and dislocations with edge components, were easily made visible.

2.6.3. X-ray Topography of Single Crystals.

Two distinct types of X-ray technique, extinction contrast and anomalous transmission, have been used for the direct observation of defects in near perfect crystals.

The extinction contrast technique was first described by Lang (1958). The section topographs, Figure 2.14a, that he obtained showed up dislocations as regions of increased diffracting power. The area that could be examined in one exposure was very small and limited to the

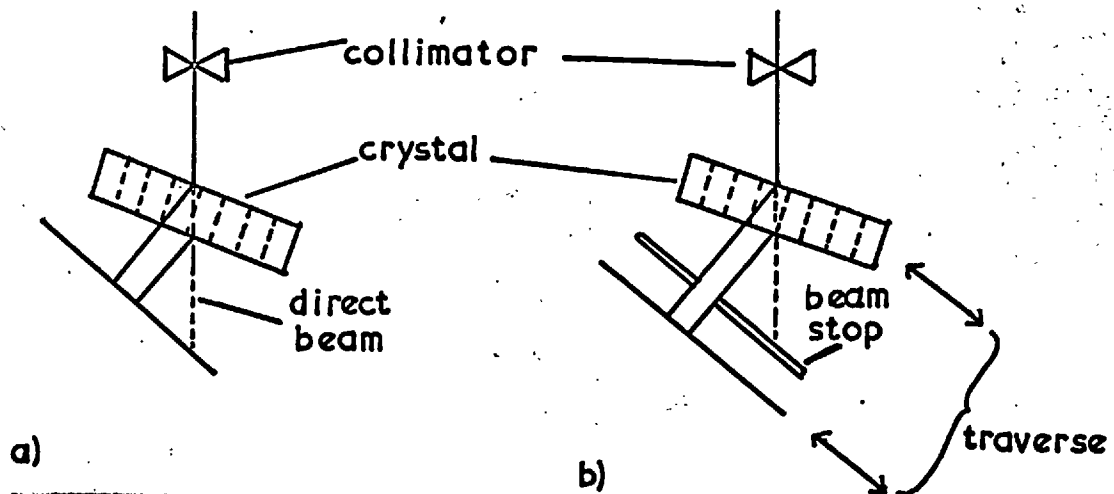


Figure 2.14 Schematic drawing to illustrate the methods used to produce a) a section topograph and b) a projection topograph.

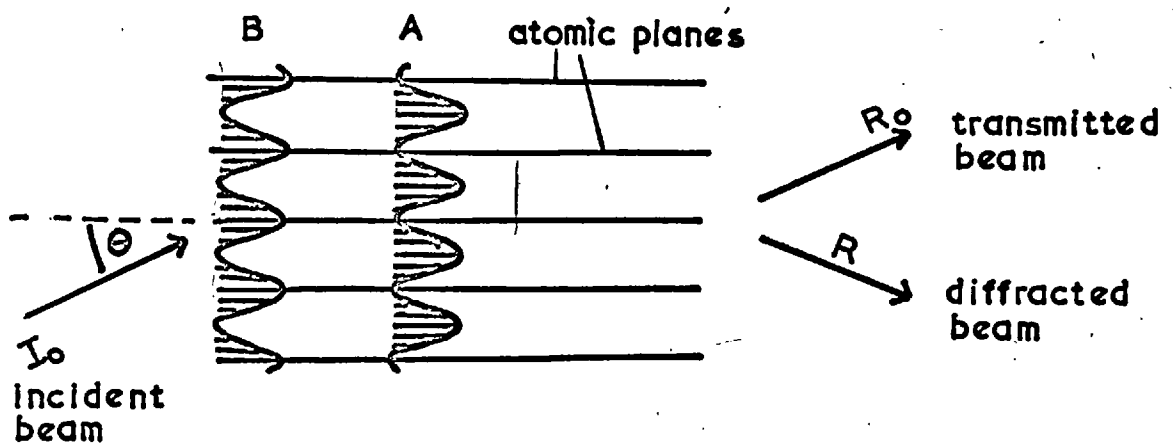


Figure 2.15 Standing wave pattern produced by two coherent travelling plane waves. Wave A has its nodes coincident with the atomic planes and is little absorbed. Wave B on the other hand has its maximum intensity at atomic positions and therefore suffers strong absorption.

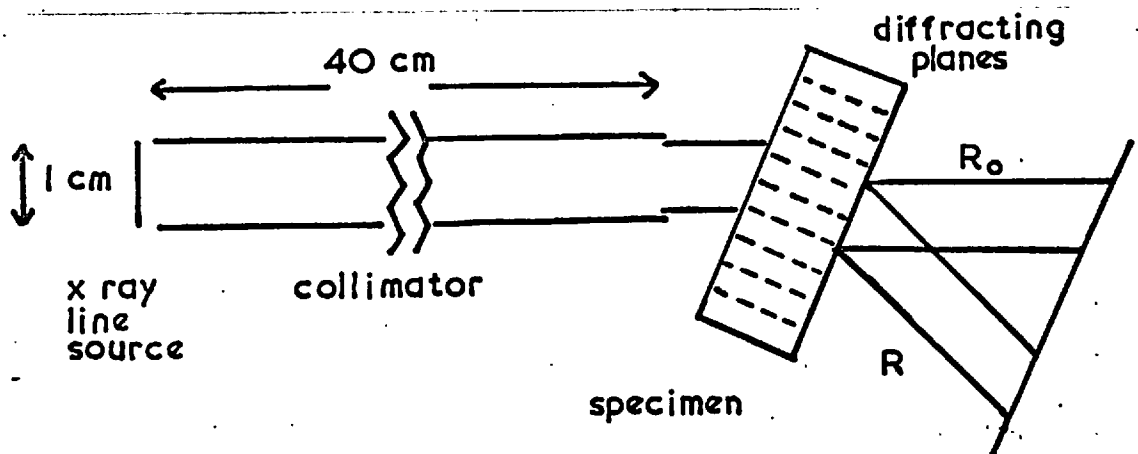


Figure 2.16 Schematic diagram of a camera for taking X-ray topographs by anomalous transmission.

narrow strip perpendicular to the plane of figure 2.14a which is illuminated by the X-ray beam. Larger areas could be examined using the projection topograph (Lang 1959). In this method, figure 2.14b, the crystal and film were traversed together. A fixed stop prevented the non-diffracted X-rays reaching the film. In this way a topograph of the whole crystal is recorded one illuminated strip at a time. For both these techniques the thickness t of the crystal must be such that $\mu_0 t < 1$ where μ_0 is the linear absorption coefficient for the X-rays in use. If this condition is not fulfilled the diffracted X-rays will be absorbed by the specimen before reaching the film. For $\text{CuK}\alpha$ radiation a specimen of GaAs must be less than 0.1 mm thick for this condition to be satisfied.

The absorption of X-rays follows the relationship:-

$$I = I_0 \exp(-\mu_0 t)$$

where I and I_0 are the intensities of the incident and transmitted beams. If the specimen thickness is such that $\mu_0 t > 10$ the transmitted intensity should be very small. However, in nearly perfect crystals of this thickness anomalous transmission occurs. This is manifested by enhanced transmission when the crystal is set for Laue reflection.

Anomalous transmission is explained using the wavefield model. The net energy flow is mostly along the atomic diffracting planes. Two standing waves as in figure 2.15 are set up perpendicular to the flow direction. Wave A has its nodes coinciding with the position of the atoms whereas wave B has its nodes halfway between planes. If the wafer is thick enough so that in practice $\mu_0 t > 10$ as noted above, wave B becomes completely absorbed by interaction with the atoms. Wave A however suffers no absorption if the perfection of the crystal is maintained throughout. At the far side of the crystal the A wave arrives with half the intensity I_0 and here separates into two

components, the diffracted beam and the transmitted beam. Defects in the periodicity of the crystal manifest themselves by strong absorption of the A wave.

The examination of crystals using anomalous transmission was first reported by Borrmann et al (1958) and Barth and Hoseman (1958). Schwuttke (1962) developed an improved technique based on the parallel beam method of Barth and Hoseman. The experimental arrangement is illustrated in figure 2.16. A long collimator tube was fixed to the port of a standard, line source, X-ray unit and the crystal was mounted on a goniometer stage at the far end. The film recorded identical topographs for the diffracted and transmitted beams R and Ro. The resolution was found comparable to that of the extinction technique.

Schwuttke and Rupprecht (1966) used extinction contrast to examine both $\{111\}$ and $\{100\}$ surfaces in Zn diffused GaAs. They found that Zn diffusion into $\{100\}$ wafers produced a crossed grid of lines lying along two perpendicular $\langle 011 \rangle$ directions. Diffusion into the $\{111\}$ plane resulted in a hexagonal network again with lines in the $\langle 011 \rangle$ directions.

Jungbluth (1965) used anomalous transmission to examine imperfections in GaAs grown by Czochralski and gradient freeze methods. The dislocation density in Czochralski grown crystals was found to vary from 10^4 to 10^5 dislocations per cm^2 . Individual dislocations could not be resolved due to the interaction of the strain fields. In the gradient freeze crystals the defect density was much lower enabling individual dislocations to be observed. In heavily doped crystals it was possible to detect precipitation. Black and Jungbluth (1967 A and B) examined Zn diffused GaAs using the same technique. They found that the diffused layers were opaque to anomalously transmitted X-rays. When the diffused layers were polished off, the

original defect structure was found to be preserved but additional defects were present including microscopic precipitation.

Iizuka (1968 b) used anomalous transmission to examine Te doped GaAs. Microprecipitates were observed throughout the material but denuded regions were found in the vicinity of dislocations. These results were substantiated by etching experiments.

The technique of Lang (1959) was used by Ladany et al (1969) to examine slices of pulled GaP produced at S.E.R.L. and also solution grown GaP platelets. In topographs of a 0.6 mm slice of pulled material no individual dislocations were resolved. After etching the density of etch pits was about 1.5×10^5 pits / cm^2 . Topographs of the solution grown platelets showed them to be nearly perfect crystals. The dislocation density was low enough for individual dislocations to be clearly resolved in the topographs. The field of X-ray topography has been reviewed by Weissmann (1968) and a review of the state of the art in anomalous transmission has been presented by Okkerse and Penning (1968).

2.6.4. Scanning Electron Beam Techniques.

Two basic types of instrument are available, the Electron Probe Microanalyser and the Scanning Electron Microscope. The microanalyser is designed primarily for the detection, spatial resolution and analysis of compositional variations. X-ray spectrometers are employed to detect the characteristic fluorescent radiation from different elements. For this purpose large beam currents are required and can be obtained only with limitations on resolution. The SEM was designed as a high resolution instrument to examine the electrical properties of materials (Oatley 1965), and it has found wide applications in semiconductor technology. Due to its large depth of focus it is of great value in the study of biological, geological and other specimens where detail

of surface topography is required.

Both instruments operate on the same principle. An electron optical system delivers a fine beam of near monochromatic electrons to a fine focus on the specimen. This beam is scanned across the specimen surface in a square raster similar to that used in television. The various signals generated by the interaction of the beam with the specimen are used to modulate the intensity of a cathode ray tube being scanned in unison. In this way images corresponding to the signal strength are formed. Various modes of operation are obtainable depending on the detection system in operation. These will be described in brief.

1. Back Scattered Electrons. These can be conveniently detected by means of Si p-n junctions suspended above the specimen surface.
2. Secondary Electrons. These low energy electrons can be detected by using a faraday cage to attract them onto a scintillator held at a high positive potential. The light output from the scintillator is monitored using a photomultiplier.
3. X-ray Fluorescence. This is detected using an X-ray spectrometer and a scintillation counter.
4. Specimen Current. The current flowing through the specimen to earth may be amplified and used to give an image corresponding to the electron absorption profile of the specimen.
5. Cathodoluminescence. Light emitted by the specimen can be detected using a photomultiplier or lead sulphide diodes.
6. Charge Collection. The current generated at a p-n junction can be used as the modulating signal. This has also been termed the short circuit current as it involves short circuiting the p-n junction through a current amplifier.

The resolution of the technique depends on the electron optics (spot size), on the particular mode of operation and to an extent on the specimen properties. The beam of incident electrons spreads out below the specimen surface due to scattering. However, secondary electrons are mostly emitted in the surface regions from an area of similar size to the beam spot and in this mode the resolution can be as good as $100 \text{ \AA}^0$ or so for a beam diameter of $60 \text{ \AA}^0$. In the cathodoluminescence mode the resolution is less because the bulk of the emission occurs from a much greater depth below the surface and hence from a broader area. This effect may be enhanced by the presence of a surface dead layer of reduced radiative efficiency (Thornton 1968).

Wittry and Kyser (1964) and Kyser and Wittry (1966) examined the polished surface of GaAs doped with Te to a concentration of $3 \times 10^{18} \text{ cm}^{-3}$. They used a photomultiplier to detect the recombination radiation emerging from the optical microscope system of an electron probe microanalyser. They observed a number of dark spots with light haloes and etching studies showed these to correlate with dislocations intersecting the surface. It was found that the infra-red recombination radiation had a component with a decay time of about 8 seconds. The magnitude of this component was a function of the time the beam was on. This indicated that trapping and thermal release of carriers was taking place and that the material had a very high trap density.

Wittry and Kyser (1965) examined p-n junctions in GaAs using the cathodoluminescent and charge collection modes of operation. An overall decrease in cathodoluminescent intensity was observed at the p-n junction. This, they proposed, was due to excess minority carriers drifting in the field of the junction, and causing a current to flow through the ohmic contacts, rather than recombining radiatively.

The charge collection signal, when monitored on a C.R.O., showed a significant peak as the beam traversed the junction region thus supporting this theory. Using a reverse bias method they determined the average energy to produce one electron hole pair as 4.6 ev. A further application (Wittry and Kyser 1967) was the measurement of diffusion lengths and surface recombination velocities from the voltage dependence of the cathodoluminescence. Czaja (1966) measured diffusion lengths in Si and GaP using the dependence of the charge collection current on the beam current and accelerating potential.

Casey (1967) used the cathodoluminescent mode to examine Te doped GaAs and found similar spot patterns to those reported by Wittry and Kyser (1964). Using a spectrometer he found that no observable spectral differences existed between areas of high and low cathodoluminescent efficiency in striated material. He proposed a theory for the contrast both at striations and in the spot patterns assuming that absorption differences were negligible.

Shaw and Thornton (1968) used the cathodoluminescence mode to examine GaAs laser material doped with Si, Se and Te. Spot patterns at dislocations were found less frequently in Se doped than in Te doped material. This they suggested was due to Te having the largest atomic misfit being 12% larger than the normal As atom compared to Se being 3% smaller. The various contrast effects observed at dislocations and striations were discussed.

Czaja and Patel (1965) used a charge collection technique to show up dislocations in the n side of a Si p-n junction. The junction was oriented perpendicular to the beam and dislocations in the thin n-type layer gave rise to shadowing on the p-n junction which acted as a detector. Such shadowing would be expected from dislocations containing dangling bonds.

Wittry (1966) used X-ray analysis in the electron probe to show

that striations in Te doped GaAs corresponded to actual Te concentration fluctuations. To do this it was necessary to average readings over a period of four hours. Black (1967) used the probe to analyse precipitates in Zn diffused GaAs. These he merely stated were Zn rich. Large inclusions in heavily Te doped GaAs with a carrier concentration of $6.4 \times 10^{18} \text{ cm}^{-3}$ were analysed by Iizuka (1968a). He found them to consist solely of Te and Ga.

GaP diodes were examined using the S.E.M. by Sulway et al (1967). The diodes were fabricated by alloying contacts onto solution grown platelets. Their results demonstrated that p-n junctions could be formed at the contacts but that in some cases junctions had formed within the platelets during growth. Thornton (1968) presents a comprehensive survey of scanning electron microscopy with particular emphasis on the Cambridge Instruments Stereoscan.

2.6.5. Transmission Electron Microscopy.

The interpretation of electron micrographs has now reached the state of a fine art. A full treatment of electron microscopy is given by Hirsch et al (1965). Principal difficulties encountered in the application of this technique to semiconductors arise in the actual thinning and handling of the specimens prior to examination. The specimen thickness an electron beam can penetrate is dependent on the accelerating voltage and the atomic number of the material. GaAs and GaP are so brittle that a uniformly thin specimen would be liable to shatter in the electron beam due to thermal expansion. This problem can be avoided by using thin areas supported by thicker material immediately adjacent. Such areas can be conveniently produced by jet thinning.

Meiran (1965) successfully thinned GaAs using electrolytic and chemical jet polishing methods. The specimen thickness was found to

be correct when yellow or orange light was just transmitted.

Biederman and Brack (1966), using a jet polishing technique, reported excellent results. They recommended a chemical polish consisting of HCl, H_2O_2 and H_2O in the ratio 40 : 4 : 1. Buiocchi (1967) reported the thinning of GaAs using a rotating beaker method. He used a chemical polish consisting of HNO_3 , HF, HCl and H_2O in the ratio 6 : 2 : 1 : 5. This polished rapidly on large {100} faces but had a negligible reaction at the edges which remained thick.

Hill et al (1968) described a technique for the automatic jet thinning of GaAs using a photomultiplier to detect the light transmitted through the specimen. When the signal from this reached a predetermined value corresponding to the required specimen thickness a solenoid was activated and the specimen was moved into position over a washing jet. Using the chemical polish described by Biederman and Brack and with improved handling techniques a very high success rate was achieved.

Several significant discoveries have been made by examination of GaAs using the electron microscope. Meiran (1965) found striations in Te doped material to consist of bands of very fine precipitates. Discrete particles were only present when the Te concentration was greater than $2 \times 10^{18} \text{ cm}^{-3}$ though the striations were visible by etching down to concentrations of 10^{17} cm^{-3} . Meiran also observed dislocation movement as the beam heated up the specimen. Abrahams et al (1967) observed precipitation in Se doped material with free electron concentrations from 4×10^{17} to $4 \times 10^{18} \text{ cm}^{-3}$. Moire fringes observed were consistent with the precipitates being $Ga_2 Se_3$. Kressel et al (1968) used electron diffraction analysis to positively identify precipitates present in Te doped GaAs as $Ga_2 Te_3$. Hill and Holt (1968) reported precipitates in Zn doped GaAs laser material. In some cases dislocations were observed which were apparently locked at

precipitates. They suggested that these dislocations resulted from the strain associated with the diffusion process.

Abrahams et al (1969a) examined misfit dislocations at graded heterojunctions of $\text{GaAs}_{1-x}\text{P}_x$ grown on GaAs substrates by vapour phase epitaxy. Their observations and conclusions were similar to those of Stringfellow and Greene (1969). The misfit dislocations present near the junction gave rise to a set of inclined dislocations that propagated through the growing crystal. The specimens were thinned first using Br methanol and then by ion beam thinning.

Twins and stacking faults were observed in vapour grown GaAs by Abrahams and Bulocchi (1967). The majority of faults seen by optical microscopy on the surface were identified as twins but stacking faults with associated Schockley partials were also found. More recent work by Abrahams and Tietjen (1969) identified stacking faults in $\text{GaAs}_{1-x}\text{P}_x$ material grown by vapour phase epitaxy as being intrinsic. Stacking faults were only observed in material doped with Se or Zn to free carrier concentrations $> 1 \times 10^{18} \text{ cm}^{-3}$. Wide variations in the length of the faults indicated that they were not introduced from the substrate and it was suggested that they might be nucleated at precipitate sites. Laister and Jenkins (1968) examined melt grown highly Te doped GaAs using transmission electron microscopy. They observed single and multiple stacking fault layers of an extrinsic nature. They suggested that these faults were due to rafts of Te atoms substituting for As on $\{111\}$ planes.

CHAPTER 3.Experimental.

The first part of this section describes the preparation of the materials actually examined in this research. With the exception of a number of laser diodes obtained from STL Harlow all the specimens were produced at the Services Electronic Research Laboratories in Baldock. The major part of the section describes the construction and use of equipment in the examination of these specimens.

3.1. Preparation of GaAs.

Bulk GaAs was grown by the horizontal Bridgeman, static freeze or Czochralski techniques. This was doped with Te, Se or Si to free carrier concentrations of $2 \pm 1 \times 10^{18} \text{ cm}^{-3}$. The ingots were polycrystalline but the large grain size enabled laser diodes to be made from single crystals. Slices were cut from the ingots and polished on a pitch plate using 2000 grit alumina powder. Zn diffusion into the slice was carried out in a quartz diffusion tube using a carefully controlled amount of Zn or ZnAs_2 as the source. The diffusion conditions were either 15 minutes at 1100°C without excess As or else 4 hours at 850°C with excess As. A p-n junction was produced on either side of the slice at a depth varying from 20 to 80 microns. One junction was removed by polishing and a gold film was evaporated onto the remaining diffused surface. The slice was then cut into strips, the narrow sides of which were polished and made accurately parallel to each other. Finally the strips were sawn into individual laser diodes and electrical and thermal contacts were formed by thermal bonding to gold plated Mo blocks. Mo was used because it has a similar thermal expansion coefficient to GaAs. The contacts were made ohmic by selective doping of the gold films.

3.2. Preparation of GaP.

GaP was grown either from a stoichiometric melt, from solution, by vapour phase epitaxy or by liquid phase epitaxy. Specimens produced by each of these methods were examined.

Large crystals were grown from the melt using the Czochralski pulling technique (Bass and Oliver 1968). The principal difficulties involved in using this technique were associated with the high melting point, 1465°C , of GaP and the high phosphorus overpressure required to prevent dissociation. Due to the inherent danger of explosion the apparatus had to be operated from a distance by remote control. Slices cut from the pulled n-type ingot were polished and used as substrates for liquid phase epitaxy. It has been found that diodes formed by growing an epitaxial p layer directly onto a pulled n-type substrate have very low efficiencies. Better quality diodes can be produced by double liquid epitaxy. In this process a Te doped layer with free carrier concentration $\sim 1 \times 10^{18} \text{ cm}^{-3}$ is first grown on the pulled slice and subsequently a Zn-O doped layer of similar free carrier concentration grown on top of this.

Liquid phase epitaxy of GaP was carried out using both the horizontal (tipping) and the vertical dip methods. The tipping method was preferred as it enabled the degree of melt-back of the substrate to be controlled more precisely. All liquid epitaxial layers were grown on the B or phosphorus $\{\bar{1}\bar{1}\bar{1}\}$ faces of the substrates which were previously chemically polished in boiling aqua regia. After the growth process the slices of material were cleaved into pieces giving junction areas from 1 to 4 mm^2 . Contacts were formed by thermally bonding Au - Zn wires to the p-type and Sn wires to the n-type material.

Material grown by vapour phase epitaxy was also examined. This

was produced using a PCl_3 , Ga, H_2 vapour transport system similar to that described by (Taylor et al 1968). The material was grown on the Λ or Ga $\{111\}$ face of a GaAs substrate which was previously polished in Br methanol. Te and S were used as dopants to produce n-type material but it was found impossible to adequately dope the material with Zn and O. Some diodes were made by liquid epitaxial deposition of Zn - O doped layers onto n-type vapour grown substrates. The diodes made in this way however, were much less efficient than those produced by a double liquid epitaxy process.

3.3. Etching and Polishing.

Metallurgical mounting plastic was used to facilitate handling of specimens. Mechanical polishing was done initially on 600 grade SiC paper. This was followed by a polish on a diamond wheel using 15 μ and subsequently finer grades of paste. Chemical polishing of GaAs was carried out using a 1% Br methanol solution in a rotating beaker. Chemical polishing of GaP was possible using the same reagent but the polishing rate was very slow. A more satisfactory reagent was found to be chlorine dissolved in methanol (Fuller and Allison 1962). This proved to be a rapid polish for the B or P $\{111\}$ faces of GaP but invariably produced etch pits on the Λ or Ga $\{111\}$ faces. This provided a convenient check on specimen orientation. To date, all chemical polishes reported for GaP give rise to similar etching effects on the Λ faces.

For the etching of surface defects in GaAs the Λ -B etchant described by Abrahams and Buiochi (1965) was used. The etching times and temperatures were taken from data given by Levene (1966).

3.4. X-ray Topography.

3.4.1. Construction of the Camera.

Using the basic design described by Schwuttke (1962) a camera

shown in figure 3.1. was constructed to take X-ray topographs, using Anomalous Transmission. A base plate was made from 'U' section Dural and machined to fit the specimen ramp of the Philips X-ray generator type PW1310. A 40 cm long by 1.2 cm diameter copper tube acted as the collimator & brass end pieces were made with 1 cm and 0.5 cm diameter apertures to produce various degrees of collimation.

The specimen stage was designed to allow specimen rotation about both the vertical and horizontal axes. The specimens were mounted over a hole in a lead disc that was then fixed in a vertical rotating bezel. The rotation of this was calibrated by a degree scale engraved round the periphery. A locking screw was incorporated to enable settings to be retained. The holder was mounted on a miniature micromanipulator block which enabled different portions of the specimen to be positioned in front of the collimator. Below the micromanipulator a steel shaft passed through a supporting bush to a gear train below the baseplate. A 360 : 1 gear ratio was employed so that one complete rotation of a handle protruding from the side of the baseplate turned the specimen through 1° about the vertical axis. The support arm for the film holder and Geiger tube was pivoted about the same axis as the specimen but could rotate independently. The rotation was indicated by a degree scale engraved on the side. A slot was machined centrally along the length of the support arm into which both the film holder and Geiger tube could be bolted. A locking screw was provided to keep the arm rigid during the alignment of the system.

The film holder was constructed from $\frac{1}{2}$ inch brass angle. A black perspex window was used in front of the film which was backed by a lead sheet and a light tight paxolin cover. A square section hole was cut in a bracket protruding horizontally from the rear of the

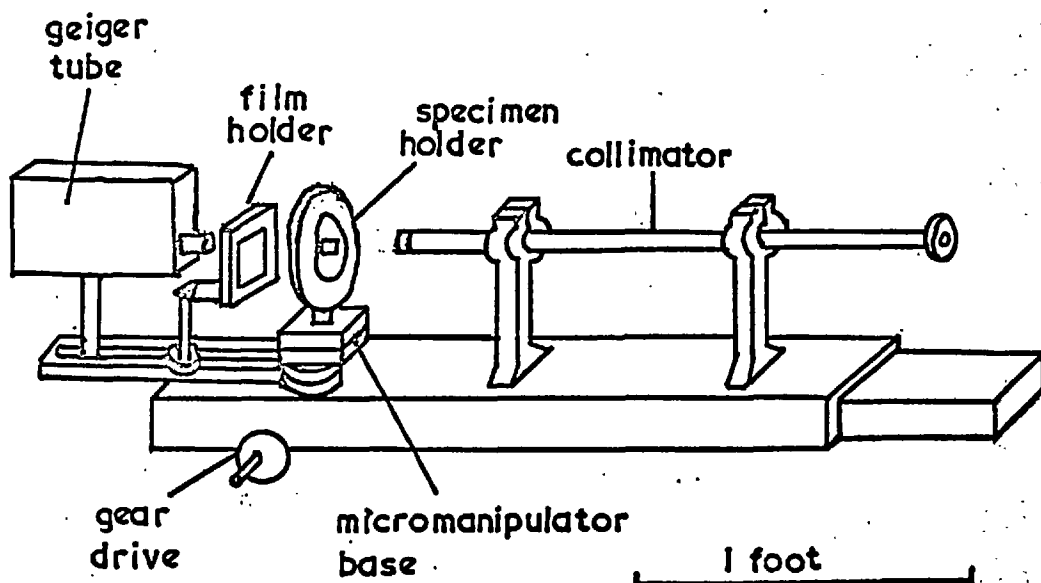


Figure 3.1 Drawing of the X-ray camera.

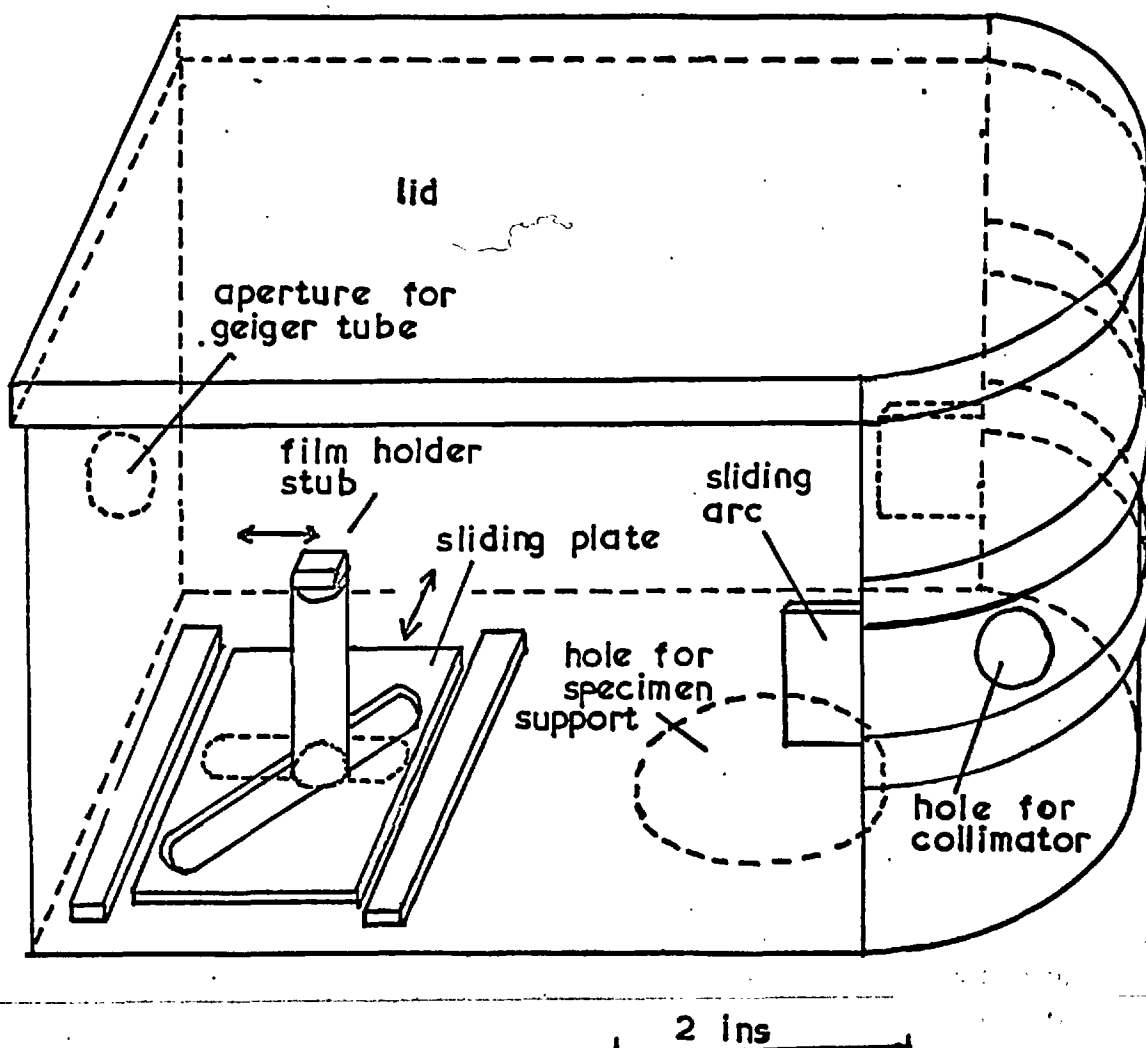


Figure 3.2 The protective screening.

film holder. This located over a peg on top of the supporting bolt and enabled the film holder to be removed and replaced without disturbing the alignment. A degree scale engraved at the bottom of the supporting bolt enabled the film holder to be oriented at a known angle to the X-rays. The general design of the camera is illustrated in figure 3.1.

Protective screening, illustrated in figure 3.2., was assembled from 16 gauge brass sheet. This consisted of a box with a removable lid, enclosing the specimen support and film holder. Facilities were incorporated to allow for the different geometrical arrangements likely to be required. The box was fixed to the film holder and geiger tube supporting arm and thus pivoted about the same vertical axis as the specimen. The side facing the collimator was of semi-cylindrical shape. Two flanges acted as guides for a sliding arc through which the collimator tube protruded. This arc remained stationary when the box was rotated and provided satisfactory screening for Bragg angles up to 30° . To allow for longitudinal movement of the film holder support peg a system of overlapping plates was used. A 45° slot was cut in the upper sliding plate through which the peg located. Movement of the film holder resulted in this plate sliding perpendicularly thus covering the lower fixed slot. To allow radiation to be detected by the geiger tube, which was mounted externally, a small hole was cut in the rear of the box. This could be covered by a shutter when the geiger tube was not in use.

3.4.2. Operation.

The camera was fixed to a port on the Philips PW1310 X-ray generator incorporating a horizontal line source and a Cu target. The geiger tube and rate meter supplied with the machine were used to detect the intensity of the anomalously transmitted X-rays.

Specimens of GaAs about 1 mm thick were stuck onto the lead disc using sellotape. The orientation of the specimen in relation to a line engraved on the disc was found by the X-ray Laue technique. The disc was clamped in the holder with the engraved line coincident with a zero marker and the specimen was then rotated about the horizontal axis till the chosen diffracting planes were vertical. This was to ensure that the diffracted beam was in the same horizontal plane as the incident beam. This is necessary from the geometry of the camera (see figure 3.3.) The Bragg angle θ was calculated for the chosen diffraction vector and the arm supporting the geiger tube moved to make an angle 2θ with the collimator. The specimen was then turned until the diffracting planes made an angle θ with the incident beam. This is fully described in section 4.1.2. The X-rays were turned on and the specimen orientation adjusted slightly to maximise the intensity of the diffracted beam as measured by the geiger tube. This final adjustment was necessary to insure the specimen was set exactly at the angle for Bragg reflection.

X-ray film or a nuclear plate (Ilford type L4) was loaded into the film holder which was placed in position. Exposure times were found to vary from $1\frac{1}{2}$ hrs for X-ray film to 6 hrs with nuclear emulsion. The development of both films and plates was carried out using standard solutions. The nuclear plates required 20 minutes development and about 30 minutes of fixing. Surface fogging was removed at the stop bath stage of the process by carefully rubbing the emulsion surface with a finger.

3.4.3. X-ray geometry in the Camera.

Ideally a broad beam of exactly parallel X-rays is required and this would be virtually impossible to obtain. An alternative is to use a horizontal line source and to have the diffracting planes

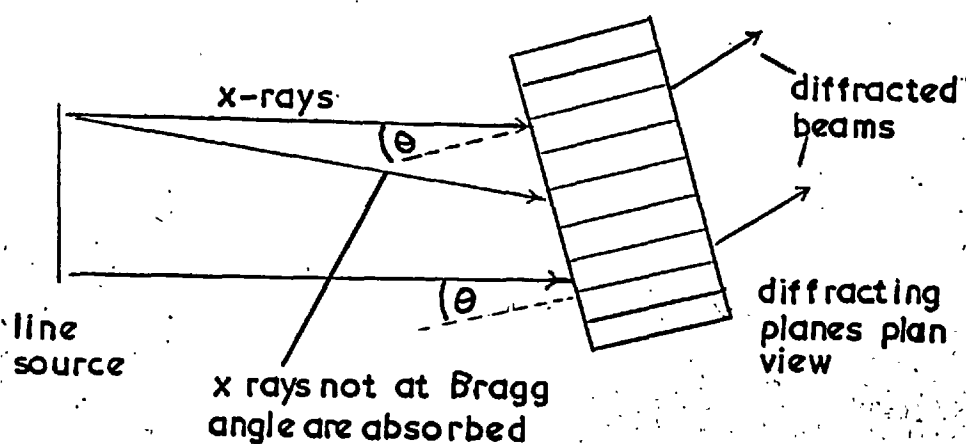


Figure 3.3 The diffraction geometry of a line source.

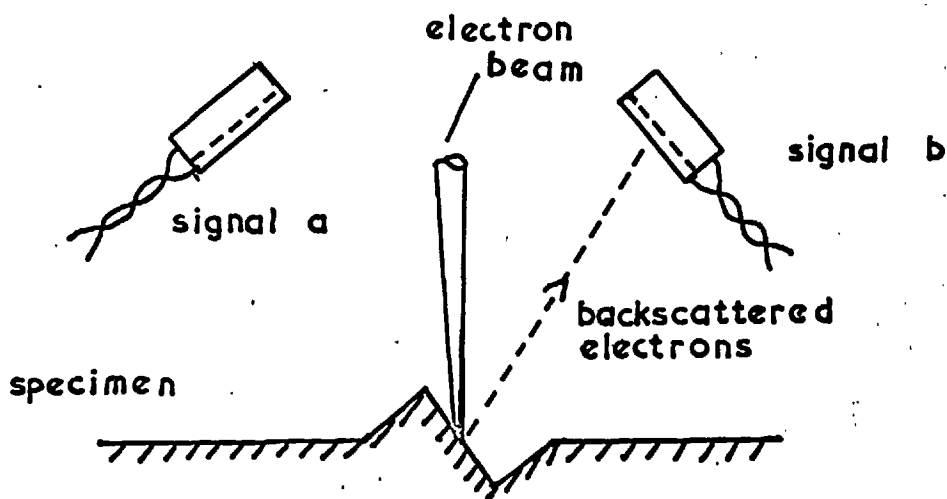


Figure 3.4 The detection of back scattered electrons in the electron probe.

vertical. Any one point on the line source would give rise to X-rays at the correct Bragg angle for a limited number of specific diffracting planes. This is illustrated in figure 3.3.

Anomalous transmission is so selective that the specimen acts as its own collimator. Any X-rays incident at other than the Bragg angle are strongly absorbed. Thus resolution is unimpaired by the relatively poor collimation of the original X-rays. The divergence of X-rays in the vertical plane is maintained in the anomalously transmitted beam & this gives rise to a distortion of the image. The degree of distortion depends on the initial collimation. To minimise distortion the source to specimen distance must be large compared to the specimen diameter.

3.4.4. Resolution.

The principal factor influencing resolution is the separation of the $K\alpha$ doublet. Schwuttke (1962) calculated a resolution of about 10μ for a similar geometrical arrangement to that reported here. The Borrmann delta effect also impairs resolution. This was first described by Borrmann et al (1955) and is a spreading of energy between the diffracting planes. The result is that imperfections near the incident face give rise to diffuse images on the film. The energy spread only occurs normal to the diffracting planes so that different diffracting planes give rise to slightly different resolutions. The specimen can also be reversed to show detail at defects previously near the incident face.

The grain size of the nuclear emulsion on the L4 plates was about 0.14μ and did not result in loss of detail. The emulsion however, was very thick (50μ) and to prevent overlapping of images it was necessary to make exposures with the plates normal to the X-ray beam.

3.5. Scanning Electron Beam Techniques.

During the initial stages of this research the only instrument available was a J.E.O.L. electron probe microanalyser and this was used to examine GaAs diodes. Shortly after the emphasis of the project had been changed to the study of GaP a Cambridge Instruments Stereoscan became available. The versatility of this instrument, a scanning electron microscope or S.E.M., made it eminently suitable for the subsequent examination of the electrical and luminescent properties of GaP diodes.

3.5.1. The Display of Surface Detail.

The two instruments differ in the means used to display topographic detail of the specimen surface. In the electron probe, back scattered electrons are detected by two Si p-n junctions suspended above the specimen (figure 3.4.) The signals from the two diodes are fed into an amplifier where they are electronically added or subtracted and the resulting signal is displayed on the C.R.T.. When the signals are subtracted the resultant is highly sensitive to the surface topography of the specimen. With addition of the signals the resultant is sensitive to the overall density of back-scattered electrons and is thus influenced by atomic weight variations in the specimen.

In the case of the S.E.M. the principal source of topographic detail is the emission of secondary electrons. For these low energy electrons a more complex detection system is required. In the Stereoscan this consists of the scintillator-photomultiplier combination illustrated in figure 3.5. The secondary electrons emitted from a surface element are pulled towards a positively charged Faraday cage. Electrons penetrating the top gauze are accelerated towards a scintillator which is coated with a layer of Al 500 Å thick

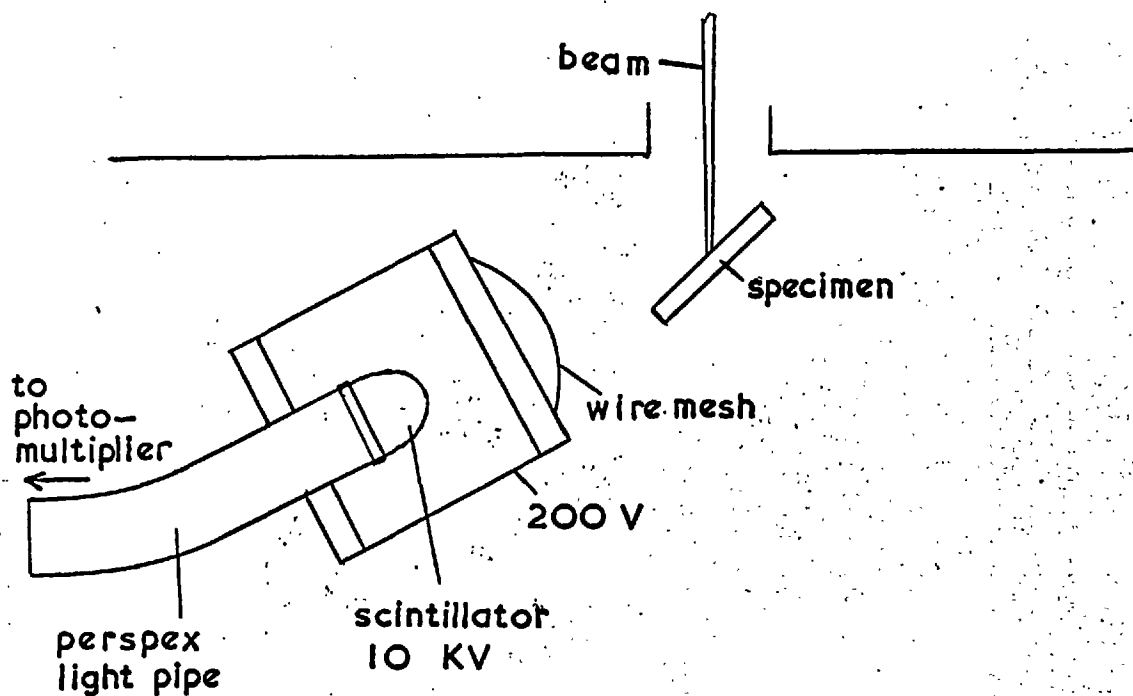


Figure 3.5 The secondary electron detection system of the S.E.M.

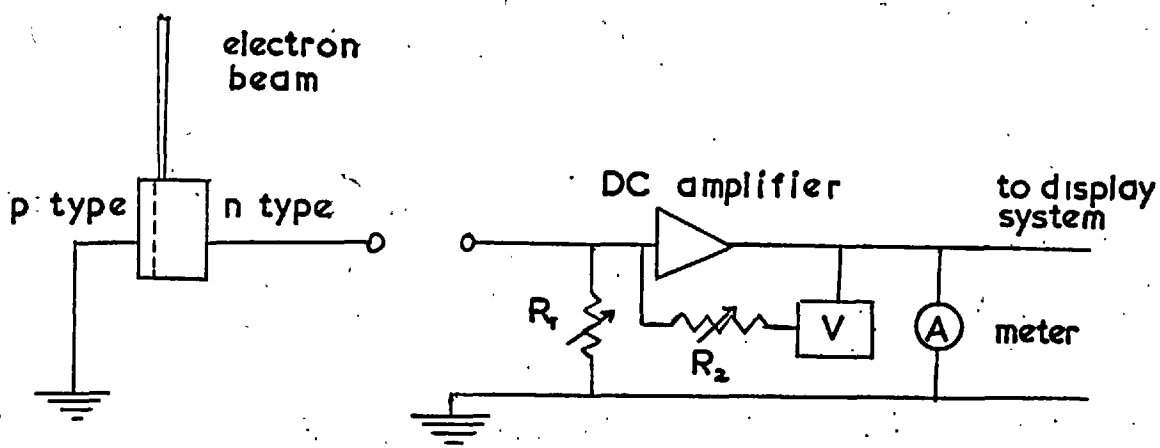


Figure 3.6 The circuit used for the detection of the charge collection current.

and maintained at a positive potential of 12 KV. Each electron reaching the scintillator therefore has a kinetic energy of some 12 KeV. This energy excites the scintillator material and a portion of the emitted light travels via a perspex light pipe to a photomultiplier. The signal from the photomultiplier is used to form an image on the C.R.T.. Back scattered electrons which are reflected into the solid angle subtended by the scintillator will also be detected. In normal use however, these form only a small fraction of the total signal. For maximum collection efficiency the specimen must be orientad so that the incident electron beam and the line joining the collector to the specimen subtend equal angles with the normal to the specimen surface. Topographic detail is observed as a change in signal intensity when localised surface fluctuations alter the ratio of these angles.

3.5.2. The Charge Collection Mode.

Both the electron probe and the S.E.M. were provided with specimen current amplifiers. In normal use these were connected directly to the specimen and used to monitor the portion of the beam current flowing through the specimen to earth. The signal thus detected is inverse in nature to that provided by secondary and back scattered electron detection systems.

To monitor the charge collection current from a p-n junction it was necessary to short-circuit the junction through the current amplifier as illustrated in figure 3.6. The "n" side of the diodes were connected to the amplifier through the specimen mount and the "p" side was connected to earth. As one side of the current amplifier is also earthed the earth return completes the circuit.

In both instruments the current amplifiers consisted of high resistance electrometer circuits with a range of shunt resistors

connected across the input. In the probe the amplifier was coupled directly to a display meter which registered full scale deflection when a potential of one volt was applied to the grid of the first valve. By switching in different shunt resistors, R1, this full scale deflection could be made to correspond to currents from 10^{-8} to 10^{-5} amps. A current suppression or back-off control was also provided. This comprised a stabilised voltage supply in series with a variable set of resistors, R2. A known current could thus be fed into the meter input in the reverse sense to that provided by the specimen. The use of this control played an important part in adjusting the contrast level of the visual display. Any background current could be backed off to zero and the sensitivity of the amplifier increased so that small fluctuations in current input showed up as large changes in contrast on the viewing screen.

In the S.E.M. the current amplifier had a greater span of current ranges from 10^{-12} to 10^{-2} amps making it more suitable for this type of work. Using the electron probe on its least sensitive range of 10^{-5} amps the charge collection signal from a GaAs diode invariably peaked. With the S.E.M. however, it was possible to observe the whole signal without any overloading of the amplifier.

3.5.3. The Cathodoluminescent Mode.

Both instruments were adapted for the detection of cathodoluminescence by the addition of photomultiplier systems. For infra-red work on GaAs a photomultiplier type 150 CVP with an S1 photocathode was fitted to the electron probe. The J.E.O.L. electron probe incorporates a good quality optical microscope. A reflecting objective is positioned above the specimen which can be observed at 200 X magnification through an eyepiece projecting from the front of the column. Illumination is provided by a lamp in a housing fitted to a port in

the side of the column. An adapter was constructed to enable the photomultiplier to be fitted to this port as shown in figure 3.7a.

The adapter was made in the form of a T piece using $1\frac{1}{2}$ inch diameter steel tubing. A stainless steel mirror was used to reflect light provided by the lamp into the microscope when specimen illumination was required. For cathodoluminescence detection the light was switched off and the mirror moved up using an external control so as to block off the tube leading to the lamp. This had the advantage of protecting the photomultiplier from damage should the light inadvertently be turned on. A direct light path was thus established between the microscope port in the column and the photomultiplier. Some initial work on GaP was done using the electron probe and for this purpose a photomultiplier type 9664B with an S10 photocathode was used.

The only suitable amplifier available on the probe was that used for specimen current amplification. This proved to be suitably matched to the photomultiplier output which was connected directly using a supplementary switch. The dark current of the infra-red photomultiplier was 3×10^{-6} amps. The suppression control enabled this to be backed off so that only the random noise remained superimposed on the detected signal. For material with a high cathodoluminescent efficiency this enabled images of good resolution to be obtained.

For work principally on GaP the S.E.M. was fitted with a 9558B photomultiplier with an S20 photocathode. To obtain optimum detection efficiency the photomultiplier was placed inside the vacuum system in direct line of sight of the specimen. A special case for the photomultiplier was constructed from $2\frac{1}{2}$ inch diameter brass tube (figure 3.7b). This was fixed to a suitable port on the side of the specimen chamber using a flange and an O-ring seal.

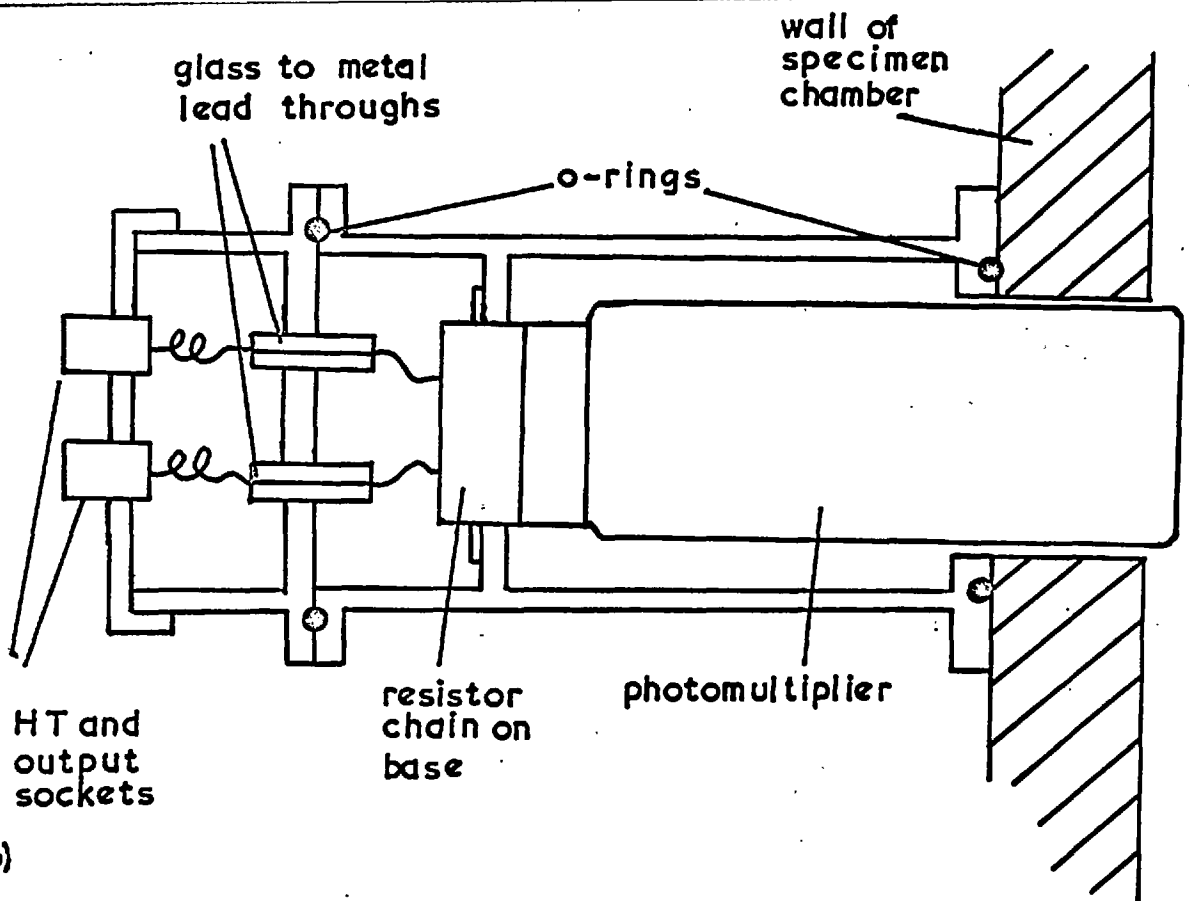
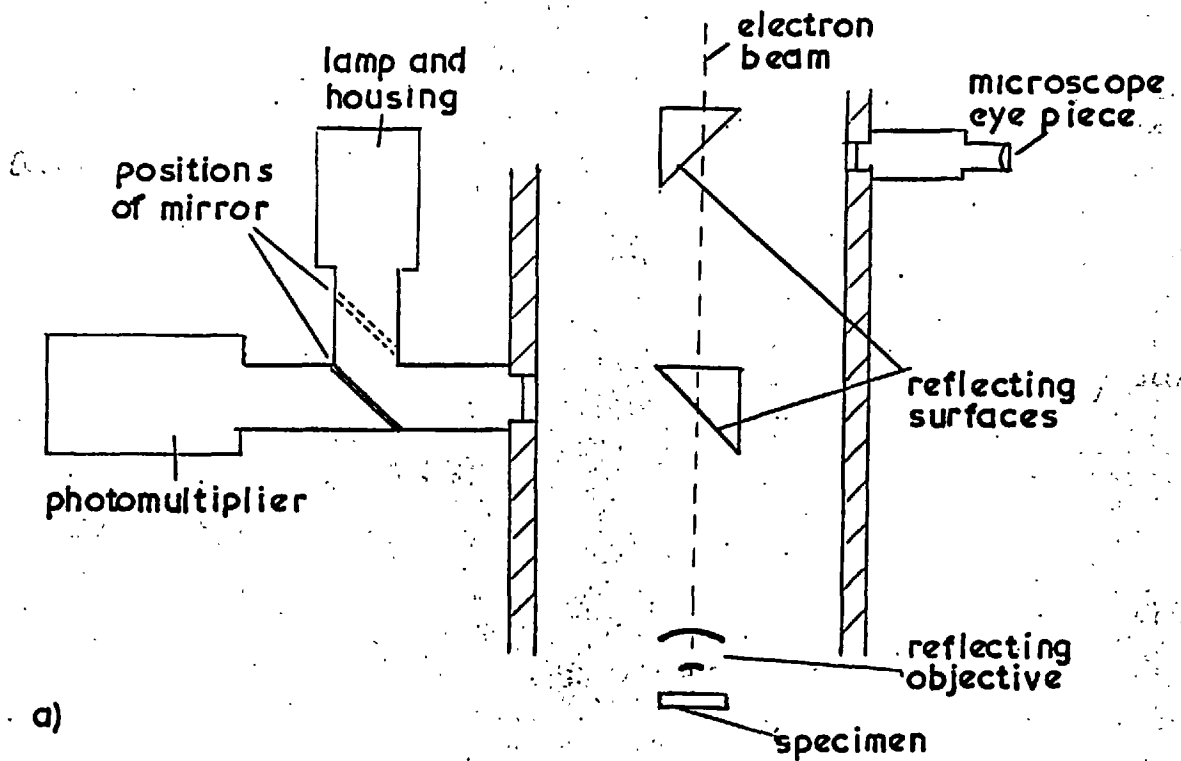


Figure 3.7 a) Schematic diagram of the system used to detect cathodoluminescence in the electron probe.
 b) Drawing (approx. half size) showing the photomultiplier mounted in the vacuum-tight case fixed to the wall of the specimen chamber of the S.E.M. and in direct line of sight with the specimen.

The leads from the photomultiplier and resistor chain inside the vacuum were connected to two glass-to-metal lead-throughs in the back plate. This was also sealed to the tube using a flange and an O-ring. A chamber open to the air behind this enabled suitable sockets to be fitted connecting with the lead-throughs.

As a photomultiplier with similar output characteristics was built in to the secondary electron detection system it was decided to use the amplifier and preamplifier associated with this for the cathodoluminescence channel. An input socket for a second channel was wired into the preamplifier and a miniature low-leakage switch used to change from one to the other. No adverse pick-up or interference effects could be detected as a result of this modification. With both the electron probe and the S.E.M., the photomultipliers were powered by a separate stabilized power pack. In the case of the S.E.M. the voltage control on the power pack was used to adjust the signal strength to an optimum level, the amplifier being of preset sensitivity. An adequate degree of back-off was still available electronically using a control built into the video amplifier.

3.5.4. Additional Features.

The X-ray fluorescence facility of the electron probe was used to analyse precipitates in Zn diffused GaAs and in Te doped GaP. The sensitivity however, was limited to impurity levels greater than 500 ppm and it was not possible to detect normal dopant concentrations of up to $2 \times 10^{18} \text{ cm}^{-3}$.

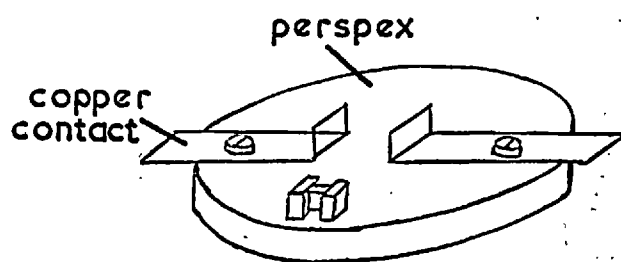
In the probe a facility existed for traversing the specimen beneath a stationary electron beam using a synchronous motor. The measured intensity of the detected signals could be connected up to a chart recorder. As the chart speed was a known multiple of the specimen traversing speed it was possible to obtain accurately

calibrated line scans as in figure 4.8. With the S.E.M., y modulated line scans could be obtained in the form of an oscilloscope trace figure 4.22. The use of multi-exposure photography enabled a direct comparison to be made between different signals. This was found to be of special interest when the beam scanned a line intersecting a p-n junction.

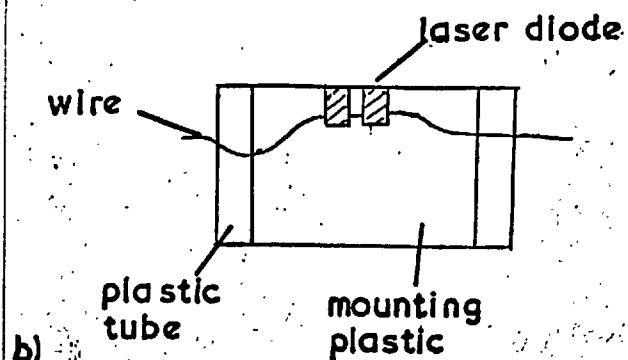
3.5.5. The Mounting of Specimens.

For the examination of laser diodes in the electron probe a small holder was made with a perspex base as shown in figure 3.8a. Diodes could be clamped between the two copper contacts, one of which was connected to the current amplifier whilst the other was earthed. For more rigorous examination diodes were set in mounting plastic, figure 3.8b. Wires were first soldered to the laser terminals and then threaded through the walls of a small section of polythene tube which acted as a mould. With the polished face of the laser pressing down on a glass slide the tube was filled with cold setting plastic. When this had hardened the glass slide was removed and any plastic covering the diode face polished off. By painting the exposed wires with lacomit it was possible to chemically polish or etch the exposed diode surface without risk of damage to the diode or its connections.

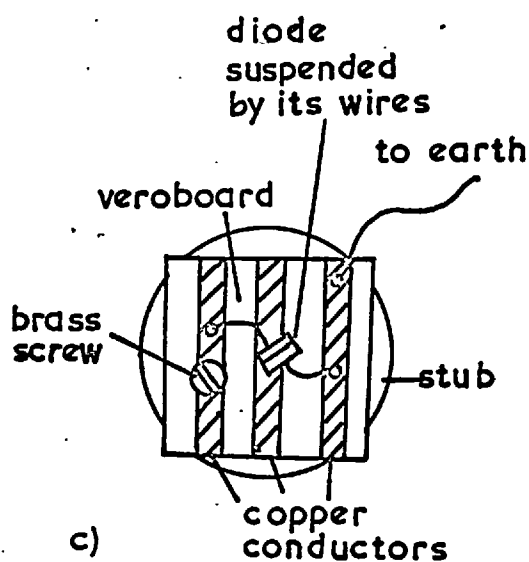
For the examination of GaP diodes in the S.E.M. it was found satisfactory to simply suspend the diodes by their wires. A hole was drilled and tapped in a specimen stub and used to fix down a 1 cm^2 piece of printed circuit veroboard. The diode was soldered into place on the contact strips with the n side connected to the current amplifier via the specimen stub. The p side was earthed using a suitable point on the specimen stage. This and an alternative method of mounting using a perspex insulator are illustrated in figure 3.8 c and d.



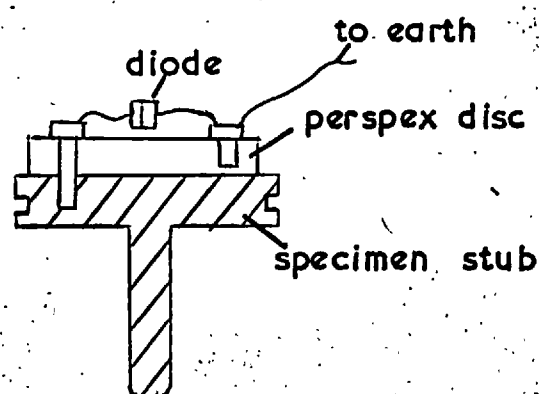
a)



b)



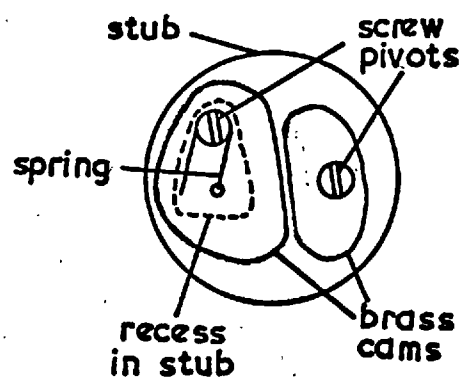
c)



d)

Figure 3.8 Diagram showing the various methods used to mount specimens for examination in the electron probe and the S.E.M.

- a) Clamp for GaAs diodes,
- b) Laser diode mounted in cold setting plastic.
- c) GaP diode mounted on veroboard
- d) GaP diode mounted on perspex base
- e) Spring loaded clamp used for holding thin transmission specimens.



e)

Some work was done using the S.E.M. in a transmission mode. Specimens were in the form of 2.3 mm discs which had already been thinned and examined in the conventional transmission electron microscope. A mount was constructed figure 3.8e in which the specimen was held in place in a vertical plane by a spring loaded brass cam. A recess was machined in a standard specimen stub to contain a small spring made from .005 inch tungsten wire. Only a very small spring pressure was found necessary to hold a specimen in place between the cam and an abutment plate. In use, the stub was tilted using the controls of the specimen stage so that the specimen was normal to the electron beam. Secondary electrons emitted from the underside of the specimen could then be detected by the scintillator.

3.6. Transmission Electron Microscopy.

A large number of specimens of GaP were examined using the A.E.I. EM6G electron microscope. The specimen stage in this instrument only allowed 10 degrees of specimen tilt and in cases where a higher degree of tilt was required a Siemens Elmiskop 1 was used. Specimens were prepared using a jet thinning technique.

3.6.1. The Thinning Apparatus.

The thinning apparatus (figure 3.9) was a modification of that described by Hill et al (1968). The reagent jet and a washing jet were enclosed in a PVC box below the level of the specimen which was fixed into a PTFE turntable. When set up, the activation of a solenoid caused the turntable to rotate moving the specimen from above the main jet to above the washing jet. A weight, connected to the turntable by a nylon cord, provided the rotational force.

The jet nozzles were drawn from glass tubing. A perspex light guide was built into the main jet to enable illumination of the specimen through the jet. This guide was sealed into the PVC box with an O-ring.

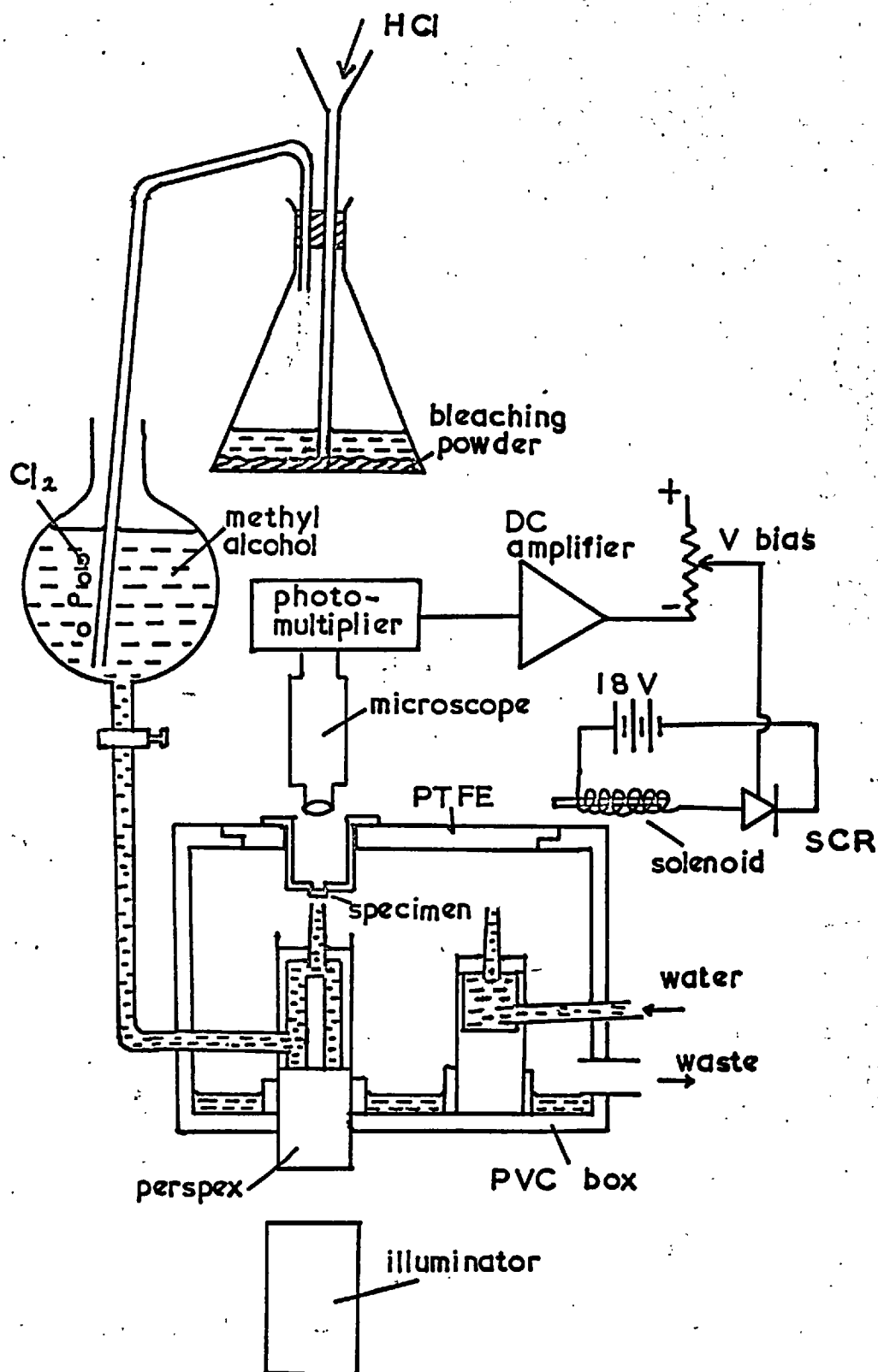


Figure 3.9 Schematic drawing of the jet thinning apparatus.

A microscope was used to position the specimen accurately over the main jet and to observe light transmitted through the specimen during thinning. A photomultiplier with an S10 photocathode could be positioned on top of the microscope in place of the eyepiece. The output from this was fed into a stabilised DC amplifier and on reaching a certain level triggered an SCR. which activated the solenoid. As a result, when the light reaching the photomultiplier through the specimen had increased by a predetermined amount the specimen was automatically repositioned over the washing jet.

The photomultiplier was sensitive to wavelengths of light which were transmitted by GaP with little absorption. To obtain adequate sensitivity it was necessary to selectively remove these wavelengths by the use of suitable filters. It was found that a Wratten filter 47B used in conjunction with a Chance OB10 metal oxide filter to remove infra-red gave satisfactory results. The details of the process are discussed in section 5.4.1. The two filters were positioned inside the photomultiplier case rather than at the illumination source to reduce the influence of extraneous light. As a result it was found possible to operate the system under conditions of normal room lighting.

3.6.2. The Thinning Process.

During the development of the thinning technique for GaP the available specimens were of vapour grown type. These had been grown on the A faces of GaAs substrates. Thinning was done from the B face or GaAs side so that the final thin area would be distant from the GaP - GaAs interface. As it is relatively simple to obtain a good polish on the B face of GaP smooth well shaped dimples with large thin areas could be formed.

The choice of a chemical reagent presented a problem. The chemical

polishes generally used for GaAs had much lower polishing rates when applied to GaP. Three of the more rapid reagents were considered. Boiling aqua regia commonly used as a polish for GaP was not found to be suitable for jet thinning. Br methanol although a satisfactory polish was unsuitable because of the effect of optical absorption by the Bromine on the light passing through the jet. With the filters in place no light could be detected by the photomultiplier even without a specimen in position. The third alternative, Cl in methanol (Fuller and Allison 1962) was found to be satisfactory. This was produced as required by the apparatus illustrated in figure 3.9. Concentrated HCl was fed into a conical flask containing bleaching powder. The chlorine gas that was evolved was bubbled through a flask containing methanol. A tap below this enabled the solution to be fed directly to the jet. The used reagent could be collected and prior to reuse was again activated with chlorine.

The thinning of GaP grown by liquid phase epitaxy presented another problem. This material was grown on the B face of pulled or vapour grown GaP substrates. In order to thin the material from the substrate side it was necessary to find a means of polishing the A face of GaP. Using Cl methanol as a chemical polish it was found impossible to form a satisfactory dimple. In general attack occurred preferentially at the edges of the specimen leaving a raised portion in the centre covered with numerous etch pits. The problem was solved by using an electrochemical technique involving the same apparatus and reagent. The specimen was connected to the positive terminal of a battery. The negative electrode consisted of a short length of tungsten wire inserted into the jet nozzle from below. With an applied potential of 120 volts the current flow was about 20 ma. With these conditions a smooth sided dimple could be produced on the A faces of specimens. The surface of the dimple was covered by a

yellowish film which could be removed by chemical action when the current was switched off for a few seconds. Unfortunately this surface film had a very high optical absorption coefficient and as a result the automatic detection system was triggered only when a hole appeared in the thin area. This was unsatisfactory and better results could be obtained using visual control. By repeatedly turning off the current to disperse the surface film the true appearance of the thin area could be observed. The specimen thickness was correct when light which appeared nearly white to the eye was transmitted. A successful alternative system was to use electrochemical polishing to produce a dimple on the A face of a specimen. The specimen was then reversed in the mount and finally thinned chemically from the B face. In this way the automatic mechanism could be used in the final stage of the process. This also had the advantage of removing any possible surface damage and meant that no special surface polishing was required prior to thinning. Some specimens were examined in the electron microscope with the yellow surface film remaining in order to try to establish its nature. In the majority of specimens it was removed by a short chemical polish. It was found possible to remove the film from the A faces without causing any detectable etching of the surface.

3.6.3. Mounting Specimens for Thinning.

The vapour grown GaP was received in the form of very thin layers. To facilitate handling small pieces were cleaved off and mounted, using silver paint, over small holes drilled in 2.3 mm diameter Ta discs. The discs were prepared by punching from .01 inch sheet using a punch and die specially made from silver steel. A No 50 drill was used to form a hole in the Ta sheet prior to this operation. A small spigot machined centrally on the punch located in this hole

so that it was automatically in the exact centre of the finished disc. Various stages of the process are illustrated in figure 3.10. The liquid phase epitaxy and pulled specimens were more robust and discs of 2.3 mm diameter were cut ultrasonically from the material as received.

The specimen holder for the jet thinner is illustrated in figure 3.10. The specimens were positioned beneath a 1.5 mm hole in a stainless steel plate. Silver paint was used to ensure electrical contact for the electrochemical process. When this had dried the metal plate and the edges of the specimen were coated with a layer of picene wax so that just the area to be thinned was exposed. This prevented current flow to regions that needed to be preserved. Lacomit, a more conventional masking paint, was found to be porous to the reagent and was thus unsuitable for this purpose. After thinning, the specimens were removed by dissolving the picene wax in trichloroethylene and peeling off the silver paint with tweezers. The specimens were then washed in hot trichloroethylene followed by a rinse in both ethyl alcohol and deionised water.

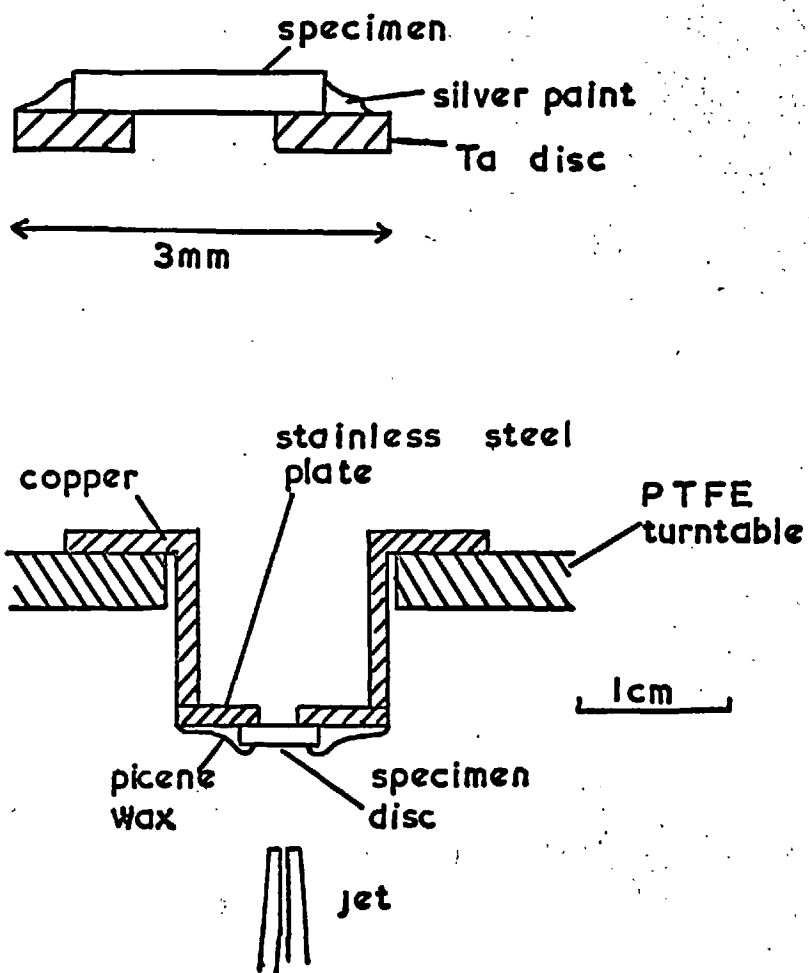


Figure 3.10 Techniques used to mount specimens for thinning.

CHAPTER 4.

RESULTS.

4.1 X-ray Topography of GaAs.

4.1.1 Diffraction Vectors.

All the slices of GaAs examined had large faces of near $\{100\}$ orientation. The strong diffracting vectors of GaAs are those characteristic of the FCC and diamond structure. The relative intensities were found from the A.S.T.M. index file and by structure factor calculation [table 4.1]. The determination of the structure factor for the various reflections in the sphalerite structure was carried out as described by Cullity (1956). The forbidden reflections hkl of the FCC structure, where h, k and l are mixed (odd and even) indices, are also forbidden in the sphalerite structure. This results directly from the fact that the sphalerite structure consists of two interpenetrating FCC lattices as described in section 2.4.1. The relative intensities for the remaining allowed hkl reflections are given by the expression:-

$$|F|^2 = 16 (f_{Ga}^2 + f_{As}^2 + 2 f_{Ga} f_{As} \cos \pi / 2 (h + k + l))$$

where f_{Ga} and f_{As} are the X-ray atomic scattering amplitudes. For the calculation, values of f_{Ga} and f_{As} were taken from tables in Cullity. The relative intensities listed in the A.S.T.M. index file are for powder specimens and thus differ slightly from the calculated values which refer specifically to a single crystal specimen set exactly on the Bragg condition.

Reflection	$I/I_{111} \times 100$. (ASTM)	$ F ^2/16$ (Calculated)
111	100	1369
200	< 1	3.2
220	35	1938
311	35	835
400	6	1345

Table 4.1 Relative intensities of different reflections in GaAs.

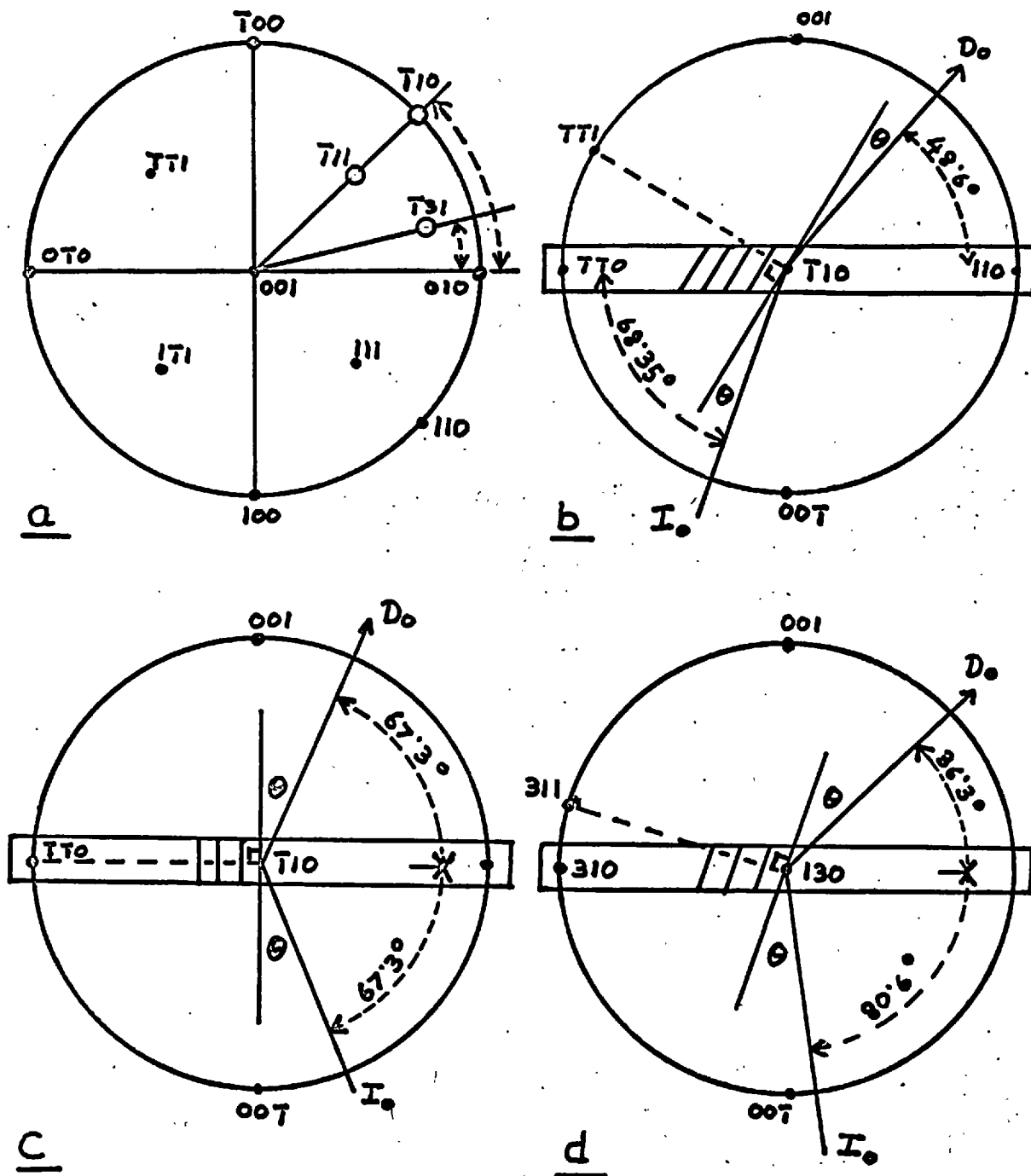


Figure 4.1

a) Stereogram of cube projection on the (001) plane. The rotations required to bring the diffracting planes to the vertical are indicated by arrows.

b), c), d). Stereograms superposed on the real image of the specimen viewed from vertically above showing the path of X-rays for different diffracting vectors.

b) 111 with $\theta = 13.65^\circ$ $2\theta = 27.30^\circ$

c) 220 with $\theta = 22.69^\circ$ $2\theta = 45.38^\circ$

d) 311 with $\theta = 26.9^\circ$ $2\theta = 53.8^\circ$

I_0 and D_0 represent the incident and diffracted beams in the horizontal plane.

It can be seen from the table that the strongest reflections are of type 111, 220 and 311. However, with $\{100\}$ specimen orientations the most practical reflection was found to be the 220. The reason for this is best illustrated stereographically. Figure 4.1 a shows the stereogram of a cube projection on (001) with the diffracting planes marked. The $\{001\}$ large faces of the specimen remained in a vertical plane by virtue of the camera geometry. During alignment the specimen was rotated about the normal to these surfaces to bring the chosen diffracting planes to the vertical. On the stereogram the line joining the normal to the chosen diffracting planes to the centre will then be horizontal. Looking down vertically onto the specimen in this position a further stereogram can be constructed with the chosen diffracting planes on its circumference. Figures 4.1 b, c and d show these stereograms for each set of diffracting planes. The real image outline of the specimen as seen from above is superposed on each stereogram together with the path of a possible X-ray beam. Here I_0 represents the direction of the incident beam and D_0 the diffracted beam. The geometry is such that this notation is interchangeable.

To prevent lateral distortion of the image, bearing in mind that the film must be perpendicular to the X-rays, the angle between D_0 and the specimen surface must be large. To provide maximum X-ray intensity over a given area the angle made by I_0 must also be large. As can be seen from the diagrams, these conditions are best met by the 220 reflection where both I_0 and D_0 make an angle of 67.31° with the surface. As a result the topographs presented here were all taken using this diffraction vector.

4.1.2 White Radiation.

Initially one of the problems encountered was the presence of high energy white radiation which was not absorbed by the material. This

gave rise to spurious images of poor resolution, obliterated the image due to the direct beam and caused overall fogging of the film. These effects are illustrated in figure 4.2. It was apparent that these white X-rays penetrated the specimens with very little absorption and that the intensity of the transmitted radiation was independent of specimen orientation, i.e. this was not an effect attributable to anomalous transmission.

The linear absorption coefficient in GaAs was measured for white radiation emitted at a tube voltage of 40KV and current 30 ma using a Cu target. To eliminate the Cu K α radiation from the measurement, a slice of GaAs, deliberately misoriented from the Bragg condition, was used as a filter. Another slice of GaAs was used as the specimen and the count rate for the incident and transmitted X-rays measured using the geiger tube. The count rates were found to be 4400 and 1020 counts per second respectively.

Using the relation $I = I_0 \exp(-\mu t)$ the value of t was found to be 1.39. With the specimen thickness of 0.05 cm this gave a value for μ of 27.8 cm^{-1} and for μ/ρ of 5.23. The absorption spectra of GaAs was plotted from mass absorption tables using the relation:-

$$(\mu/\rho)_{\text{GaAs}} = 0.5 (\mu/\rho)_{\text{Ga}} + 0.5 (\mu/\rho)_{\text{As}}$$

This curve is shown in figure 4.3 together with the Cu X-ray emission spectrum. The measured value of μ/ρ was compared with this absorption spectrum and was found to correspond to X-rays of wavelength near $0.4 \text{ \AA}$.

To produce radiation down to a wavelength λ it is necessary to use a voltage on the tube given by the expression $\lambda V = 12,400$ (Cullity 1956). For a wavelength of $0.4 \text{ \AA}$ the corresponding value of V is 31,000 volts. This effect is illustrated in figure 4.3 by the two spectra corresponding to voltages of 60 kV and 30kV. It was found that by using voltages of 29 kV or less on the tube, the white radiation was limited to

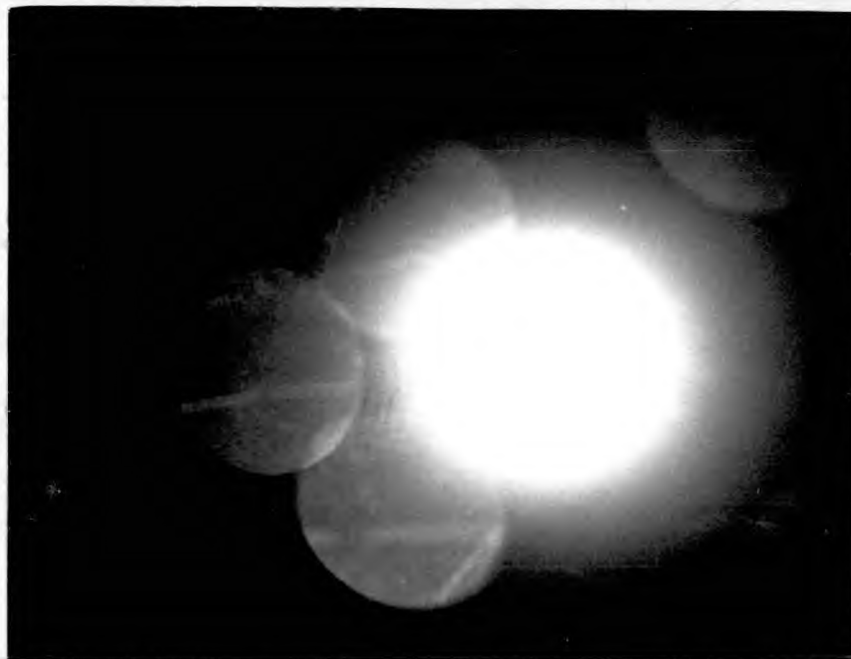


Figure 4.2 X-ray topograph showing multiple images and fogging caused by the presence of high energy white radiation.

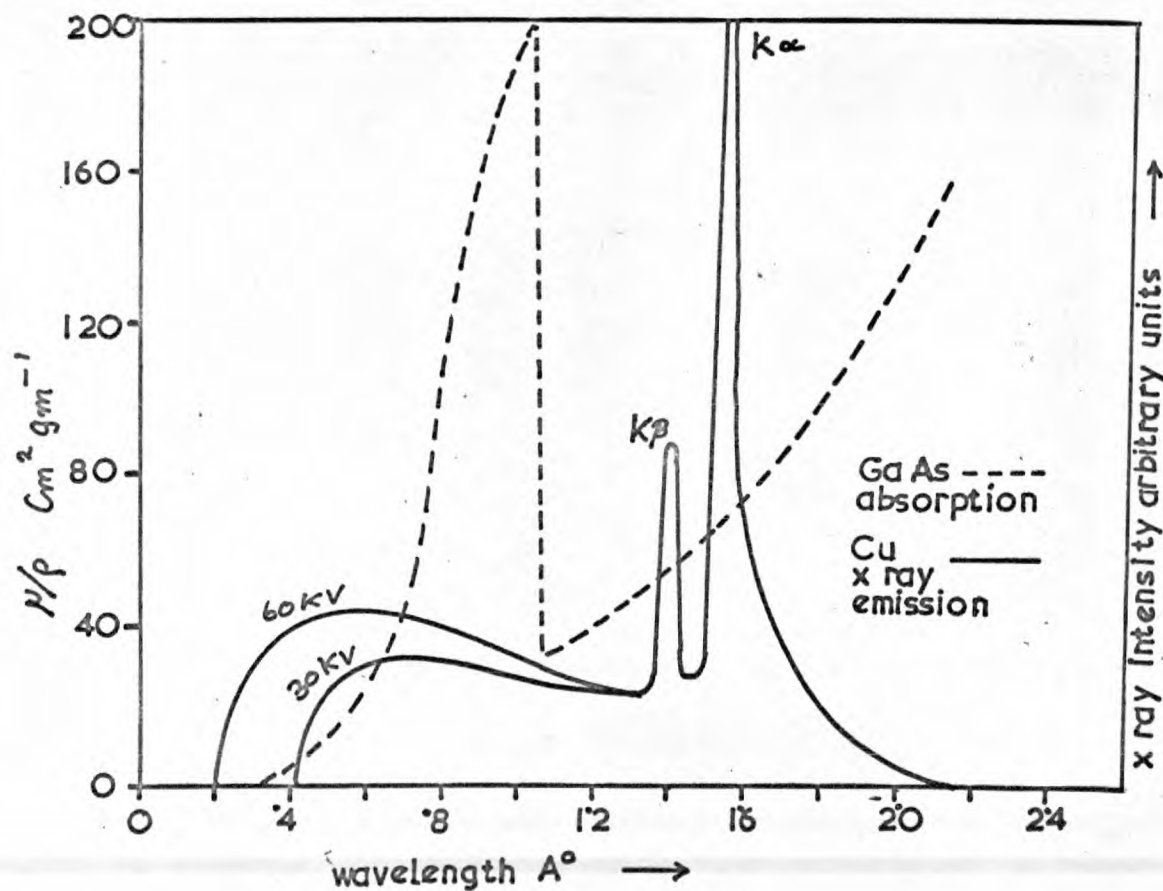


Figure 4.3 The Cu X-ray emission spectrum showing the relation of the high energy white radiation to the GaAs absorption spectrum.

frequencies that were completely absorbed by the specimen and the undesirable effects as illustrated in figure 4.2 were eliminated.

4.1.3 Topographs.

Two polished slices from Si doped GaAs ingots were examined. In the S.E.R.L. notation these were Si, 661 slice 12 and Si, 643 slice 2. Both were grown by the static freeze technique. The former was shown by a Laue diffraction pattern to be polycrystalline and as a result no satisfactory topographs were obtained. The other specimen was more satisfactory and using the 220 reflections good resolution topographs were obtained. Topographs taken from either side of the specimen are shown in figure 4.4. Figures 4.4 a and b illustrate the identity of images formed by the direct and diffracted beams. A comparison with figure 4.4 c taken from the other side of the specimen shows evidence of the Borrmann delta effect. For example those images indicated by numbers 1 and 4 appear sharp in figures 4.4a and b but appear blurred in figure 4.4c. Conversely those indicated by numbers 2 and 3 appear sharp in figure 4.4c and blurred in figures 4.4a and b. The degree of blurring gives some indication of the depth of the defects with respect to the emergent face.

Surface scratches are visible in the topographs as fine sharp lines. The large irregular shaped dark blobs were interpreted as being due to the presence of precipitates or inclusions. No evidence of these could be detected by optical inspection of the surface. A large ring like defect complex is also visible in the topographs.

For comparison the specimen was etched using the A-B etchant, Abrahams and Buicchi (1965). The resulting surfaces are shown in figures 4.4d and 4.4e. A large proportion of the detail shown in the topographs was also revealed by the etch. In particular the

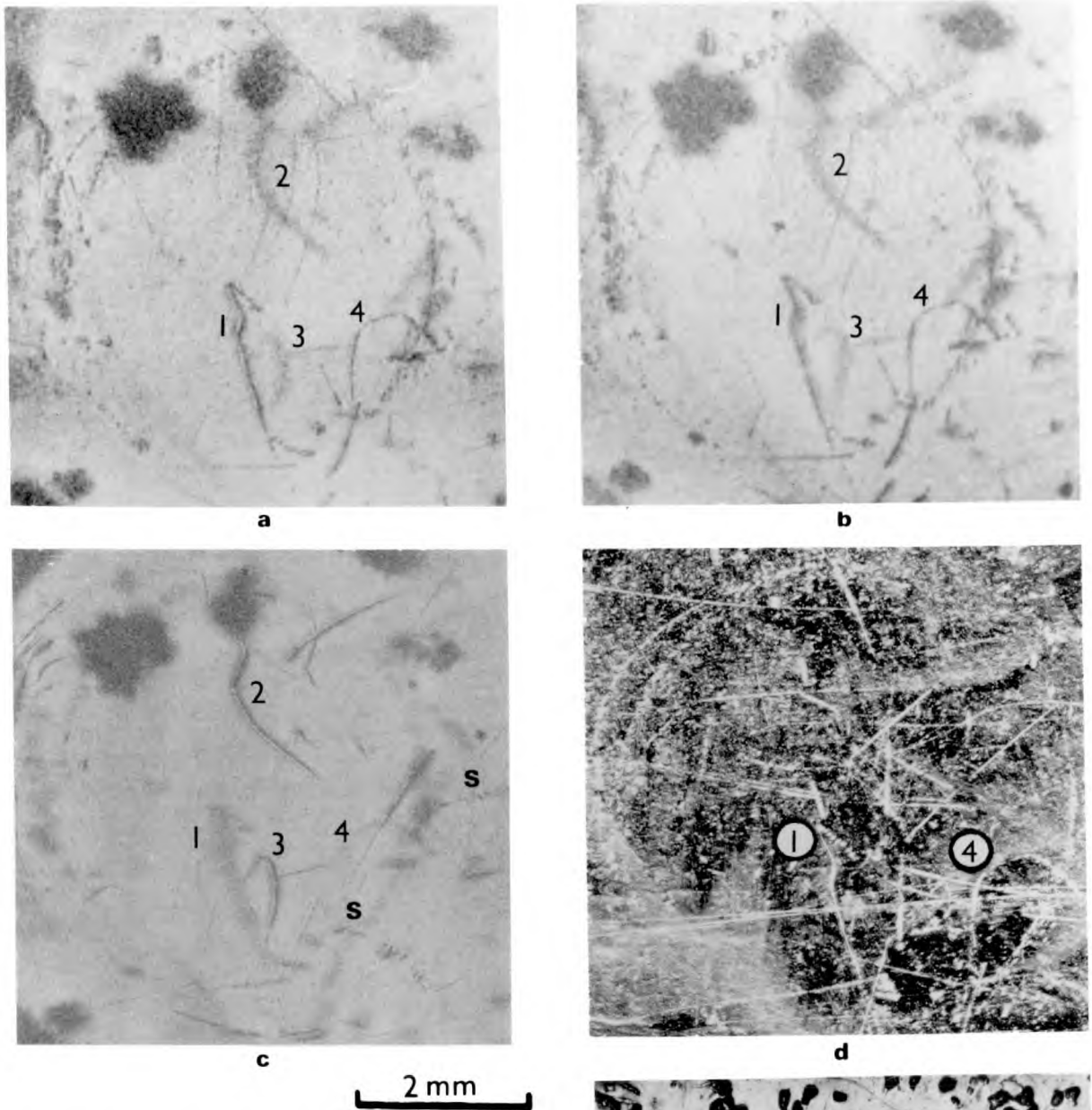


Figure 4.4 X-ray topographs and etched surfaces of GaAs Si doped slice no 643/2.

a) and b) are X-ray topographs formed using the direct and indirect beams respectively and the images exhibit identical contrast

c) An X-ray topograph of the same area as a) and b) but taken with the other side of the specimen facing the film.

d) Etched structure of the side of the specimen nearest to the film in a) and b).

e) Etched structure of the side of the specimen nearest to the film in c). Features marked 1 and 4 are sharp in a) and b) and also appear on the etched surface in d) whereas features marked 2 and 3 are sharp in c) and are also revealed by the etch in e). The features marked s in c) may be **helical** dislocations.

features numbered 1 and 4 are revealed as being on the surface shown in figure 4.4d and those numbered 2 and 3 as being on the surface in figure 4.4e. The specimens were examined with the surfaces in the state as received from S.E.R.L. with a high polish. It is possible however, that the extensive surface damage revealed by the etch may have obscured detail from the interior of the specimen in the X-ray topographs. The surface shown in figure 4.4d was only lightly etched and most of the detail appears to be due to surface damage. That of figure 4.4e was etched for a longer time and most of the surface damage has been removed.

4.2 Inclusions in Zn Diffused GaAs.

A Zn diffused slice SJC 563 of $\{100\}$ orientation was examined in the optical microscope. Both surfaces had been Zn diffused and one of these was polished down slightly on the diamond wheel to remove gross surface contamination. A micrograph of this polished surface figure 4.5 shows a large number of inclusions. A number of these can be seen to follow definite lines across the surface as shown at higher magnification in figure 4.6. It is probable from the nature of these lines that the inclusions form preferentially at defects associated with surface scratches or at subgrain boundaries in the original material.

Figure 4.7 shows a series of micrographs which illustrate the individual types of feature present. Small rectangular inclusions were prominent throughout the surface and these were all formed with the long sides lying mutually parallel in a $[011]$ direction. Also present were larger polyhedral inclusions. These displayed a certain amount of surface detail whereas the rectangular inclusions displayed none. In some cases the rectangular inclusions were observed associated with the edges of polyhedral inclusions as in figure 4.7c. The background

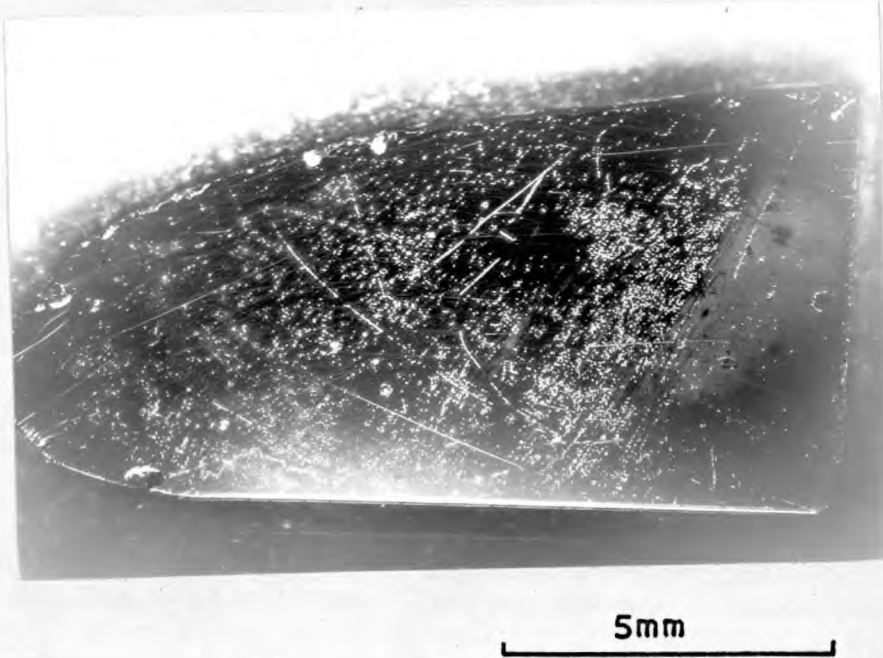
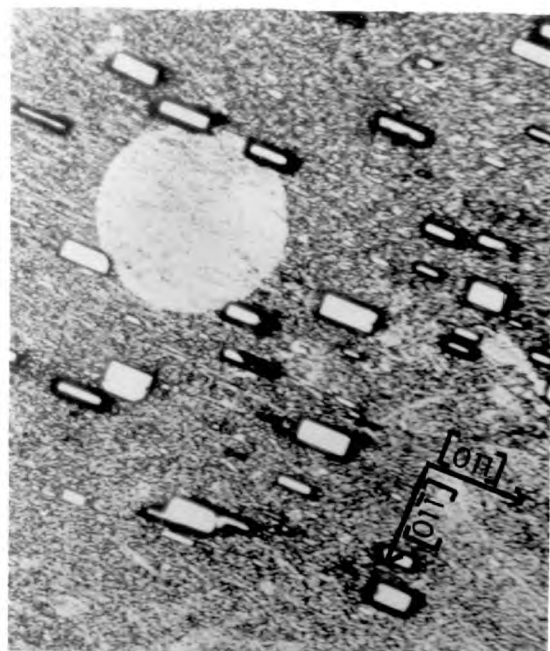


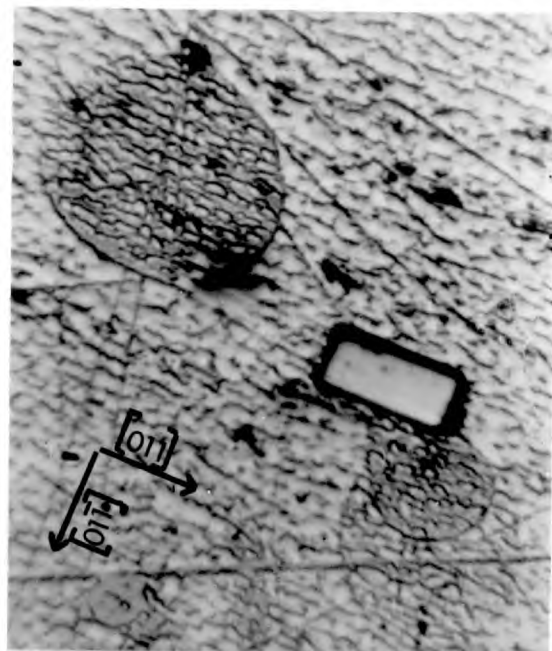
Figure 4.5 Optical micrograph of the surface of Zn diffused slice SJC 563 showing the overall distribution of inclusions.



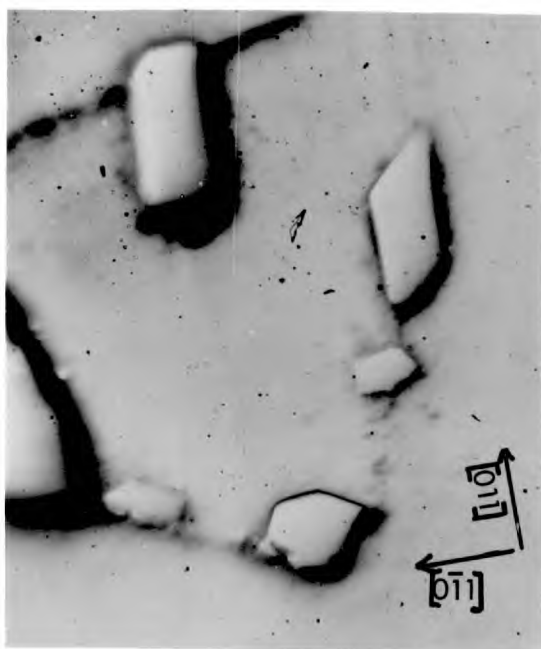
Figure 4.6 A line of rectangular shaped inclusions.



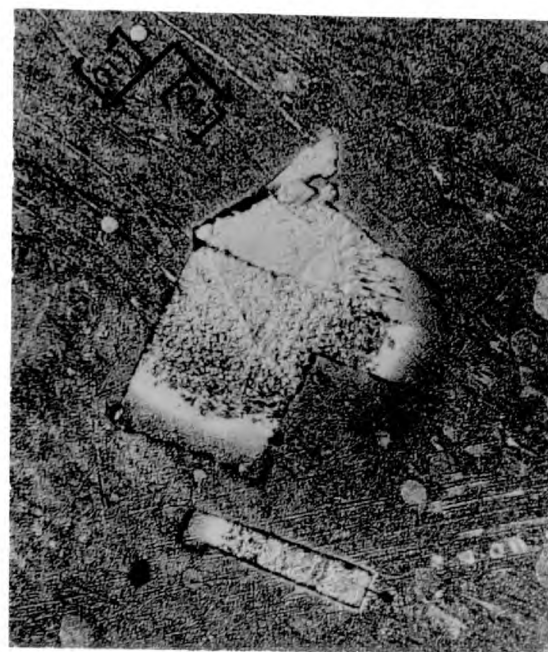
0.5mm



0.2mm



0.2mm



0.5mm

Figure 4.7

Optical micrographs of the Zn diffused surface of GaAs slice SJC563.

- a) and b) show rectangular inclusions and circular structures.
 c) shows rectangular inclusions, some with modified shapes, at the edges of a polyhedral structure. d) shows a polyhedral structure.

when observed at high magnification took on a rippled appearance and in certain areas of circular section (figure 4.7a and b) this rippling gave rise to different contrast. The line of the rippling was parallel to the long sides of the rectangular inclusions and to certain sides of the polyhedra.

The inclusions were microanalysed using the electron probe. No compositional difference could be detected between the rectangular inclusions and the matrix, but an analysis of the polyhedral inclusions showed them to contain 60 at % Zn, 40 at % As and no Ga. This would be consistent with them being precipitates of Zn_3As_2 . The overall Zn content of the surface was found to be near 0.5 at %.

The same slice was examined in the electron probe using the cathodoluminescence mode. The background noise was found to be abnormally high and little detail could be resolved in the image. On looking through the optical microscope whilst scanning was in progress it was found that light, appearing blue to the eye, was being emitted for a considerable time after the beam had passed. This phosphorescence appeared predominantly at the edges of the rectangular inclusions, and provided a virtually constant source of light for the photomultiplier, in effect raising the noise level. As a result, the normal cathodoluminescence in the infra-red was swamped and could not be resolved. This phosphorescence indicates that despite the compositional equivalence between the rectangular inclusions and the matrix, the interface between the two possesses distinctive recombination properties.

4.3 The Examination of GaAs Laser Diodes in the Electron Probe.

4.3.1 Charge Collection.

Laser diodes were mounted in the electron probe with one mirror face towards the electron beam. The p-n junction was thus normal to the surface under examination. A chart recorder was used to monitor

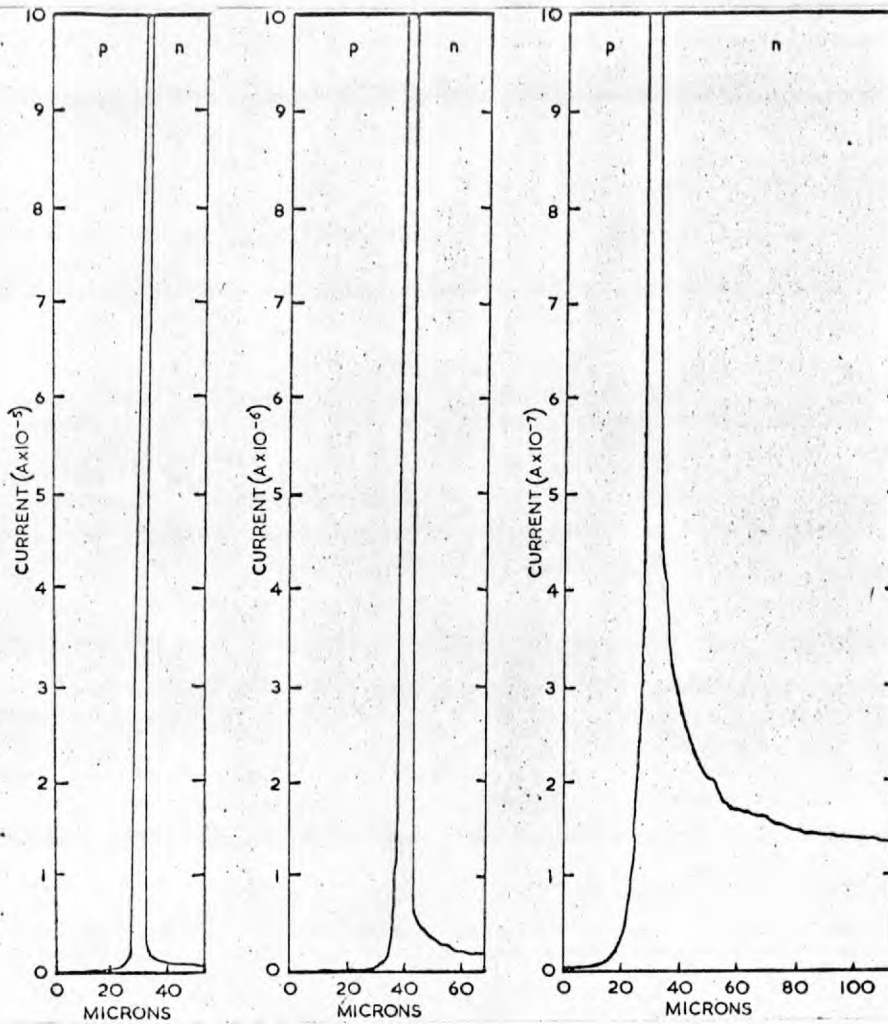
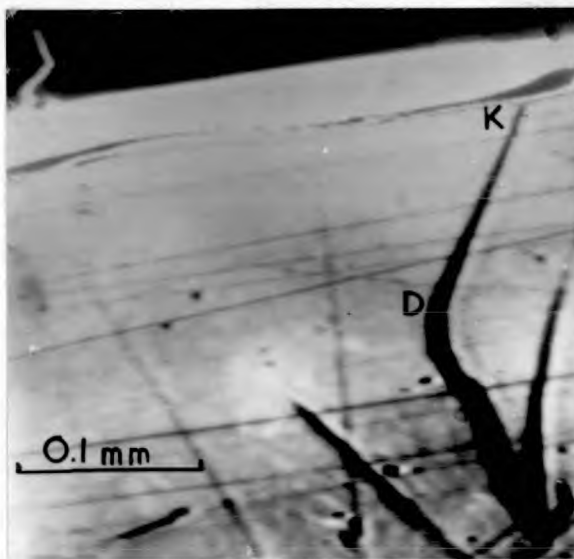
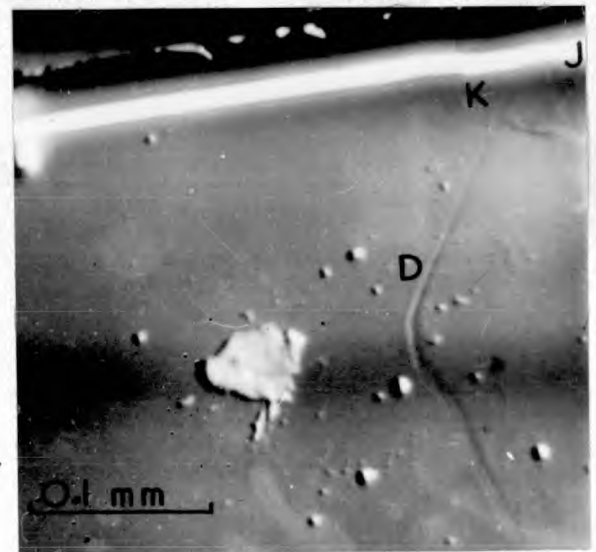


Figure 4.8 Signal strength versus distance for a line scan and a series of decreasing settings of the amplifier range.



a



b

Figure 4.9 a) Charge collection micrograph of diode from slice SJC 602 diffusion 535 taken at 10^{-7} amps FSD and 2×10^{-8} amps back off. b) Topographical image of same area as in a) with charge collection image of junction taken at 10^{-5} amps FSD superimposed.

the charge collection signal as the specimen was traversed beneath the stationary beam. This gave a calibrated trace of the current profile along a line normal to the junction. Traces for three different settings of the meter are given in figure 4.8.

Charge collection images were displayed on the C.R.T. using the normal scanning raster. With the amplifier sensitivity set to 10^{-5} amps the p-n junction was seen as a broad bright line. The width of this line corresponded to the width of the peak in figure 4.8a at an intermediate current value. When the sensitivity of the amplifier was increased, detail began to appear in the n-type material adjacent to the junction. This contrast would be represented in figure 4.8c by fluctuations in the plateau on the n side of the junction. Contrast could be optimised by using the suppression control to back off to zero the current represented by this plateau.

Figure 4.9 shows two micrographs taken using the charge collection technique. Prominent in figure 4.9a, for which contrast has been maximised, is a profusion of straight black lines. Also visible in this micrograph is a prominent curved feature D. This same feature is visible in figure 4.9b which is a topographic image of the same area with the charge collection image of the junction superimposed. This feature appears to be connected with a kink K in the image of the p-n junction. The visibility of this feature in the topography suggests that it may be a sub-grain boundary which has been polished preferentially.

In figure 4.9b the position of the p-n junction in relation to the diffused surface at the top of the micrograph can be clearly seen. A comparison shows that in figure 4.9a all the contrast comes from the n-type material with the Zn diffused region above the junction remaining dark. In both micrographs particles of dirt on the surface are visible but the long straight lines are only shown up in figure 4.9a.

Also visible in figure 4.9a is a double dark line running close to the junction on its n side. This feature was an artifact which only appeared when the sensitivity of the amplifier was increased beyond 10^{-6} amps. At this sensitivity the image on the screen appeared at maximum brightness when the signal reached about 5×10^{-7} amps. The exact value however depended on the settings of the brightness and contrast controls on the video display unit. The peak of the charge collection trace, figure 4.8, was at about 10^{-4} amps so in the region of this maximum there was considerable overload. The artifact was a direct result of instability induced in the amplifier by this overload on each successive line scan. The shape of the artifact, which did not alter with the time the beam was on, had different characteristics for each junction examined. When the beam was scanned across the junction in other relative directions the artifact was found to appear on the side of the junction in the direction of the scan. In all cases the direction of scan was from left to right so the artifact invariably appeared to the right of the junction. In fig 4.9a the direction of scan (horizontally across the micrograph) was nearly parallel to the junction. As a result the two lines of the artifact, separated by a constant distance in the scan direction, are seen more clearly at the kink K.

A set of micrographs taken using different amplifier settings are shown in figure 4.10. The scanning direction in each case is horizontally across the micrograph. Comparison of figures 4.10 a), b), c) and d) shows that as the sensitivity of the amplifier is increased the bright line at the junction broadens as would be expected from the evidence of figure 4.8. The width of the artifact (the dark line) also increases with amplifier sensitivity. In figure 4.10f it can be seen that kinks shown up in the artifact appear to be associated with straight

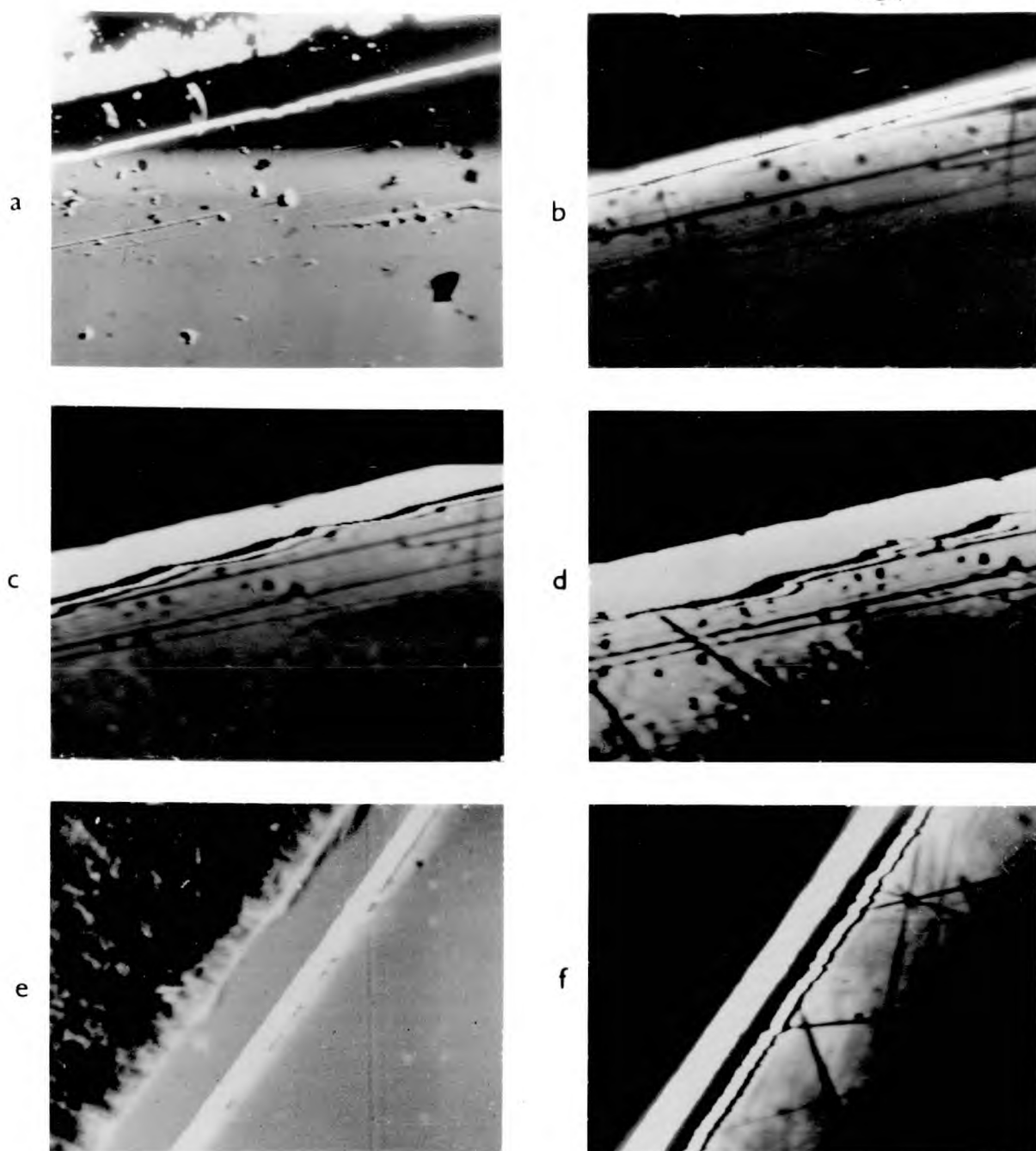


Figure 4.10

Charge Collection micrographs taken using different current amplifier settings and junction orientations to illustrate the behaviour of the artefact.

- a) 10^{-5} amps FSD No back off Superimposed on topographical image.
 - b) 10^{-6} amps FSD 2×10^{-7} amps back off.
 - c) 10^{-7} amps FSD No back off.
 - d) 10^{-7} amps FSD 2×10^{-7} amps Back off
 - e) 10^{-5} amps FSD No back off. Superimposed on topographical image.
 - f) 3×10^{-7} amps FSD 2×10^{-7} amps back off.
- a) b) c) and d) are of diode from slice SJC602. Diffusion 535
and e) and f) of diode from ingot SB74 diffusion 519.

black lines shown up in the n-type material. It is also apparent that irregularities in the outline of the artifact are far greater than any seen in the image of the junction at low amplifier settings. It is probable that this variation in shape of the artifact is a manifestation of changes in the charge collection efficiency of the p-n junction along its length. Any increase in charge collection efficiency would correspondingly increase the degree of overload of the amplifier and hence influence the size and position of the artifact.

4.3.2 Te Doped Material.

Te doped diodes were found to show different contrast effects in the bulk n-type regions to diodes doped with Si or Se. In all Te doped diodes examined in the charge collection mode there appeared black dots and lines which did not correspond to any topographical detail. In some cases, figure 4.11, the dots and lines were surrounded by white haloes.

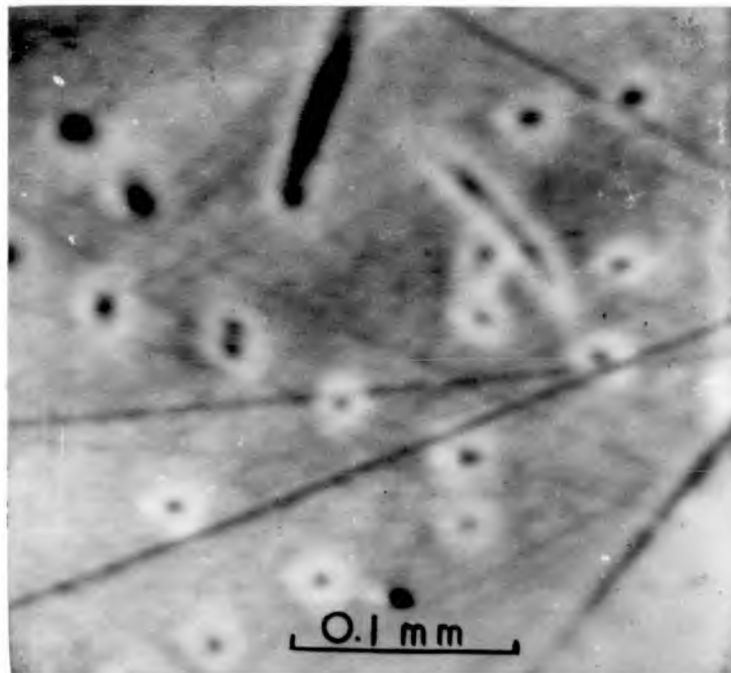


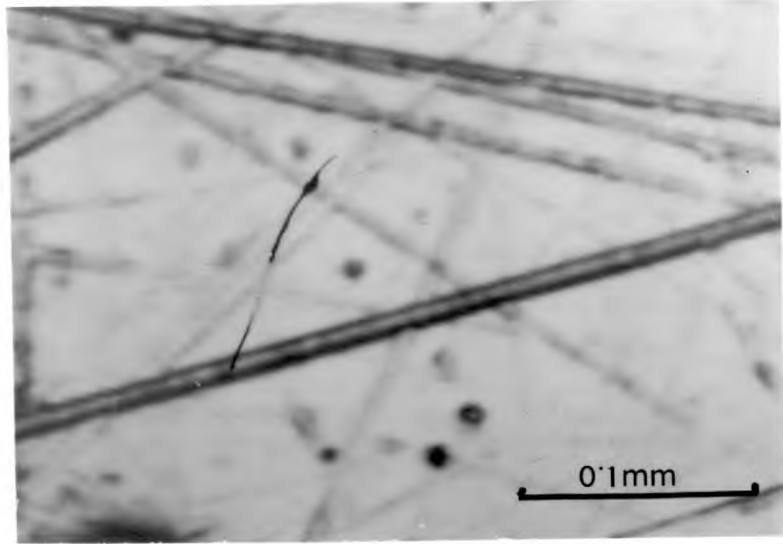
Figure 4.11 Charge collection micrograph of diode 3434/1 showing white haloed spots and lines together with surface scratches.

To determine the nature of these spots the surface of a diode was etched using the A.B etchant. Figure 4.12a shows the etched surface of the diode and figure 4.12b is a charge collection micrograph of the same area prior to etching. The white haloed spots seen in the latter are clearly revealed by the etch. Figure 4.12c at higher magnification shows the spots to have etched in a manner distinct from that of the overall surface damage. This is consistent with them being due to segregation phenomena. The dark straight lines displayed on the charge collection micrograph correspond with the lines of polishing damage revealed by the etch. The majority of these lines were not visible in the topographic image and must therefore represent sub-surface damage.

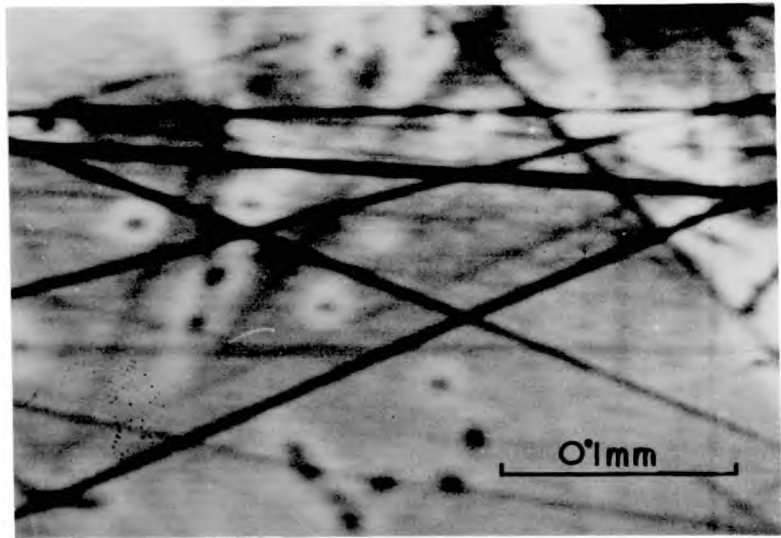
The spots with white haloes were also observed in similar material using the cathodoluminescence mode. These spots together with black lines representing surface scratches are shown in figure 4.13. The overall graininess of the micrograph is due to random noise in the photomultiplier.

The infra-red transmission micrograph (figure 4.14a) of Te doped Czochralski grown diode No 3434/4 shows up a number of impurity striations. These striations are also shown up in the cathodoluminescence image figure 4.14b. Comparison of the two micrographs shows that regions of low infra-red absorption (bright areas in figure 4.14a) correspond to areas of high cathodoluminescent efficiency (bright areas in figure 4.14b). In figure 4.14a a large opaque region can be seen towards the right hand side of the micrograph. This is not visible in the cathodoluminescence image so must have been located below the maximum penetration depth of the electron beam. This particular diode had a very low p-n junction resistance and exhibited no rectifying properties. This was attributed to a short circuit of the junction probably associated with the opaque defect.

a



b



c

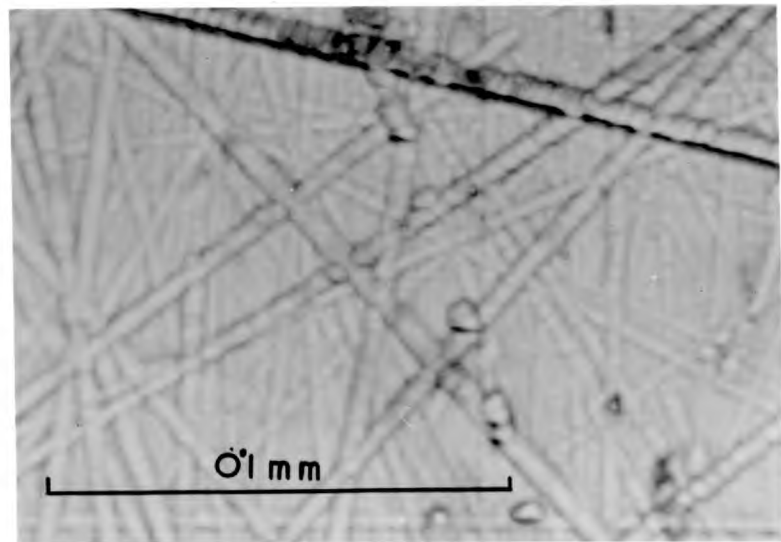


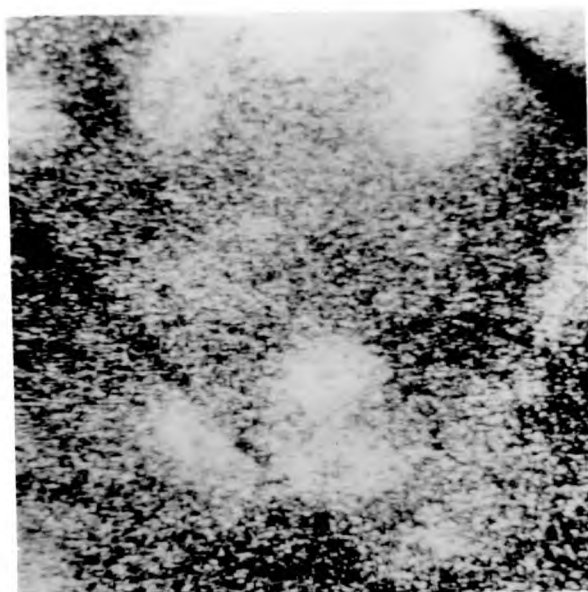
Figure 4.12

Te doped Czochralski diode 3434/2.

a) Etched surface.

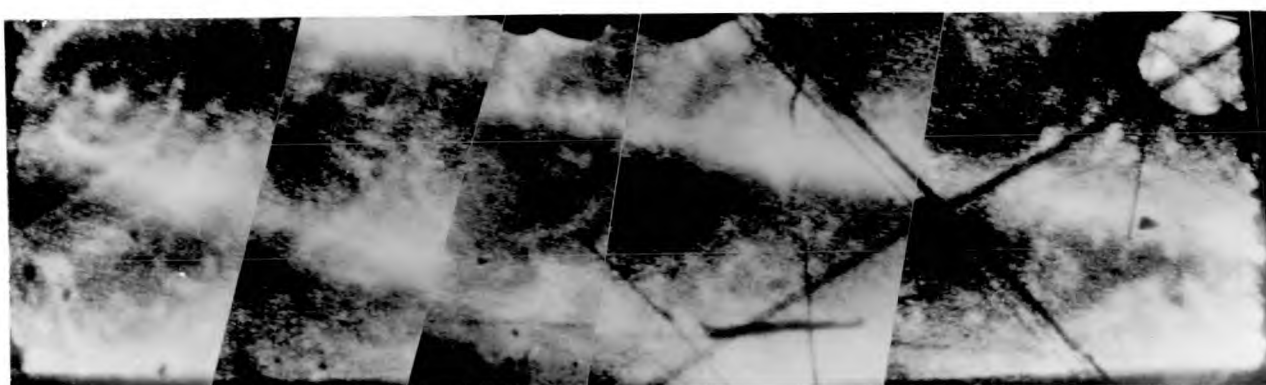
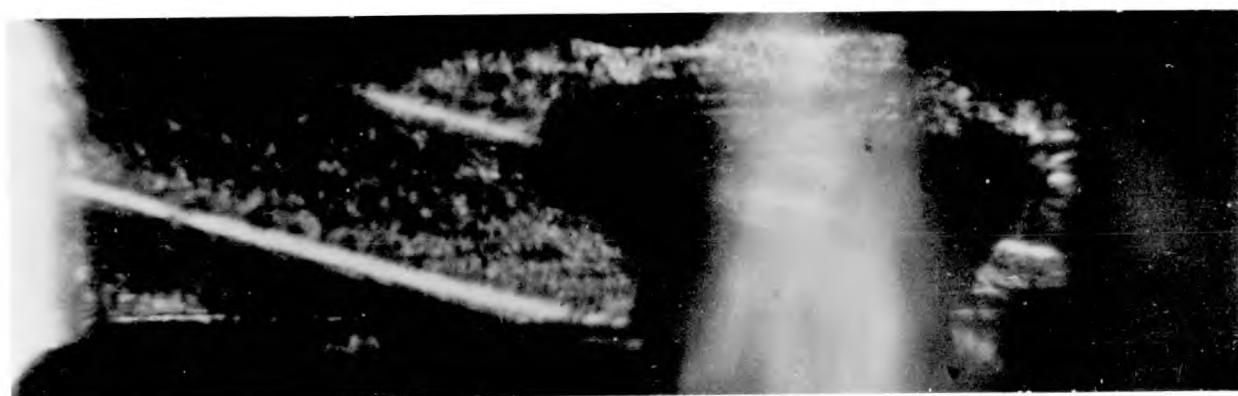
b) Charge collection micrograph of same area.

c) Higher magnification of etched surface.



20 μ

Figure 4.13
Cathodoluminescence micrograph of Te doped
Czochralski grown material in diode 3434/4.



0.2 mm

Figure 4.14
a) Infra red transmission micrograph of Te doped Czochralski
grown diode 3434/4.
b) Composite cathodoluminescence micrograph of the same diode.

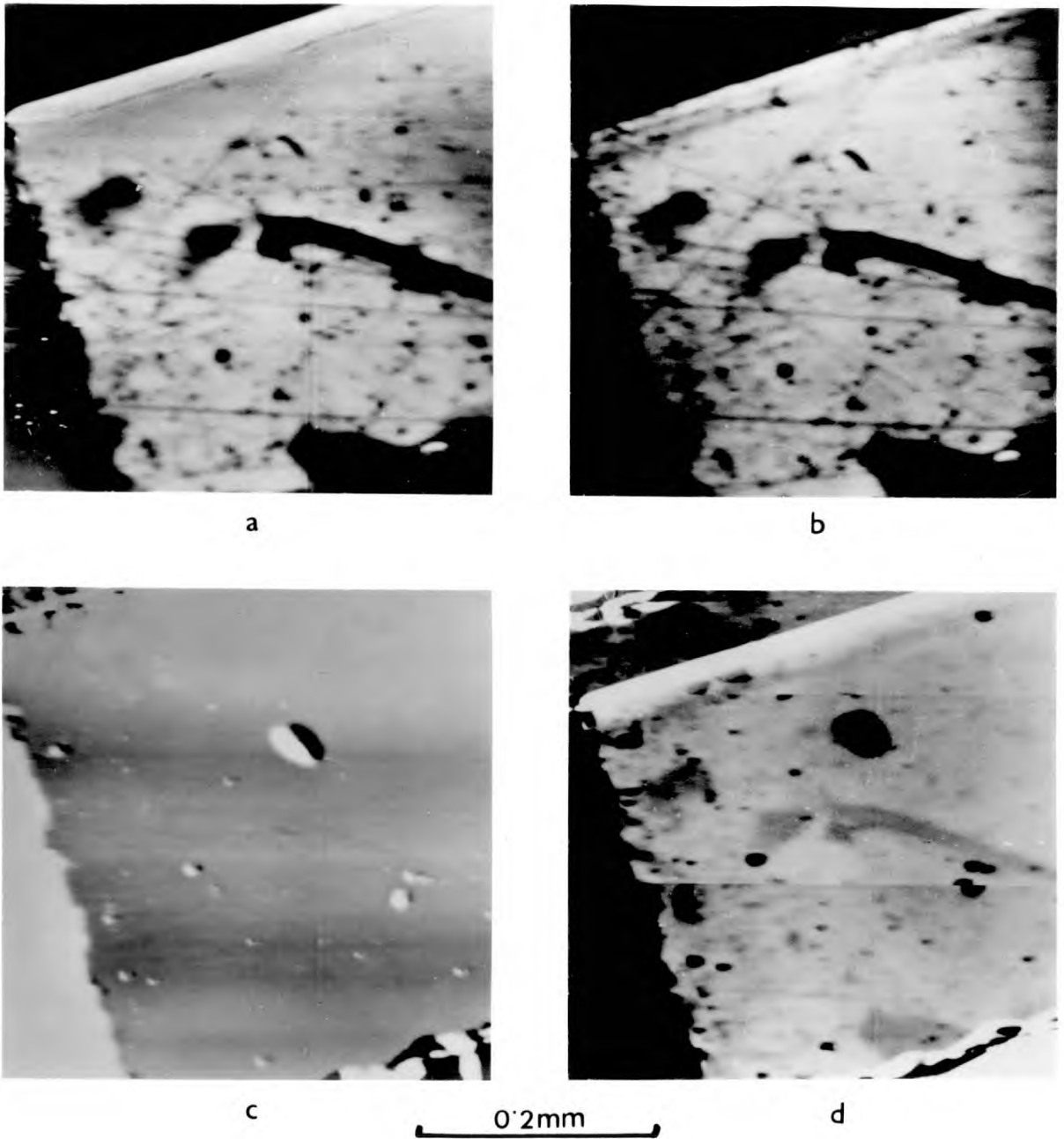


Figure 4.15

- a) Charge Collection micrograph taken at 10^{-6} amps FSD setting
- b) Cathodoluminescence micrograph
- c) Topography
- d) Compositional image with charge collection image of junction taken at 10^{-5} amps FSD superimposed.

All micrographs are of the same area of Te doped, Bridgeman grown diode no 2659/1.

4.3.3 Comparison of Charge Collection and Cathodoluminescence Micrographs.

Figure 4.15 shows a set of micrographs, all taken of the same area on the mirror face of a Te doped, Horizontal Bridgeman grown diode. The charge collection and cathodoluminescence micrographs (figure 4.15 a and b) show virtually similar detail apart from ~~the~~ the immediate region of the p-n junction. Here the charge collection micrograph displays the junction as a bright band with a dark artifact beneath. The cathodoluminescence micrograph however shows the junction region as two bands, each containing detail. In neither micrograph is any detail displayed in the p-type layer above the junction. In contrast to the previous specimens the spots visible in both micrographs have no white halos. In infra-red transmission growth striations were a very prominent feature but these are not visible in either of these micrographs.

The quality of the cathodoluminescence micrographs from this diode was very good. There was no graininess as in figure 4.13 and surface scratches appeared sharper. This improvement was associated with a much greater cathodoluminescent efficiency in this material. The detected signal was stronger so the effects of photomultiplier noise were not noticable in the image. Topographical and compositional micrographs of the same area are presented for comparison (figure 4.15 c and d). The topographical image shows no comparable detail but a number of common features can be resolved in the compositional image, figure 4.15d. The explanation for this is that the Si p-n junctions used to detect back scattered electrons are also sensitive to infra-red. The infra-red emitted by this specimen was sufficiently intense to give rise to a detected signal comparable with that due to back scattered electrons. In other diodes this effect was not observed.

Quantitative measurements of the signal to noise ratio of the photomultiplier were made for the two diodes 3434/4 and 2659/1.

To the nearest whole number this was 2 : 1 and 4 : 1 respectively. The dark current in each case was 3.3×10^{-6} amps at a photomultiplier voltage of 1200 V.

4.4 Scanning Electron Microscopy of GaP.

The initial investigations on GaP were carried out using the electron probe microanalyser. The principal disadvantage of this instrument was that the minimum available magnification was 300 X. This meant that a large number of micrographs had to be taken in order to cover an area equivalent to the surface of a GaP diode. The S.E.M. however gave a continuous magnification range from 20 X to a theoretical 120,000 X. The resolution in the higher magnification ranges was however severely limited by the finite beam diameter and the spread of electrons into the specimen as described in section 2.6.4. The S.E.M. proved an ideal instrument for the examination of diodes and apart from the initial microanalyser work was used exclusively.

4.4.1 The Examination of Pulled Material in the Electron Probe.

A slice of pulled GaP doped with Te (S.E.R.L. number PEO 24) was examined in the electron probe. The surface was in the unpolished condition as received. Overall the cathodoluminescence (CL) efficiency was small and no satisfactory micrographs could be obtained using the S10 type photomultiplier. At some small localised positions however, very intense light emission was detected. These positions were found to be associated with larger inclusions seen in the back-scattered electron image. A series of micrographs showing one of these inclusions is presented in figure 4.16. Due to the roughness of the surface the topographic image shows little detail but the outline of the inclusion can be clearly seen in the X-ray fluorescence images. The X-ray images indicate that the composition of the inclusion is not

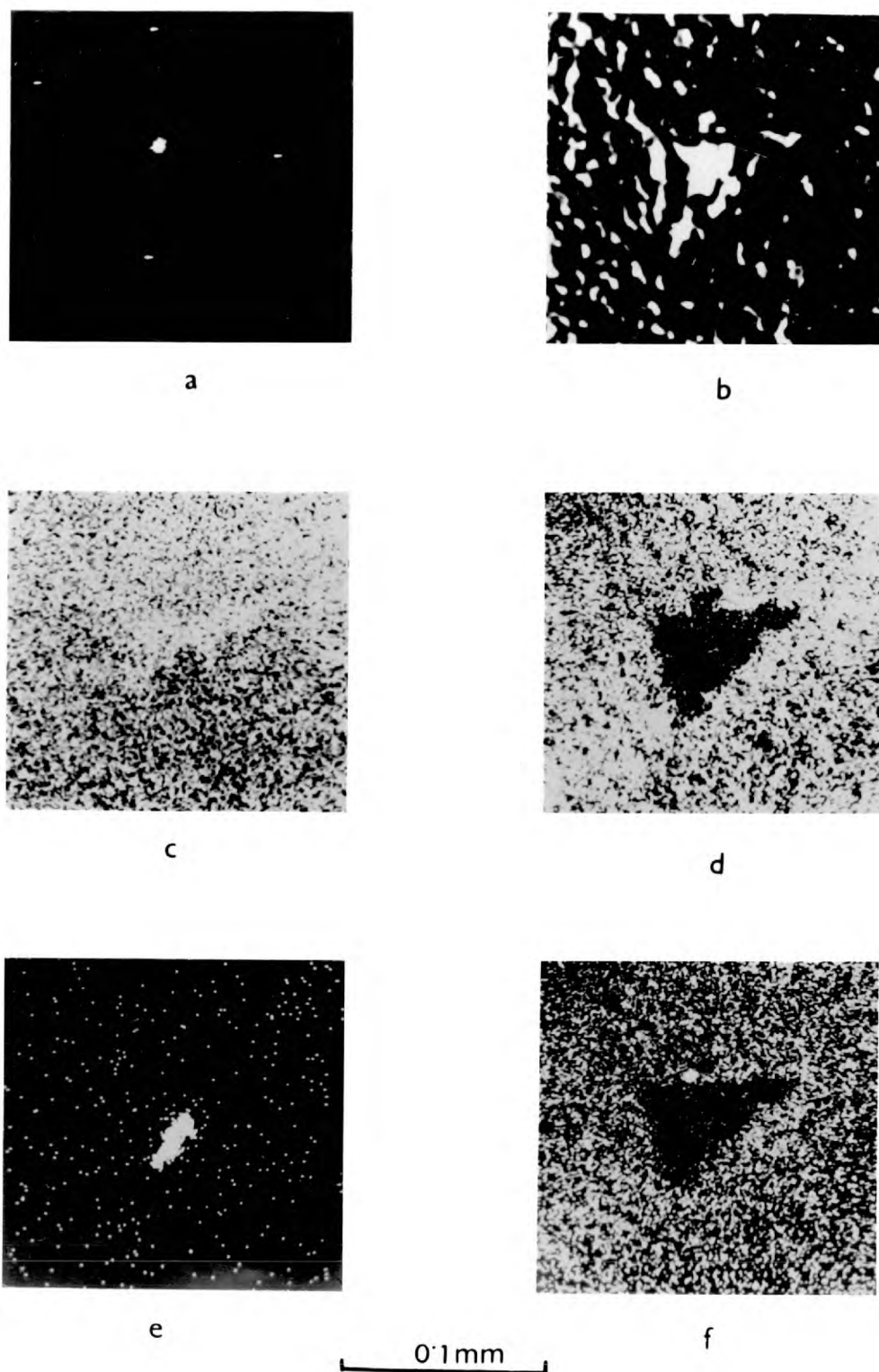


Figure 4.16

Cathodoluminescence and compositional effects in a slice of Te doped Czochralski pulled GaP.

- a) Cathodoluminescence image. b) Topographical image.
 c) Ga X-ray fluorescence image. d) P X-ray fluorescence image.
 e) Te X-ray fluorescence image. f) P X-ray + cathodoluminescence image.

uniform throughout. There is an overall deficiency of P but Ga and Te are concentrated in different regions. The upper part of the inclusion as seen in the micrographs is Ga rich whereas in the lower portion the Ga concentration is of the same order as in the matrix. Also in the lower part the X-ray image indicates a region of high Te concentration. The final micrograph of the series is a double exposure showing the relation of the points of high CL efficiency to the outline of the inclusion as evidenced by the X-ray image of the phosphorus content. These points occur predominantly at the edges of the inclusion but do not otherwise appear to be connected with any particular impurity concentrations. It is possible they are associated with other impurities, not investigated in this experiment.

4.4.2 The Examination of GaP Diodes.

The initial investigations on GaP diodes were carried out using the Electron Probe. At this stage in the work only relatively poor diodes with external quantum efficiencies less than about 0.1% were available. These diodes were made by liquid epitaxial growth of a Zn-O doped layer directly onto a substrate cut from a Czochralski pulled crystal. Figure 4.17a is a CL micrograph taken in the probe using the photomultiplier with the S10 photocathode. To achieve a high level of contrast the signal was backed off in the current amplifier. Immediately obvious from the micrograph is that the Zn-O liquid epitaxial layer exhibits striations of similar nature to those seen in Te doped GaAs grown by the Czochralski technique (figure 4.14). Also of significance is the fact that the overall CL intensity decreases with distance from the p-n junction.

The same diode was also examined in the SEM. Figure 4.17b is a CL image formed using the S20 type photomultiplier. Here it was not possible to back off the output to the same extent as in the electron

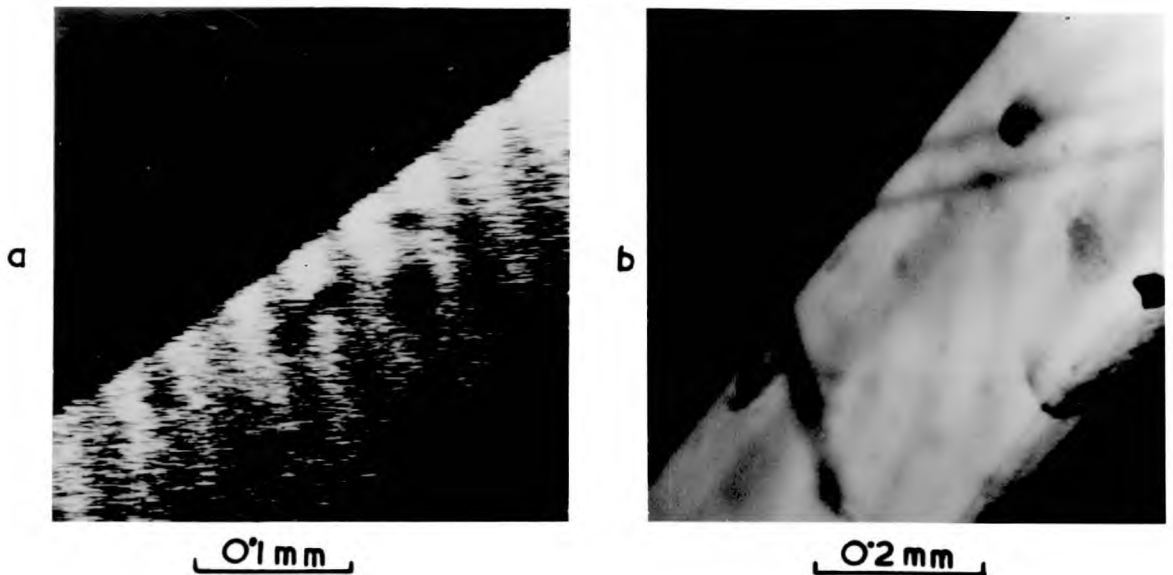


Figure 4.17 Cathodoluminescence micrograph of diode No L 136 showing growth striations in the p layer. This diode was made by growing a liquid epitaxial layer, doped with Zn and O, directly onto a Te doped substrate.

- a) Micrograph taken in the electron probe using the S 10 photomultiplier.
- b) Micrograph taken in the S.E.M. using the S 20 type photomultiplier.

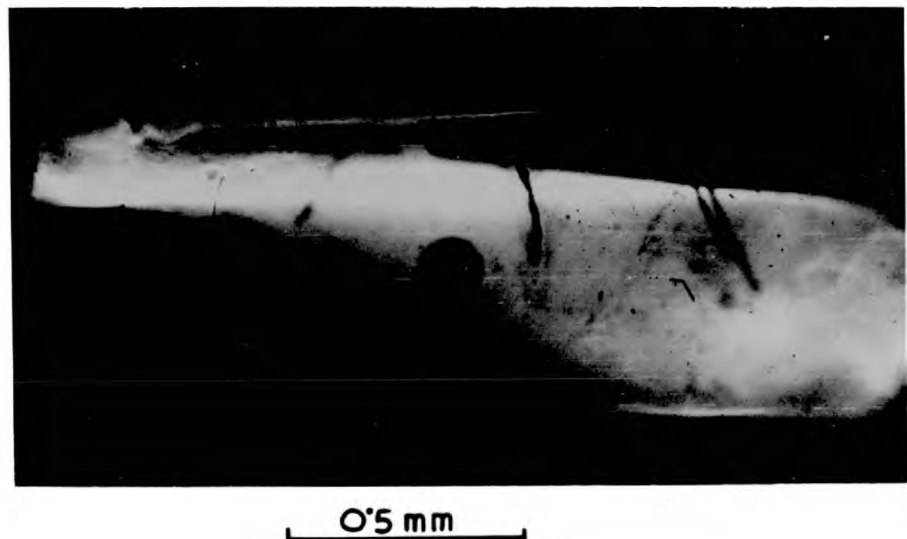


Figure 4.18 An optical micrograph showing the near field electroluminescence pattern from diode No L 136. There is no evidence of a periodic fluctuation in intensity associated with the striations displayed in figure 4.17.

probe and the striations are only faintly visible. Carbon contamination from the electron probe has obscured the striations near to the p-n junction and only those in a region further out are visible. The long dark lines also visible are a result of carbon contamination in the probe during a line scan across the surface and provide convenient markers. The results of the line scan were inconclusive probably due to this contamination and no regular variations in CL intensity were recorded.

The electroluminescent output of the same diode was photographed through an optical microscope (figure 4.18). No intensity fluctuations corresponding to the striations were observed. This was not unexpected as the striations were only made visible in the electron probe and the S.E.M. by electronically increasing the contrast. Also the emission seen during electroluminescence represents an integrated intensity from all parts of the junction. That is to say, the light emitted at any one point on the specimen surface may originate anywhere on the junction plane and reach the surface either directly or by one or more internal reflections. Thus the influence of striations on the emission pattern will be minimal.

One feature of all diodes examined was the non planar surface of the Zn-O doped liquid epitaxial layers. A typical surface is illustrated in plan view in the secondary electron image of figure 4.19. When examined in cross section it was found that the troughs and grooves in the surface sometimes extended down nearly as far as the p-n junction. Figure 4.20 is a double exposure showing the relation of the p-n junction, revealed by charge collection, to the positions of some of these defects. It can be seen that the junction tends to be displaced deeper into the n-type material immediately below the troughs. In other diodes, such as in figure 4.21, the troughs were not so deep



FIGURE 4.19

0.2 mm

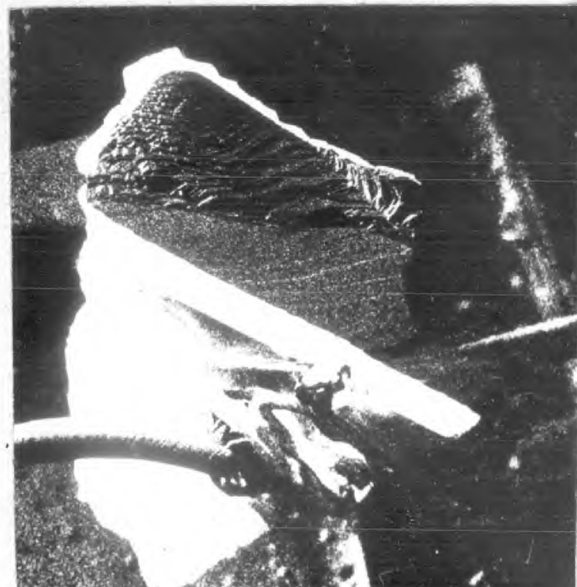


FIGURE 4.20

0.5 mm

Figure 4.19 Secondary electron image of Zn-O doped face of diode L322 showing troughs and grooves formed during the liquid epitaxial growth.

Figure 4.20 Double exposure (secondary electron + charge collection images) of diode L474/4 showing deviations in junction planarity associated with troughs in the Zn-O liquid epitaxial layer.



0.5 mm

Figure 4.21 Micrographs of diode no L322 showing the presence of the Zn-O doped p layer on three sides of the diode.
 a) Secondary electron + charge collection images
 b) Cathodoluminescence image.

and no displacement of the p-n junction could be detected. In the n-type liquid epitaxial layers these troughs did not occur to the same extent. It appears (Wight 1970) that such surface effects are a common feature of liquid epitaxial layers of GaP doped with oxygen.

In some inefficient diodes it was found that the Zn-O epitaxial layer was not limited to a single surface of the diode. Figure 4.21a shows a diode where the p-n junction extended over three sides. The same diode is shown in the CL image of figure 4.21b; here the Zn-O doped layer appears as a bright band. One of the contact wires can be seen in the lower left of both micrographs. This particular diode gave no electroluminescence and the micrographs indicate that this was because the contacts were short circuited by the p layer. Such overlap of the p layer is not a serious problem in practice as any extraneous material can be removed by mechanical polishing prior to the formation of contacts.

4.4.3 Line Scan Observations.

The Y modulation facility of the SEM was used to make cathodoluminescence and charge collection scans across the p-n junctions of a number of diodes. For accuracy the time for each individual scan was made greater than four seconds. With a fast scan speed of say 0.01 seconds the traces were distorted and as the scan speed was changed both the shapes of the traces and the position of the charge collection peak were found to alter. At these rapid scan speeds the position of the peak of the charge collection trace was found to be dependent on the sensitivity range and time constant of the amplifier. Using scanning times greater than four seconds it was found that any distortions or displacements of the traces were so small as to be negligible.

By making a double exposure it was possible to obtain both the cathodoluminescence (CL) and charge collection traces on the same

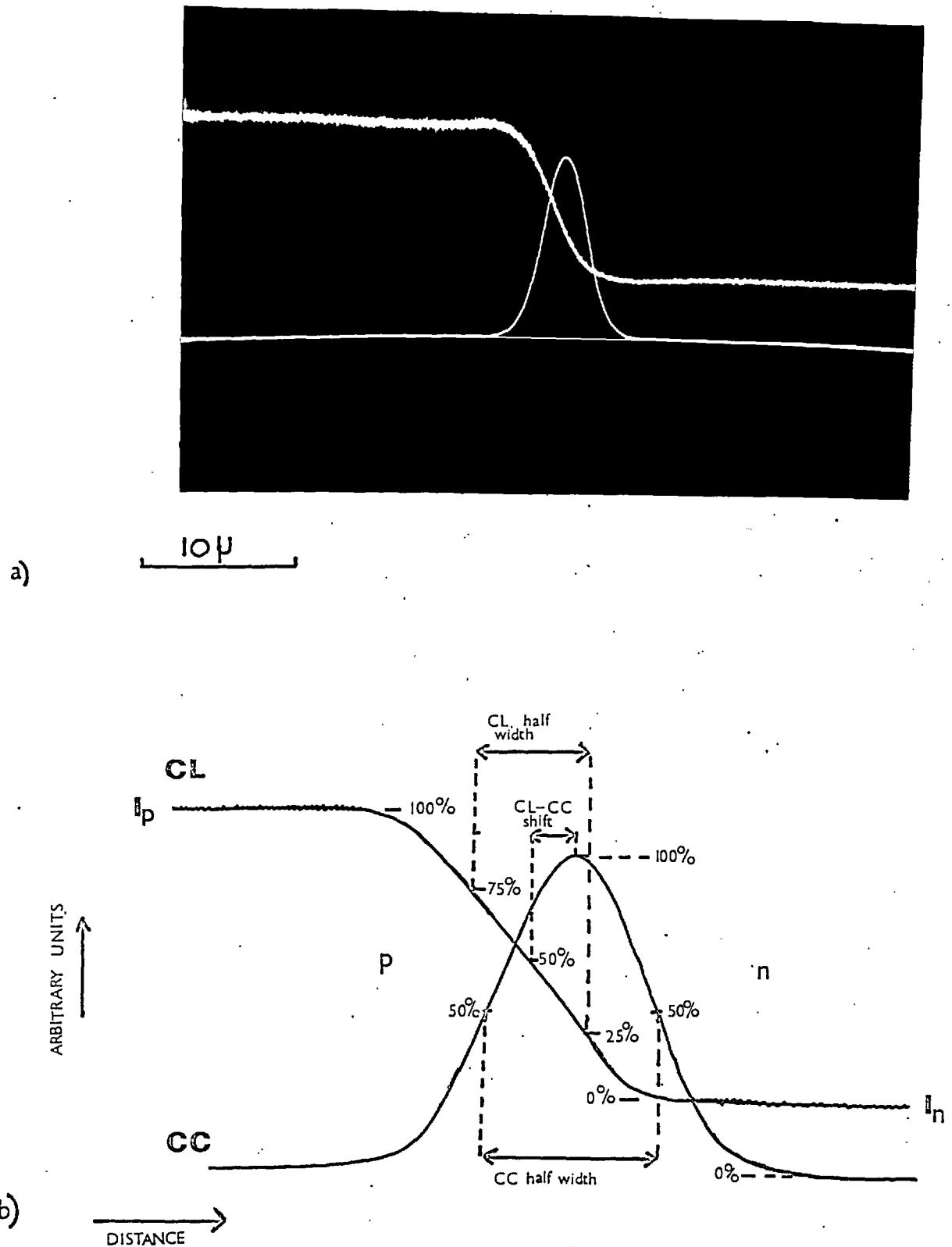


Figure 4.22 a) line scans obtained from diode L475/6.
 b) Diagram showing how the measurements of table 4.2 were obtained.

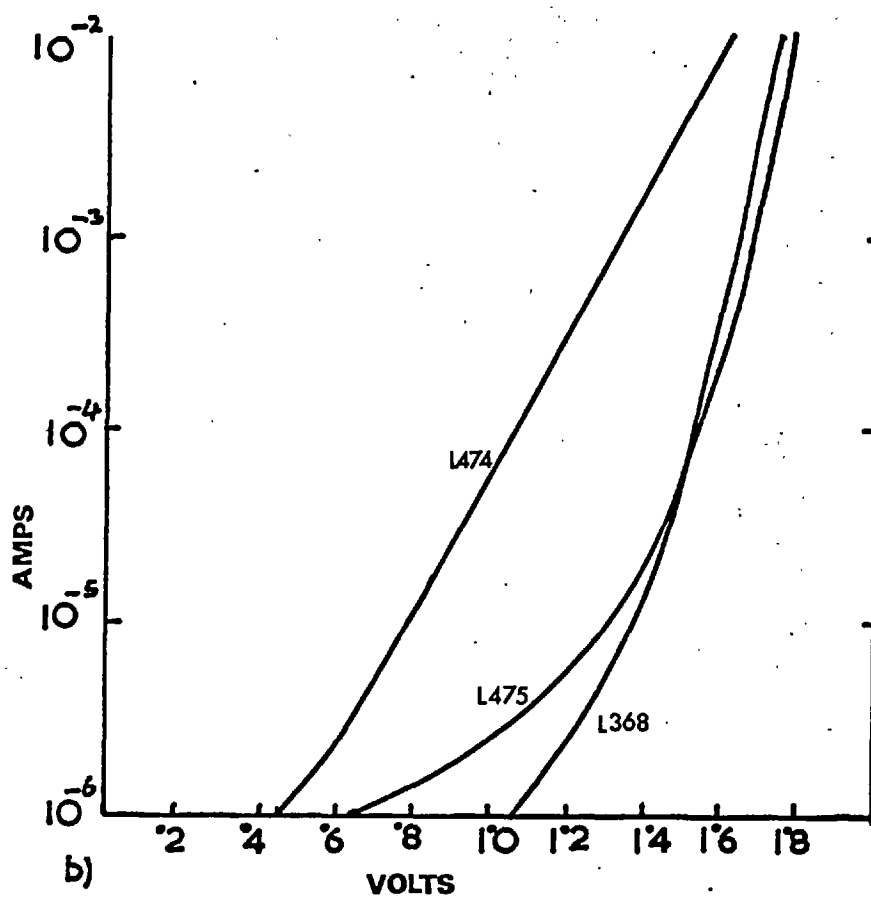
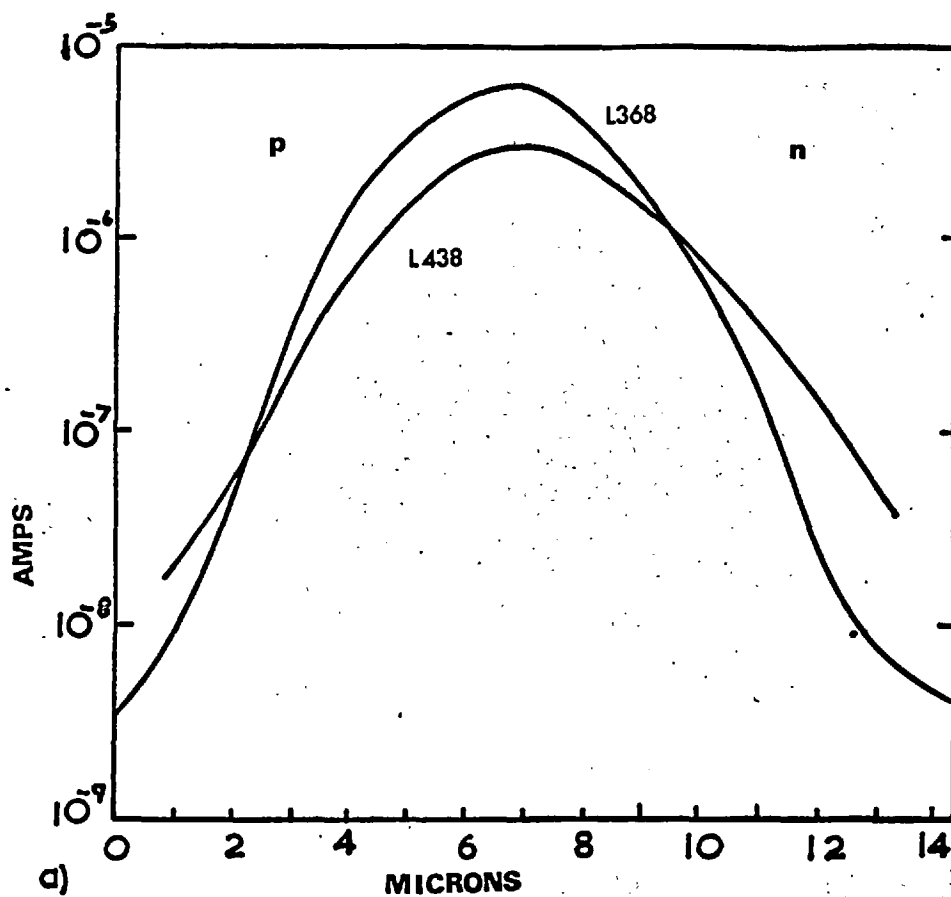


Figure 4.23 a) Logarithmic plot of the charge collection trace for diodes L368/3 and L430/5.
 b) I-V curves for diodes L474/4, L475/6 and L368/3 as measured at room temperature.

negative (figure 4.22). The two traces obtained are thus exactly equivalent in the x direction and direct comparisons can be made between them. In all diodes examined it was found that a finite displacement existed between the position of the peak of the charge collection trace and the centre of the CL trace. The latter was defined as the position on the trace half way between the levels of intensity from the bulk material either side of the junction. These measurements are plotted in table 4.2, and it can be seen that a general inverse relationship exists between the displacements and the diode efficiency.

The half width of the charge collection peak was measured for each diode and, for this purpose, only traces where the signal had not been backed off were used. Also a half width was measured for the CL trace. If the intensities from the p and n sides are denoted I_p and I_n , this half width was defined as the separation in the x direction between points on the trace at intensity levels given by $I_n + 0.75 (I_p - I_n)$ and $I_n + 0.25 (I_p - I_n)$. In the majority of diodes the two half widths measured as above were of similar magnitudes (Table 4.2). The implications of the differences that exist will be discussed in section 5.3.5.

The charge collection trace for each diode was replotted logarithmically as in figure 4.23a. The slope m was measured for the straight line portions of each graph and the value of the minority carrier diffusion lengths L_p and L_n found using the expression: $L = 0.4343/m$. The justification for the use of this expression and the relevance of the results is discussed in section 5.3.2. In the more efficient diodes the minority carrier diffusion length in n-type material, L_p , was found to be fractionally greater than the diffusion length L_n in p-type material. In diodes of low efficiency the reverse was generally true.

Diode Number	Efficiency	Junction Shift CL-CC μ	Half Width μ		Diffusion lengths μ		β
			CL	CC	L_n	L_p	
L136 ^x	Low	5	2.0	3.0	1.0	.9	1.6
L129	Low	7.5			.9	.8	6.0
L322	.06%	4	4.5	3.5	.63	.65	3.8
L222	.07%	3.2	10.0				3.1
L377/4	.10%	0.8	2.0	2.2	.65	.55	2.5
L368/3	.12%				.4	.6	2.0
L480/6	.32%	3	4.0				2.0
L438/5	.4%	0.3	2.1	2.5	.8	.92	1.7
L475/6	.56%	0.9	2.4	3.6	.8	.9	2.0
L206	.7%	0.5	1.5				
L474/4	.7%	D.8	2.6	2.3	.8	.98	4.2

Table 4.2 List of diodes examined in the S.E.M. arranged in increasing order of efficiency. The parameters listed for each diode are as described in the text.

4.4.4 I - V Characteristics of GaP Diodes.

The I-V characteristics of a number of diodes were measured under forward bias conditions and at room temperature. For each diode the I-V curve was plotted logarithmically as in figure 4.23b. The majority of curves displayed a well defined straight line region and for this, in each case, the value of β in the expression $I = I_0 \exp ev/\beta kT$ was determined by measuring the slope of the trace m . Here

$$m = \frac{d \log I}{dV} = 0.4343 e/\beta kT$$

and for $T = 300^\circ K$, $\beta = 16.8/m$.

The values obtained for β are listed in table 4.2 together with the

parameters determined using the SEM. In general the values obtained were close to or greater than 2. This indicated (Sah et al 1957) that space charge recombination was the dominant process in these diodes. The scatter of results is too great to enable any correlation of β with device efficiency.

4.5 Transmission Electron Microscopy of GaP.

Specimens of GaP grown by the three different techniques, liquid epitaxy, vapour phase epitaxy and Czochralski pulling from the melt, were examined in the transmission electron microscope. As the method of growth is relevant to the interpretation of micrographs the results are presented separately for each class of material.

The electron microscopes used in this investigation were an A.E.I. EM6G and a Siemens Elmiskop 1. The latter was used only when large angles of specimen tilt were required and allowed tilts of up to $\pm 22^\circ$. The A.E.I. EM6G was fitted with a $\pm 5^\circ$ tilt stage which also allowed a 360° specimen rotation. This proved perfectly adequate for the majority of the work.

The micrographs unless otherwise stated were taken using a two beam condition with a single operating diffraction vector. Kikuchi lines were present in the diffraction patterns from all specimens and enabled two beam conditions to be selected with a high degree of precision. Dark field micrographs were taken using the high resolution dark field facility of the A.E.I. EM6G which enabled the incident electron beam to be tilted through a predetermined angle using electromagnetic deflection.

4.5.1. GaP Grown by Vapour Phase Epitaxy.

The specimens examined are listed in table 4.3. All specimens were doped with Te.

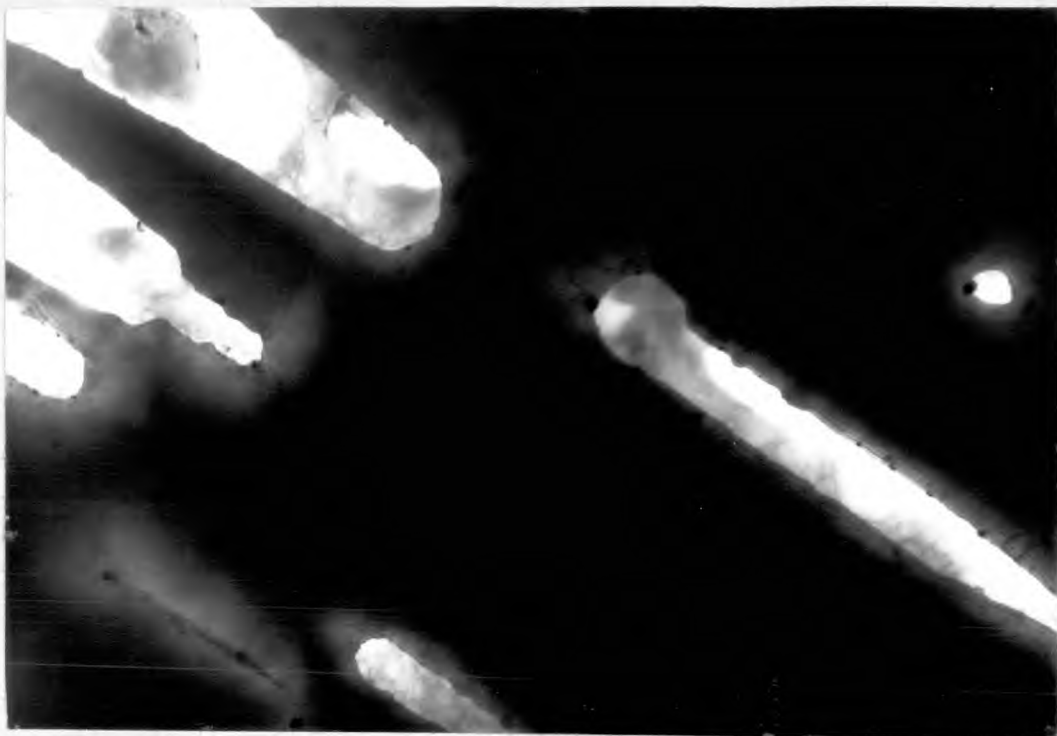
Table 4.3

<u>Specimen (S.E.R.L. No)</u>	<u>Free Electron Concentration cm^{-3}</u>
AP 64/2	Intrinsic
VP 571/2	6×10^{16}
VP 574/3	1×10^{17}
AP 118/2	$10^{17} - 10^{18}$ estimate
AP 133/4	2.2×10^{17}
AP 143/2	2.2×10^{17}
AP 136/7	1.1×10^{18}

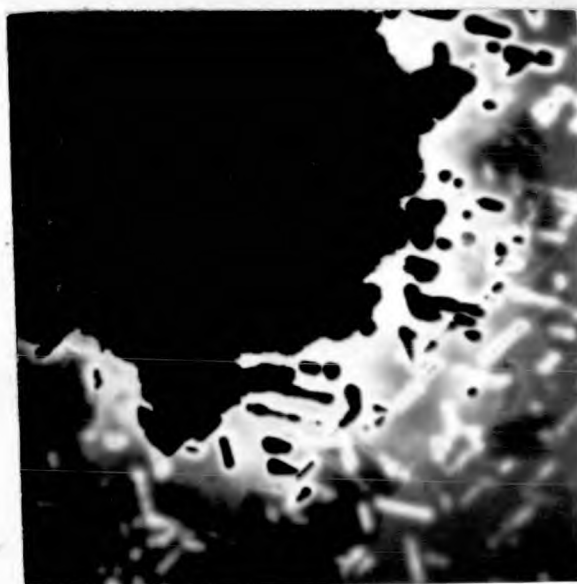
Table 4.3 List of the vapour phase epitaxy specimens examined in the transmission electron microscope. All the specimens were doped with Te and are arranged in increasing order of free electron concentration.

Difficulty was experienced in chemically jet thinning specimens with low free electron concentrations. There was a tendency for a rough rather than a polished surface to form at the bottom of the dimple. From the electron micrographs of specimen VP 571/2 (figure 4.24a) it is evident that preferential attack has occurred at certain planar defects. These defects could also be resolved in the scanning electron microscope used in the transmission mode (figure 4.24b). No additional diffraction spots were visible in selected area diffraction patterns from these defects. This was consistent with the defects being stacking faults rather than twins. However, as pointed out by Chang et al (1962) preferential thinning of the foil at twins could make the detection of twinned material impossible. In addition the large degree of inelastic scattering, as evidenced by the predominance of the Kikuchi lines observed in the diffraction pattern, means that any additional reflections would have to be of a very high intensity to be visible.

The more highly doped specimens with carrier concentration



a)

20 μ 

b)

100 μ

Figure 4.24 a) Electron micrograph of thinned specimen from vapour grown sample VP571/2
b) Transmission micrograph taken using the S.E.M. from the same thinned specimen.

$N > 2 \times 10^{17} \text{ cm}^{-3}$ were easier to thin and no preferential etching at defects was observed. The most common defects were identified as stacking faults. The majority of these were linear in nature but in some specimens tetrahedral faults were also observed (figure 4.25). Bright field and dark field micrographs of a linear stacking fault are shown in figure 4.26. Analysis of these showed that the faults were intrinsic in nature. For such purposes care was taken to choose a single fault rather than a series of overlapping faults which would give ambiguous results. It was established that tetrahedral faults such as shown in figure 4.25 were also intrinsic. The method used for the analysis was that described by Amelinckx (1964). If the reflection is of the type 400, 220 or 111, and if the diffraction vector with its origin at the centre of the fault points towards the dark fringe in the dark field image, the fault is intrinsic as in figures 4.25b and 4.26. The reverse is true for reflections of type 200 and 222.

In determining the direction of g in relation to the real image, account was taken of the extra inversion undergone by the real image with respect to the diffraction pattern. (Hirsch et al 1965, page 14). When using high resolution dark field the direction of g was opposite to that of the corresponding bright field image. This occurred due to the shift of the diffraction pattern in relation to the Kikuchi line pattern which remained stationary. As illustrated in figure 4.27 for a 220 reflection, the central spot of the diffraction pattern was shifted from one side of a Kikuchi line pair to the other. The operating diffraction spot appeared on the remaining Kikuchi line and was therefore on different sides of the central spot for the two cases.

More complex stacking faults were found in specimen AP 118/2. An analysis was made of the burgers vectors of the dislocations associated with the faults shown in figure 4.28. The plane of the foil

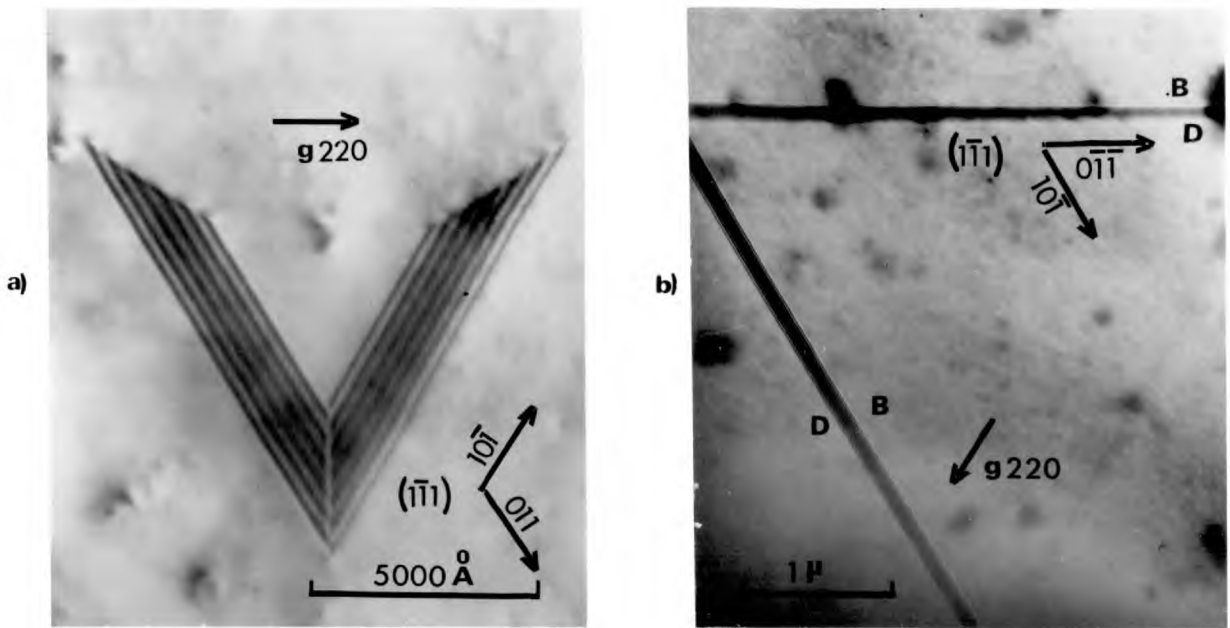


Figure 4.25

Tetrahedral stacking faults in vapour phase grown GaP.

a) Bright field image.

b) Dark field image. The 220 diffraction vector points towards the dark fringe therefore the fault is intrinsic.

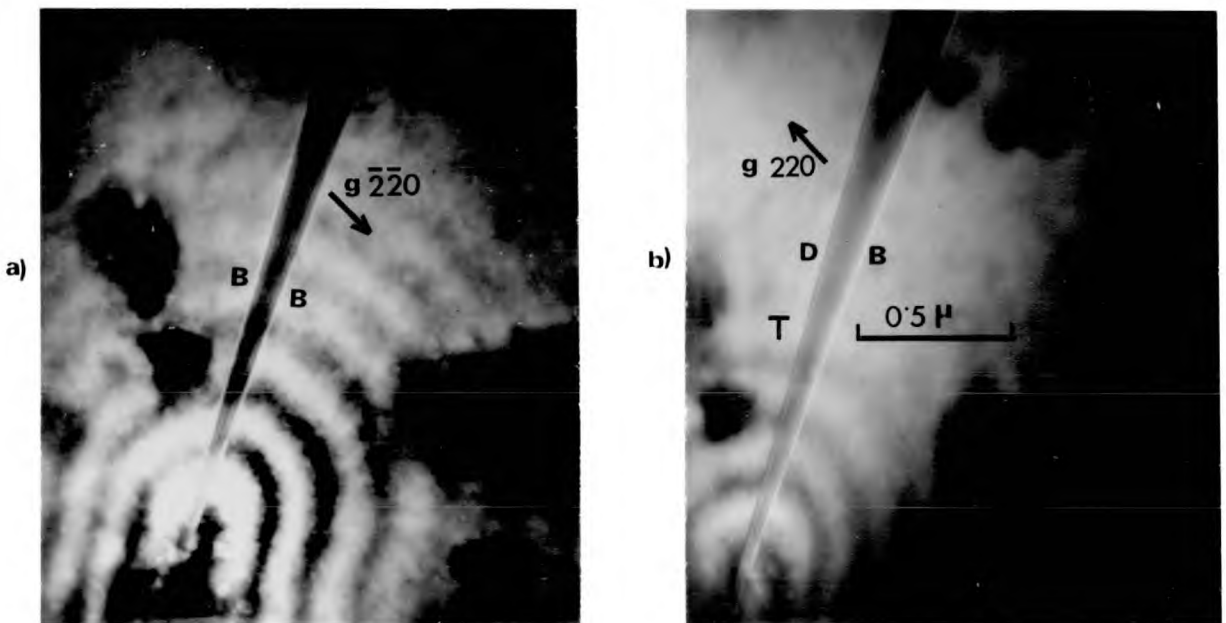


Figure 4.26

a) Bright field image and b) dark field image of a linear stacking fault in vapour phase grown GaP.

In the dark field image the 220 diffraction vector g points towards the dark fringe therefore the fault is intrinsic.

Due to the reversal of g between the two micrographs the top edge of the fault, marked T, shows fringes of different contrast in each micrograph.

was close to a $\{111\}$ orientation and was arbitrarily assigned the indices $(\bar{1}11)$. The faults gave no fringe contrast when observed in bright field using the 220 reflection (Figure 4.28a). For this to occur $\underline{R} \cdot \underline{g} = 0$ (Hirsh et al 1964), and thus the fault displacement vector $\underline{R}$ can only be of type $\pm 1/3 [\bar{1}11]$ or $\pm 1/3 [1\bar{1}\bar{1}]$. When the faults were observed using the 202 reflection (figure 4.28b), fringes were visible, i.e. $\underline{R} \cdot \underline{g} \neq 0$. Thus the fault vector $\underline{R}$ was of type $\pm 1/3 [\bar{1}11]$ or $\pm 1/3 [111]$. Only the value $\underline{R} = \pm 1/3 [\bar{1}11]$ is consistent with both observations and therefore the faults lie in the $(\bar{1}11)$ plane.

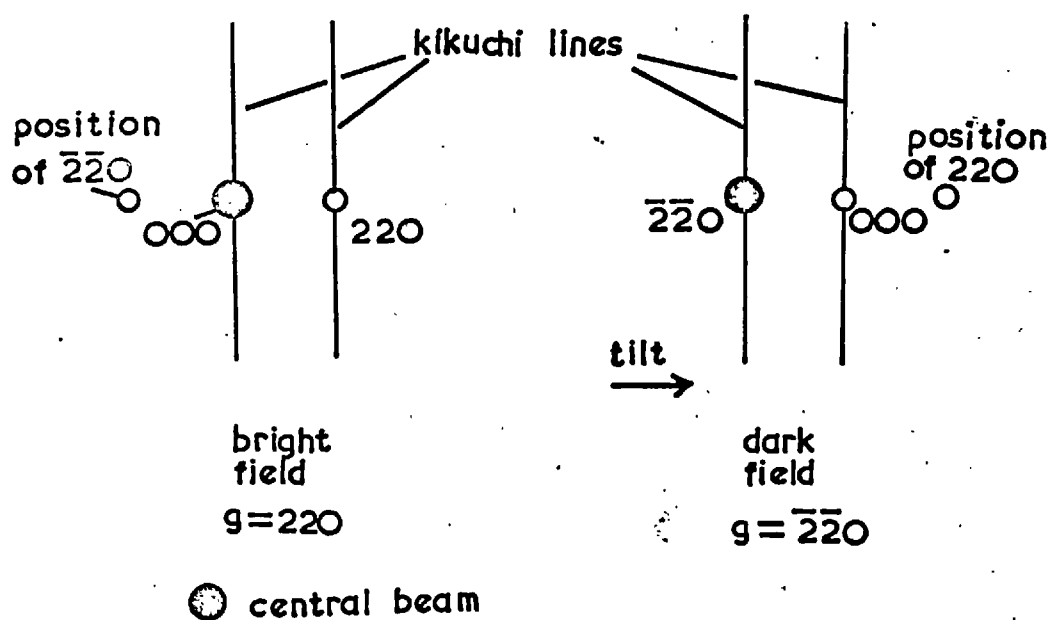


Figure 4.27 Diagram illustrating the reversal in sign of the diffraction vector $\underline{g}$ between the bright and dark field cases.

It is worth noting at this point that the terminology and theory relating to stacking faults in FCC materials can be applied directly to the sphalerite structure. The justification in principle is that the sphalerite structure consists of two interpenetrating FCC lattices

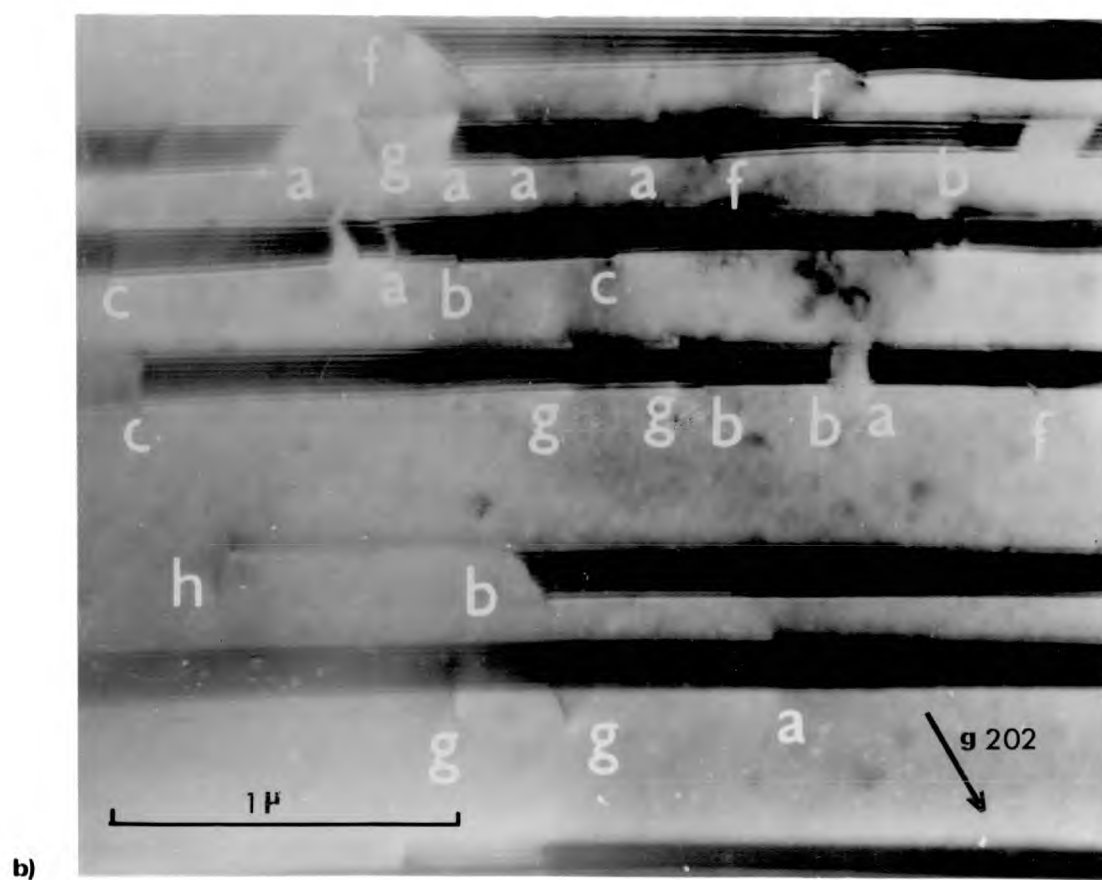
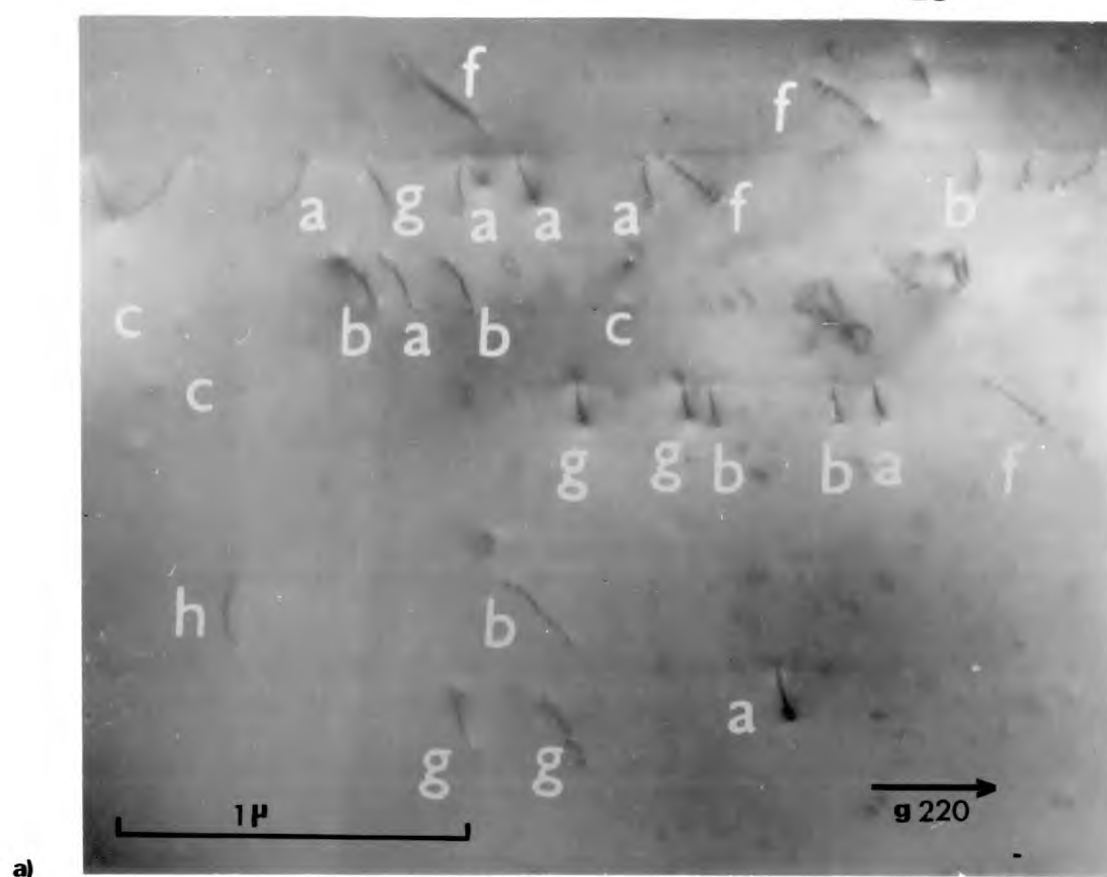


Figure 4 28

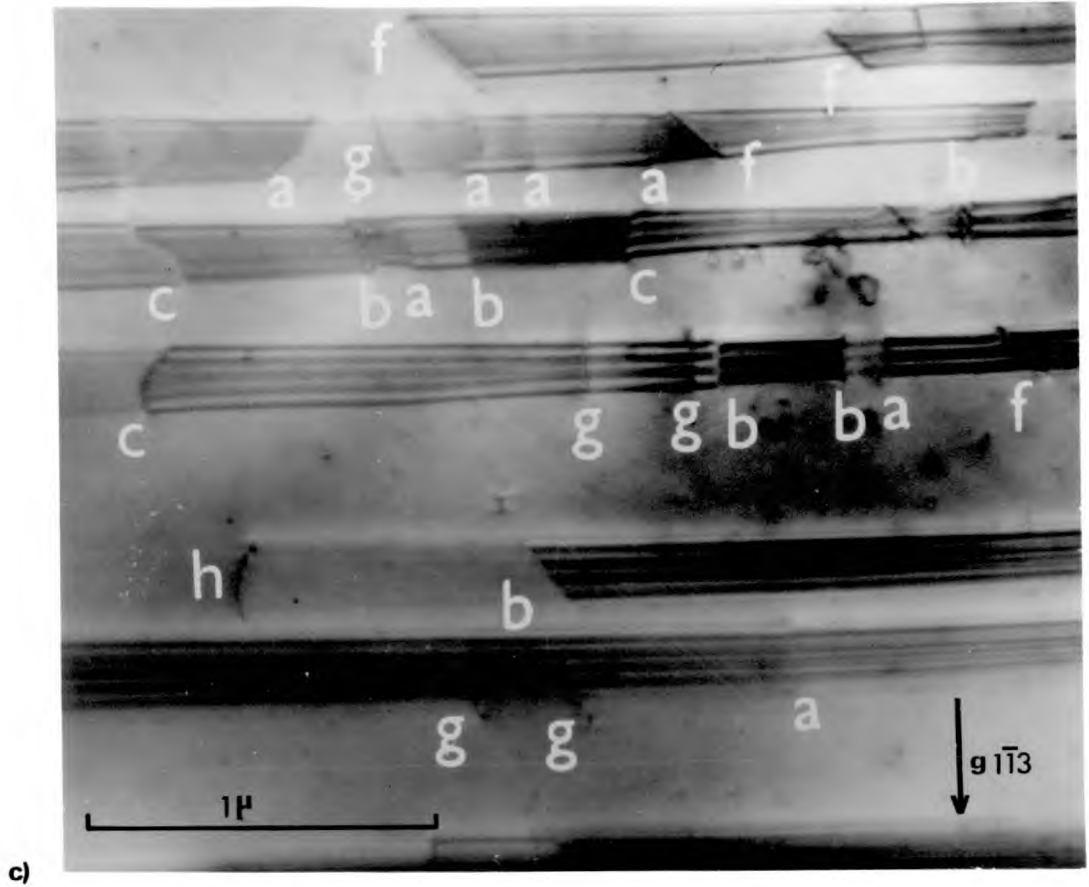


Figure 4.28 (cont).

Bright field micrographs of a stacking fault complex in vapour grown GaP slice no AP136/7. Te doped 1×10^{18} donors cm^{-3} .

a) Taken using the 220 reflection. The stacking fault fringes are out of contrast ie $g \cdot R = 0$ see text.

b) Taken using the 202 reflection.

c) Taken using the $1\bar{1}3$ reflection.

Micrographs a) and b) were taken with the electron beam close to the $[111]$ direction. Micrograph c) was taken with the specimen tilted so that the beam direction was close to $[3\bar{3}2]$.

composed of atoms of different type and displaced from one another by vectors of the type $\langle \frac{111}{444} \rangle$. The atomic arrangement at stacking faults in the diamond structure was discussed by Hornstra (1957). He demonstrated that faults in the **diamond** structure were similar in nature to faults in the FCC structure. In the FCC structure, the stacking sequence is built up of planes containing a single layer of atoms, whereas in the **diamond** structure, planes consisting of a layer of pairs of atoms must be considered, the atoms in each pair being joined by a bond in the $\langle 111 \rangle$ direction. Holt (1962) extended this treatment to the sphalerite structure and demonstrated the possibility of two types of fault, upright and inverted, the latter being a high energy structure with bonds between like atoms occurring both above and below the fault plane. In the present work no evidence was seen to suggest the presence of inverted faults and all the observed contrast effects could be explained in terms of upright faults analogous to those of the FCC structure. It is not certain whether an inverted fault would be expected to display any characteristic contrast effects. The fringe contrast exhibited by a stacking fault results essentially from differences in the phase angle in material above and below the fault plane. Any additional contrast due to the wrong bonds within an inverted fault would be limited in extent because only a layer two atoms thick is involved.

The burgers vectors of the partial dislocations associated with the faults of figure 4.28 were determined using the invisibility criteria as described by Silcock and Tunstall (1964). A table was made out to show the value of $\underline{g} \cdot \underline{b}$ for possible dislocations in the $(\bar{1}\bar{1}1)$ plane. (Table 4.4). For a perfect screw dislocation the invisibility criterion is that $\underline{g} \cdot \underline{b} = 0$; the presence of an edge component can however make the dislocation visible even under these conditions. For a Shockley type partial dislocation with no edge component the invisibility criterion

is that $\underline{g} \cdot \underline{b} = \pm 1/3$. For values $\underline{g} \cdot \underline{b} = \pm 2/3, \pm 4/3$, the dislocation will be visible. When an edge component is present, the dislocation will only be invisible when $\underline{g} \cdot \underline{b} = \pm 1/3$ if the value $E_g S_g$ is small. Here E_g is the extinction distance and S_g is the distance in reciprocal space of the reciprocal lattice point from the sphere of reflection measured parallel to the beam (see Amelinckx 1964, P.126). For a Frank partial, which is an edge dislocation, the invisibility criterion is less well defined. Even when $\underline{g} \cdot \underline{b} = 0$ the dislocation can still be intensely visible due to the finite value of $\underline{g} \cdot \underline{b} \wedge \underline{u}$, where $\underline{u}$ is the unit vector in the dislocation line. Invisibility can only be expected for the case where $\underline{g} \cdot \underline{b} \wedge \underline{u} = 0$. This condition takes account of the lattice displacement characteristic of an edge dislocation and has been treated theoretically by Howie and Whelan (1962). As a result of this, the Frank partial with $\underline{b} = 1/3 [\bar{1}\bar{1}1]$ will be visible in the 220 reflection even though $\underline{g} \cdot \underline{b} = 0$.

Reflection	$\underline{b} = 1/6 [2\bar{1}\bar{1}]$	$1/6 [\bar{1}2\bar{1}]$	$1/6 [\bar{1}\bar{1}2]$	$1/3 [\bar{1}\bar{1}1]$	$\frac{1}{2} [\bar{1}10]$	$\frac{1}{2} [\bar{1}0\bar{1}]$	$\frac{1}{2} [011]$
202	1/3	2/3	2/3	4/3	1	0	1
220	1	1	0	0	2	1	1
422	4/3	5/3	1/3	4/3	1	1	1
$\bar{2}42$	-5/3	-4/3	1/3	4/3	1	1	1
$1\bar{1}3$	-1/3	1/3	2/3	5/3	0	-1	1

Table 4.4 Values of $\underline{g} \cdot \underline{b}$ for dislocations lying in the $(\bar{1}\bar{1}1)$ plane.

For Shockley partials ($\underline{b} = \frac{1}{2} \langle 112 \rangle$) invisibility will occur only where $\underline{g} \cdot \underline{b} = 0$ or $\pm 1/3$. Total dislocations of screw nature ($\underline{b} = \frac{1}{2} \langle 110 \rangle$) will be invisible only when $\underline{g} \cdot \underline{b} = 0$. The Frank partial ($\underline{b} = 1/3 [\bar{1}\bar{1}1]$) possesses strong edge character (see text) and will be visible even for the case $\underline{g} \cdot \underline{b} = 0$.

In order to perform a valid analysis of Shockley partial dislocations it was necessary to determine the experimental limits of the value of $E_g S_g$. According to Silcock and Tunstall (1964) the criterion for unambiguous results is that $E_g S_g < \sim 0.3$.

To calculate E_g the expression

$$E_g = V \cos \theta / \lambda F_g.$$

was used (Hirsch et al 1964, page 102). Here V is the volume of the unit cell, λ the wavelength of the electrons, F_g the structure factor and θ the Bragg angle. The structure factor was calculated using the expression

$$|F_g|^2 = 16 [f_{ga}^2 + f_p^2 + 2 f_{ga} f_p \cos \pi/2 (h + k + l)]$$

[Cullity 1956]. The atomic scattering amplitudes for electrons f_{ga} and f_p were taken from tables given by Hirsch et al and were relativistically corrected for 100 kV electrons. For this purpose the relevant parameter $(\sin \theta) / \lambda$ was calculated using the Bragg equation $\lambda = 2d \sin \theta$. The wavelength of 100 kV electrons was taken as $0.037 \text{ \AA}$ and the lattice parameter of GaP as $5.4505 \text{ \AA}$ (Geisecke 1966). The calculated extinction distances for the relevant reflections are given in table 4.5. The accuracy of the calculated values of E_g is limited by uncertainty in the scattering amplitudes which are not known to better than a few per cent. Other possible errors involved in the calculation are discussed by Hirsch et al. The calculated values can be judged correct only to within about $\pm 10\%$.

Reflection	$\frac{\sin \theta}{\lambda} \text{ \AA}^{-1}$	f_{ga}	$f_p \text{ \AA}^{-1}$	$F_g \text{ \AA}^{-1}$	$E_g \text{ \AA}$	$\frac{\Delta x}{x}$
220	0.26	3.48	2.48	23.8	577	0.053
113	0.30	3.03	2.04	14.6	941	0.024
224	0.45	2.04	1.15	12.8	1072	0.01

Table 4.5 Calculated values of E_g for various reflections and values of $\Delta x/x$ for $E_g S_g = 0.3$. For notation see text.

The value of S_g can be determined by observation of the Kikuchi line pattern (Amelinckx 1964 page 125). When Δx is the displacement on the plate of the Kikuchi line in relation to the diffraction spot and x is the distance of the spot from the centre of the pattern:-

$$S_g = \Delta x \lambda / x d_{hkl}^2.$$

For each reflection this expression was used to calculate values of $\Delta x/x$ which would satisfy the condition $E_g S_g = 0.3$; these are listed in the table. It is apparent that as the reflections increase in order it becomes more difficult to align the specimen within the critical condition. In practice it was found that for the 220 and 113 reflections an adequate degree of accuracy was achieved.

From measurement of the projected widths of the faults the specimen thickness was calculated to be near $4000 \text{ \AA}$. This gave rise to a very intense Kikuchi pattern which for values of $\Delta x/x$ greater than about 0.2 completely obscured the diffracted spots. It was found that when $\Delta x/x$ was varied about zero the intensities of both the direct and diffracted spots went through distinct maxima. This provided a convenient way of minimising $\Delta x/x$ and all micrographs were taken with the spots at maximum intensity. Measurements on the diffraction patterns showed that the values of $\Delta x/x$ were within the limits for the condition $E_g S_g < 0.3$ to hold. For the higher order reflections of type 422 it was found that the maxima of the two spots occurred at slightly different angles of tilt. This made exact alignment very difficult and measurements on the diffraction patterns gave values for $\Delta x/x$ greater than 0.5 and outside the acceptable limits. As sufficient information was available from the lower order reflections for dislocation analysis the 422 reflections were not used.

A check that $E_g S_g < 1$ can be simply made by observation of the fringes in the stacking fault. Whelan and Hirsch (1957) showed that

when $E_g S_g \leq 0.5$, dynamical conditions of diffraction result in each stacking fault fringe having a double minimum. This can be seen clearly in figure 4.28c where each fringe appears as a double dark line.

The observed visibilities of a large number of dislocations in different reflections were compared with the predicted visibilities in table 4.4. It was found that the majority of dislocations were Shockley partials with a burgers vector of type $\underline{b} = a/6 [21\bar{1}]$. These are denoted by the letter 'a' on the micrographs. It can be seen that all dislocations so marked in figure 4.28 are visible in the 220 reflection and are either invisible or exhibit very faint contrast in the 202 and $1\bar{1}3$ reflections consistent with the predictions of table 4.4. Similarly those of type $\underline{b} = a/6 [\bar{1}21]$ and $\underline{b} = a/6 [\bar{1}\bar{1}2]$ are denoted by the letters 'b' and 'c' respectively.

Some dislocations were found which were visible in all reflections. Comparison with the table indicates that these will either be perfect dislocations or else Frank partials. A Frank partial must bound a region of stacking fault and, even in a system of overlapping faults such as here, can be distinguished from a perfect dislocation by the change in nature of the fault fringes either side. Frank partials with $\underline{b} = a/3 [\bar{1}\bar{1}1]$ and exhibiting the above contrast are denoted by the letter f. Perfect dislocations with no associated change in fringe contrast are denoted by the letter 'g' but there was insufficient data for burgers vector determination. The dislocation at 'h' was visible in all reflections and gave the appearance of terminating a stacking fault. The stacking fault immediately adjacent gave only very faint fringe contrast so no unambiguous analysis could be made.

Certain dislocations were found to have well defined line directions. In particular all the Frank partials lay along the $[10\bar{1}]$ direction. The Schockley partials were found to lie variously along the $[011]$,

$[\bar{2}13]$, $[1\bar{1}2]$ and $[1\bar{2}3]$ directions with no particular correlation between the direction and the assigned burgers vector. As a large number of the Shockley partials were bowed, the directions were taken as parallel to the line joining the points of intersection with the top and bottom of the foil.

The most complex defect structure was found in specimen no. AP 136/7 which also had the highest doping level. Figure 4.29 is a dark field micrograph illustrating some of these defects. The plane of the foil was found to be close to $\{114\}$. Two sets of stacking faults are present but one set lying parallel to the $[\bar{2}20]$ direction is out of contrast. It can be seen that the apparent nature, intrinsic or extrinsic, of the stacking faults varies along their length. For example at A the position of the bright fringe indicates an intrinsic fault whereas that at B indicates an extrinsic fault. This is interpreted as a case of faults on adjacent planes overlapping one another. Whelan and Hirsch (1957) showed that the fringe contrast of a stacking fault is governed by the phase angle $\alpha = 2\pi \underline{g} \cdot \underline{R}$, where $\underline{R}$ is the displacement vector of the fault. If $\alpha = +2\pi/3$, a single fault in bright field will show bright edge fringes, and dark edge fringes for $\alpha = -2\pi/3$. If two intrinsic faults overlap on another on closely adjacent planes the total phase angle is simply the sum of the individual phase angles. If α is $2\pi/3$ for each fault individually it is $4\pi/3$ for the pair; this is equivalent to $-2\pi/3$. Thus α changes sign and the fringes from the pair reverse in the sense that light fringes become dark fringes and vice versa. This applies equally in dark field so that the pair together is equivalent to an extrinsic fault. For three overlapping faults $\alpha = 6\pi/3$ which is equivalent to $\alpha = 0$ and no fault contrast would be expected. In practice a finite spacing between fault planes results in faint fringes appearing such as at C and D in figure 4.29.

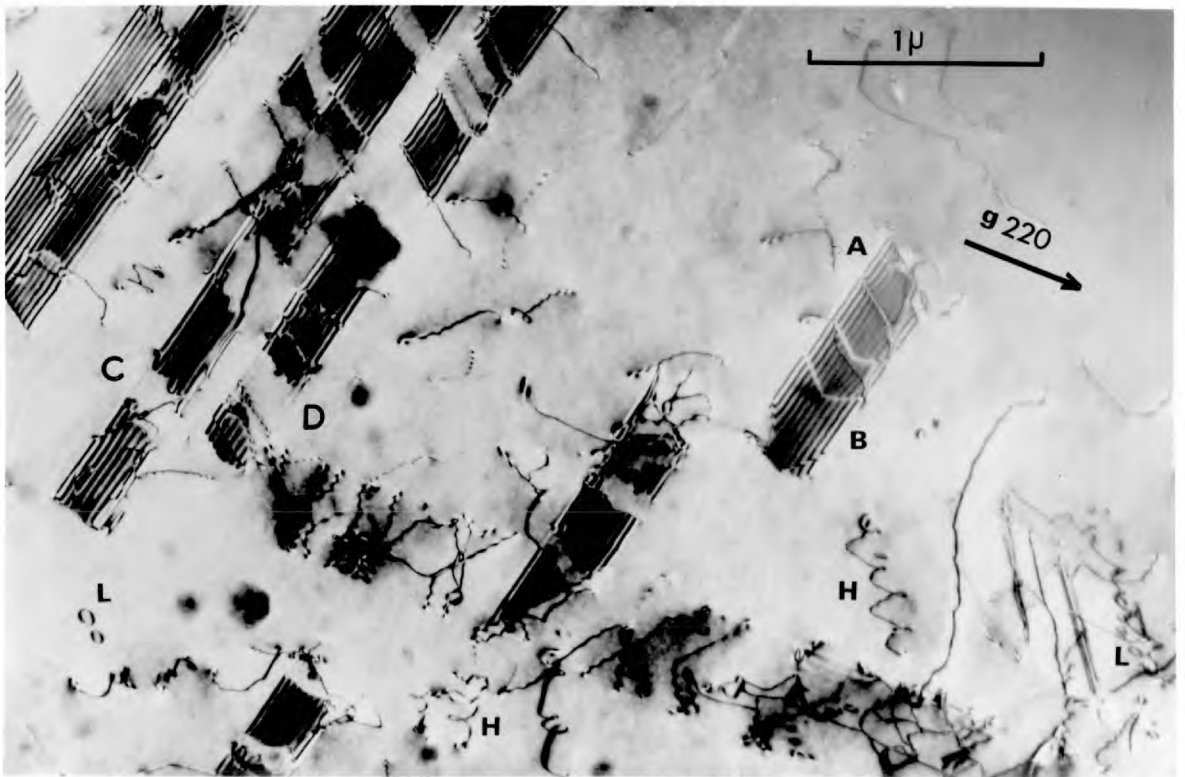
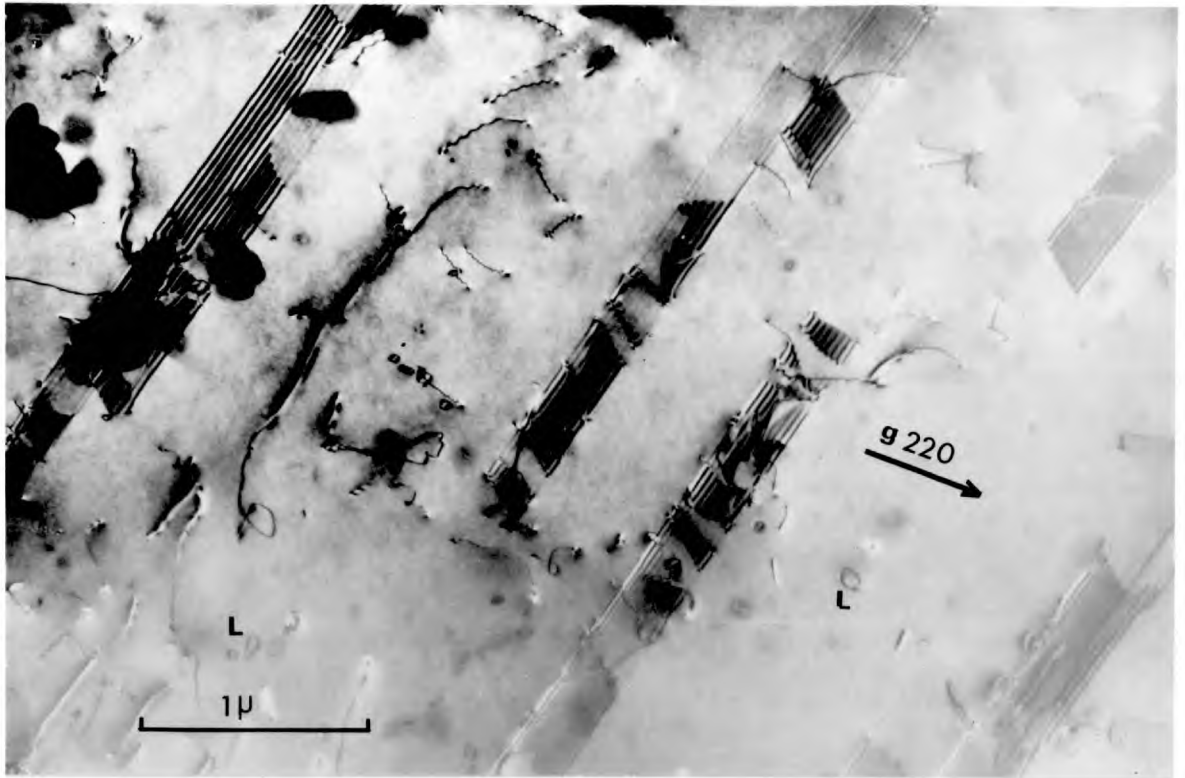


Figure 4.29 Dark field micrographs showing defects in vapour phase grown specimen AP 136/7. Helices are marked h and dislocation loops l.

Also visible in the micrograph are a number of helical dislocations and dislocation loops *l*. Stereo pair analysis was used to show that the helices were in fact helical dislocations and not just a series of dislocation dipoles.

Other interesting defects were found in a different region of the same specimen. Figure 4.30a shows a dislocation complex associated with a subgrain boundary. The tilt across the boundary could be detected in the electron microscope by a small rotation of the selected area diffraction pattern as the boundary was traversed. Of interest are the different types of interface which were shown by trace analysis to be of types (111) , $(\bar{1}\bar{1}\bar{1})$ and (122) when the normal to the foil had the indices $[114]$. A good example of a cross slip loop marked *l* is seen on the (122) plane. The dark lamellae also visible in the micrograph gave extra spots in selected area diffraction. This identified them as microtwins as distinct from stacking faults which would not be expected to give rise to extra spots. The finite width of these features which lie in the (111) plane can be observed by comparison with the projected image of one of the associated dislocations. Another example of a microtwin is seen in figure 4.30b. Here characteristic wedge fringe contrast can be observed at the edges even though a multibeam diffraction condition was operating. Figure 4.31a is a bright field image illustrating a stacking fault complex of a slightly different nature to those of Figure 4.29. Two main overlapping fault lines are visible. The one on the right hand side in the micrograph exhibits distinct sections showing a number of different types of fault contrast. This is clearly characteristic of a number of overlapping faults on closely adjacent planes. On the other hand, the fault line on the left exhibits only two types of fringe contrast. In the one, fringes are clearly visible whilst in the other the fringes are very faint. The

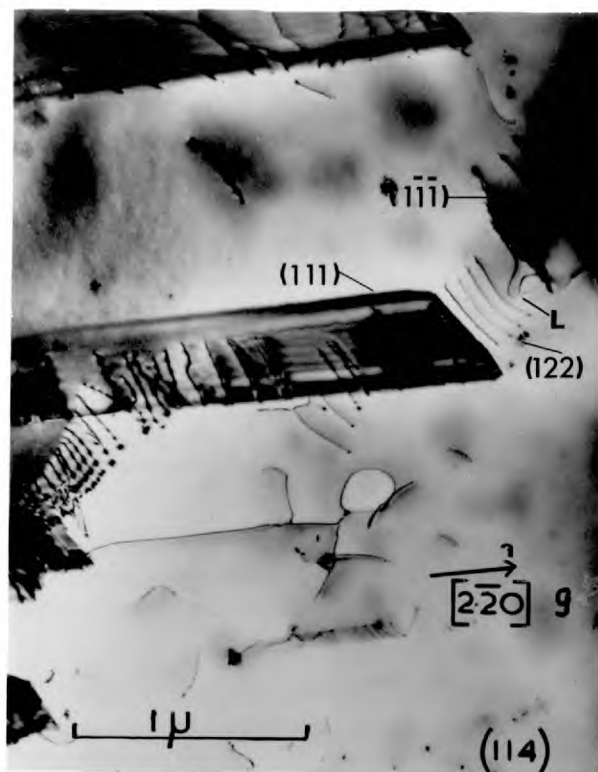


Figure 4.30 a) Electron micrograph showing defects at a subgrain boundary in specimen AP 136/7. The interface planes as determined by trace analysis are indicated along the boundary. A cross slip loop is marked L.
b) A micro-twin present in a different area of the same specimen (multibeam reflection).

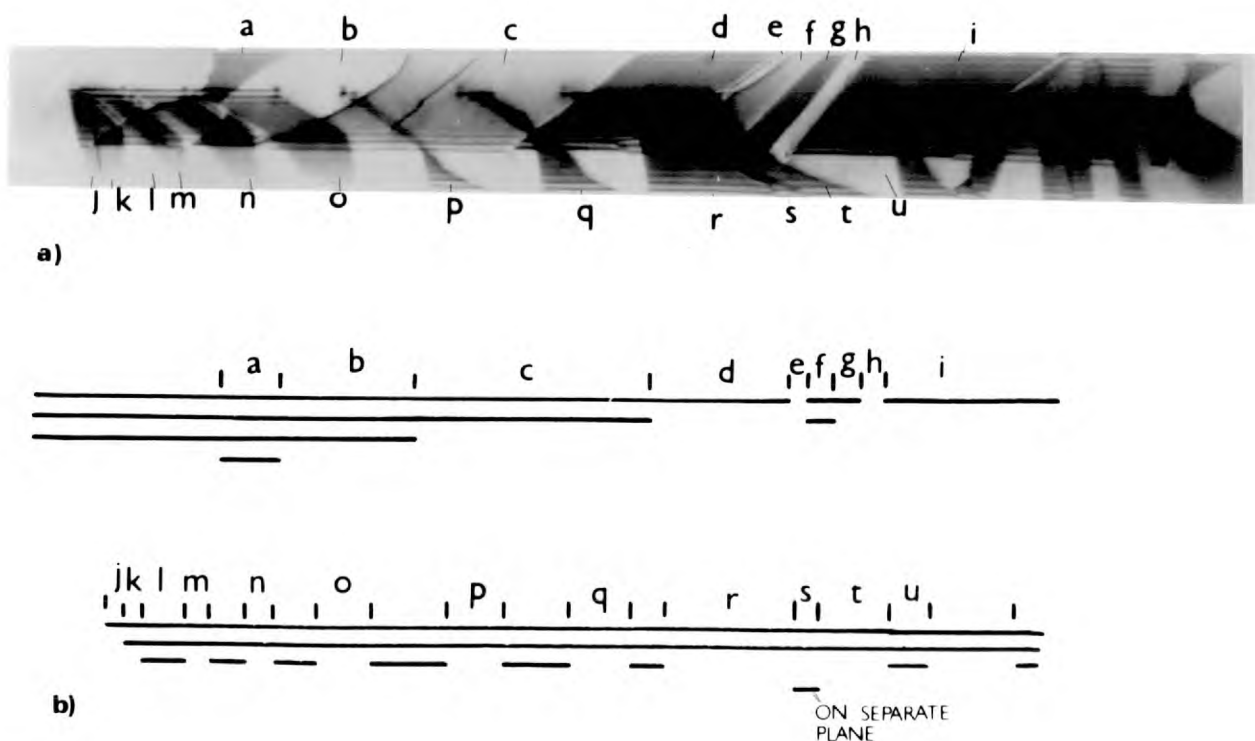


Figure 4.31 a) Complex stacking fault structure in specimen No AP 118/2.
b) Diagram drawn looking parallel to the plane of the faults showing possible arrangements of single intrinsic faults to give rise to the observed contrast.

suggested explanation for this contrast is that a number of total dislocations have moved into an atomic plane or planes close to an original fault system. These dislocations have subsequently dissociated to give a number of small regions of stacking fault bounded by partial dislocations. Examination of the lower edge of the fault at point j in the micrograph indicates that the original system may have consisted of a pair of overlapping intrinsic faults such that for the two $\alpha = 4\pi/3$. The dissociation of a total dislocation to give a further region of intrinsic fault would give a sum total of $\alpha = 6\pi/3$ and ideally no fringe contrast would be seen. A finite atomic separation between the fault planes can result in faint fringes appearing as in the present case. Figure 4.31b is a schematic drawing showing how systems of overlapping intrinsic faults could give rise to the fringe contrast observed in the fault complex.

4.5.2 Pulled Material.

Pulled material is currently produced at S.E.R.L. mainly for use as substrate material for liquid phase epitaxy. In a device it provides electrical contact to the overgrown n + layer and as such must itself be n-type material with a high conductivity. In general the material is doped with Te or S to a free electron concentration of about $1 \times 10^{18} \text{ cm}^{-3}$. The specimens subjected to examination are listed in table 4.6.

In the undoped specimen PEO2, preferential attack occurred at planar defects during the thinning process. An example of this can be seen at the linear stacking fault in figure 4.32. A number of these faults were analysed and all found to be intrinsic. Stacking fault tetrahedra were also found together with dislocations (figure 4.33). In this micrograph no stacking fault fringes are visible as a multi-beam reflection was used.

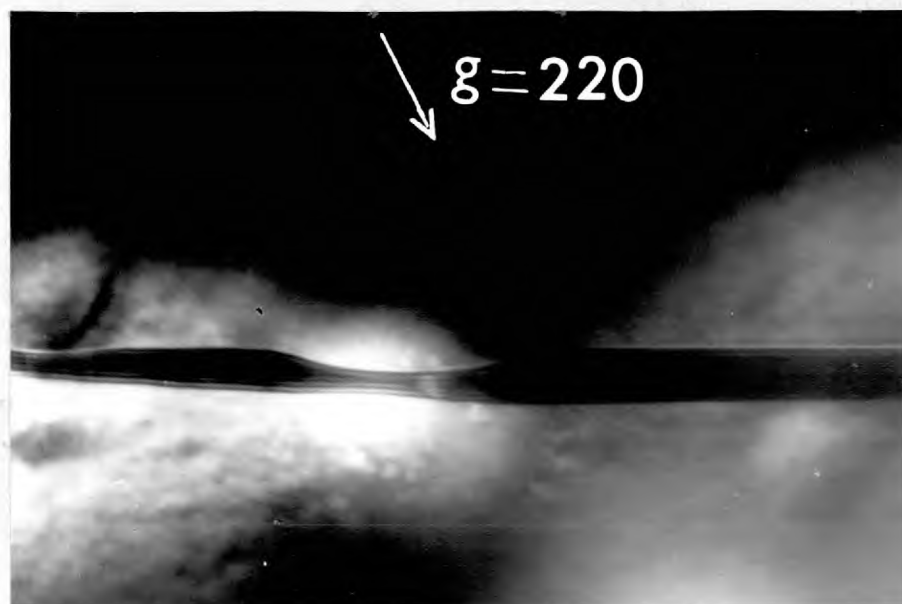


Figure 4.32 Dark field micrograph showing evidence of preferential polishing at a stacking fault in specimen PEO 2.

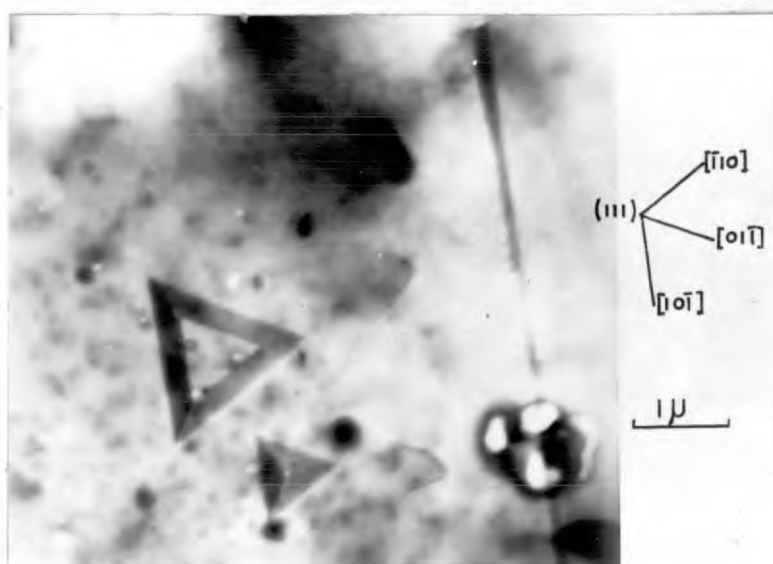


Figure 4.33 Micrograph showing stacking fault tetrahedra in specimen PEO 2.

Specimen (S.E.R.L. No)	Doping	Free electron conc ⁿ cm ⁻³
PEO 2	Undoped	-
PEO 77	S	9×10^{17}
PEO 53	S	1×10^{18}
PEO 78	S	1×10^{18}
PEO 73	S	2×10^{18}
PEO 24	Te	3×10^{17}
PEO 47	Te	1×10^{18}
PEO 48	Te	1×10^{18}

Table 4.6 List of the GaP specimens grown by Czochralski pulling
(liquid encapsulation) from the melt.

In all the sulphur doped material there was evidence of what could be precipitation. This is shown up in figure 4.34, a micrograph of specimen PEO 77, as a series of small dark spots. The use of a stereo pair showed these spots to be actually inside the material and not simply surface features. The larger inclusion shown in the same micrograph was examined in selected area diffraction and a ring pattern indicated an amorphous structure.

A similar dotted background was visible in micrographs from the other S doped specimens. In figure 4.35 (specimen PEO 53), these spots can be seen together with some larger angular particles which were shown to be on the surface and are probably due to contamination. The small spots were measured as about $40 \text{ \AA}^0$ diameter and appear to show an interaction with the extinction contours. This would be consistent with them being precipitates, made visible by the structure factor contrast mechanism (Hirsch et al P336). An order of magnitude estimate was made of the total volume of the precipitates shown in this micrograph. The average diameter of the precipitates was measured



Figure 4.34 Micrograph showing precipitation effects and an inclusion in sulphur doped specimen PEO 77.

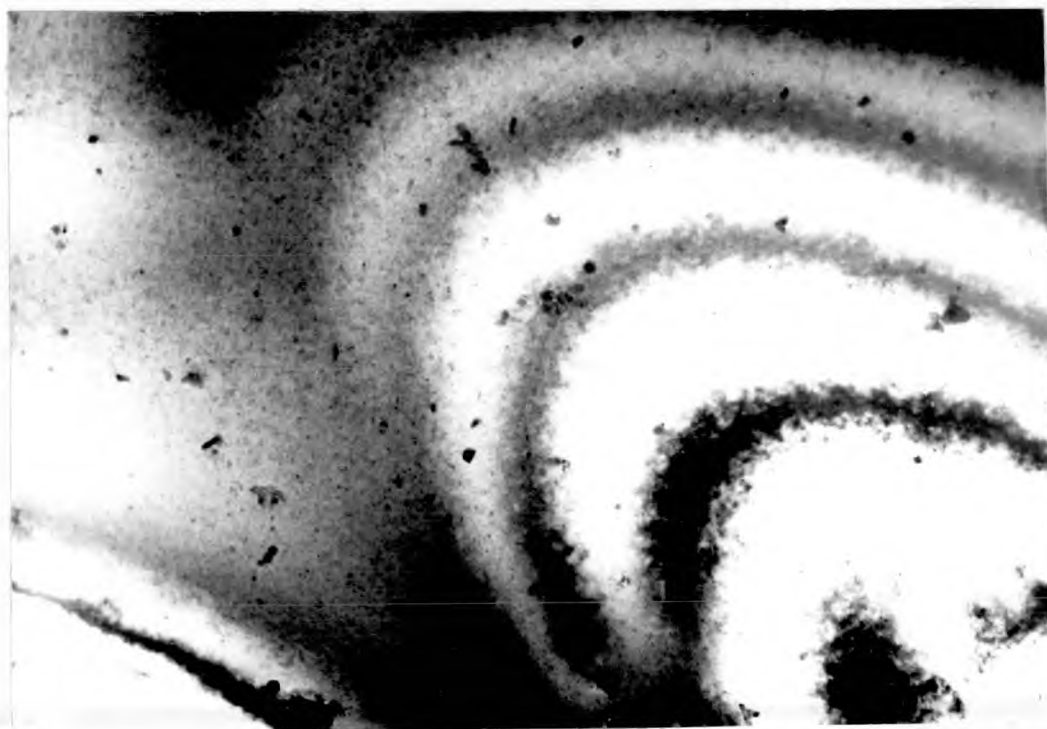


Figure 4.35 Micro-precipitates in sulphur doped specimen PEO 53.

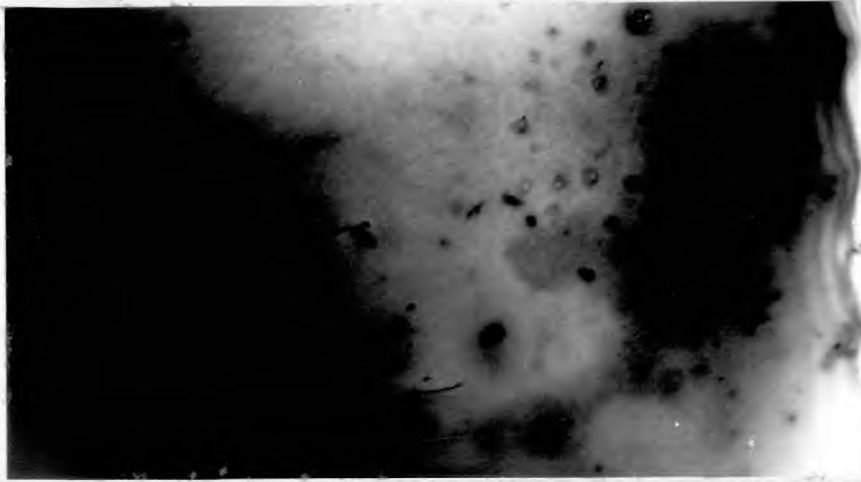
as near $40 \text{ \AA}^0$ and the density measured as 5 particles per 10^{-10} cm^2 area. The specimen thickness was estimated as $5000 \text{ \AA}^0$ and this gave a precipitate density of 1 part in 3×10^4 by volume. This is equivalent to about 1.5×10^{18} precipitate atoms / cc. The accuracy of this figure is however limited by the difficulty of measuring the precipitate diameters which are only just within the resolution of the electron microscope. Also the estimate of the specimen thickness may not be very accurate.

In the Te doped material little evidence of precipitation was found. In one specimen (PEO 48) a number of dark spots were observed and some of these can be seen in figure 4.36. Again stereo pair analysis showed these to be in the material itself. Also present in this micrograph is a dislocation with a single helical loop. Some precipitation is apparently associated with this defect.

4.5.3 GaP grown by Liquid Phase Epitaxy.

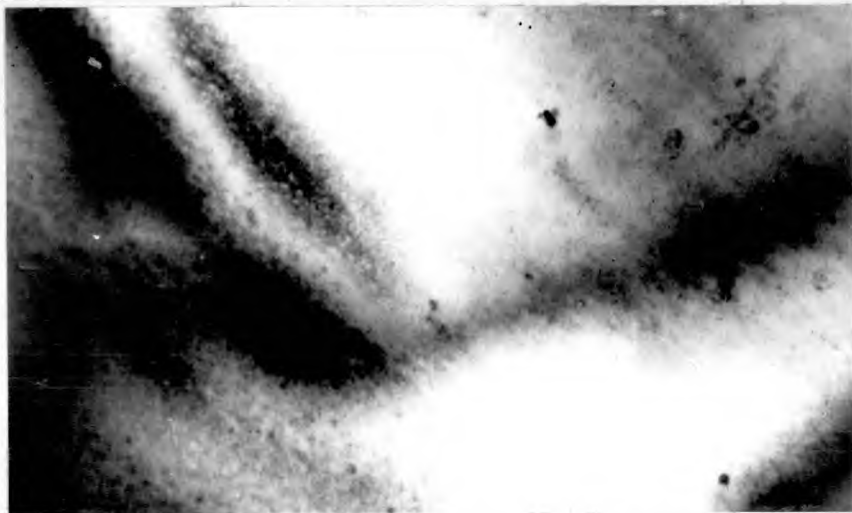
GaP diodes were fabricated at S.E.R.L. by a double epitaxial process using pulled material as the substrate. An n + layer, doped with Te or S, was grown by liquid epitaxy onto the substrate and a p layer (Zn-O doped) was overgrown onto this. Some specimens were received with both the n + and p layers and others with just the n + layer (table 4.7). Thinning of the specimens with Zn-O doped p-type layers was made difficult by the pitted nature of the surface.

The nature of this surface can be seen in figure 4.19 which was taken using the S.E.M. During thinning, holes formed first at these pits and the subsequent formation of a suitable thin area was only occasionally found possible. The depth of the pits was found to be too great to allow a suitably flat surface to be produced initially by mechanical polishing without danger of reaching the p-n junction. In general, the liquid epitaxial Te or S doped layers were found to be



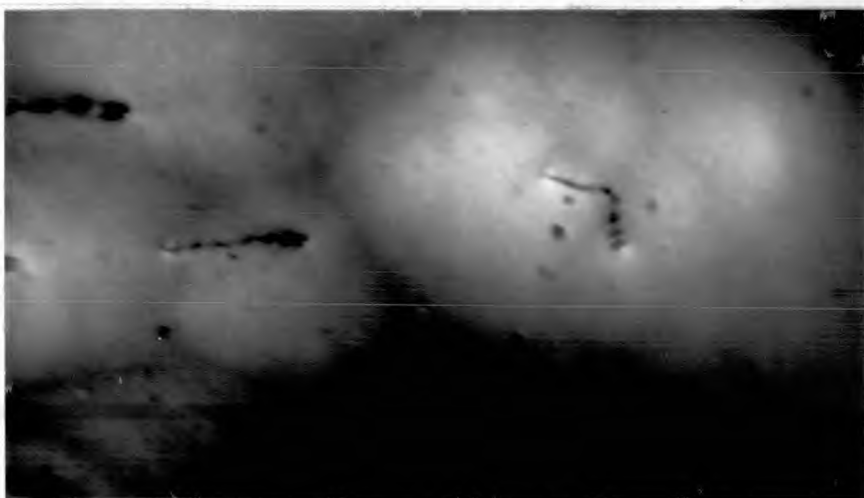
1μ

Figure 4.36 Dislocations and precipitates in specimen PEO 48/14. A helical dislocation is present in the centre of the micrograph and apparently has some precipitation associated with it.



1μ

Figure 4.37 Precipitation in Te doped liquid epitaxial layer of slice L322.



1μ

Figure 4.38 Dislocations in p-type layer of slice L222.

of much better quality and little difficulty was experienced in producing adequate thin areas. On the microscopic scale these n + layers were found to be of very good quality. No stacking faults or dislocations were observed in any specimen. In some layers however, evidence of precipitation was found (figure 4.37).

Specimen (S.E.R.L. No)	p Layer	n + layer.
JN 162	-	1×10^{18}
JN 64	-	1×10^{18}
JN 151	-	1×10^{18}
JN 148	-	1×10^{18}
L 322	1×10^{18}	$2-4 \times 10^{18}$
L 222	1×10^{18}	$2-4 \times 10^{18}$
L 343	1×10^{18}	1×10^{18}
L 317	1×10^{18}	1×10^{18}

Table 4.7 List of liquid epitaxial specimens examined in the electron microscope. All were grown on pulled GaP substrates and the n + layers were doped with Te and the p layers with Zn-O.

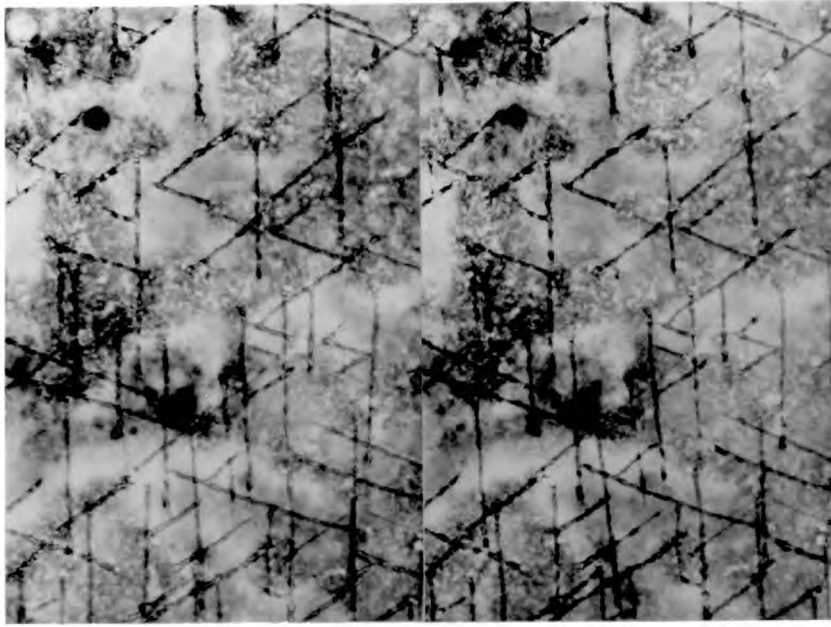
The Zn-O doped layers were, on the microscopic scale, found to be less perfect than the n + layers. In all the specimens dislocations were observed (figure 4.38). The overall dislocation density was estimated at about $4 \times 10^6 \text{ cm}^{-2}$. Evidence of precipitation can also be seen in this micrograph in the form of a number of isolated spots. As with the n + layers no stacking faults were observed.

4.5.4 Electrochemical Polishing.

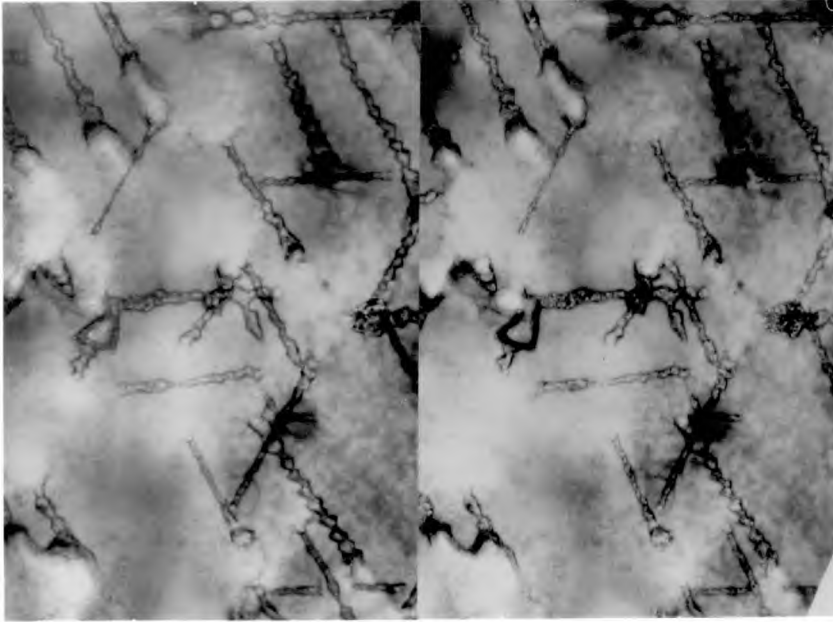
As mentioned in section 3.6.2 it was found impossible to satisfactorily thin GaP from the A face using chemical polishing alone.

A combination of electrochemical and chemical polishing was developed to overcome this problem. Electrochemical polishing was used to produce a smooth, well shaped, dimple and the final thinning was accomplished by chemical means alone. This final stage lasted about 15 seconds and was sufficient to remove the orange coloured surface film and other effects of the electrochemical reaction yet did not lead to any undesirable etching.

To examine the nature of this orange surface film specimens were prepared using electrochemical polishing alone. Examination in the electron microscope revealed the presence of a dense network of linear features which were only visible in specimens with this surface film remaining. Examination using a stereo pair (figure 4.39) shows that the features form a three dimensional array with each one penetrating the foil from top to bottom. The stereo pairs were taken using the specimen tilt stage of the microscope to give about 8° difference in tilt between the two micrographs. To achieve identical contrast in each micrograph the tilting was carried out whilst observing the diffraction pattern. The same two beam condition was used for each micrograph and the tilt was such that the central and diffracted spots remained on the same pair of Kikuchi lines throughout. Selected area diffraction patterns from regions with heavy concentrations of the features, showed no additional diffraction spots. This ruled out the possibility of the presence of a second phase or of extensive precipitation. It was concluded that the features were etch or corrosion tunnels possibly of a similar nature to those observed in LiF (Westwood and Rubin 1962) or in Cu_3Au alloys (Swann 1969). The scattering of light from these networks of tunnels is thus the explanation for the translucence of the orange surface film and the diffuse nature of light reflected from it when observed in the optical microscope.



1 μ



0.5 μ

Figure 4.39 Stereo pairs to illustrate the 3D array of tunnels. Angle of tilt between each micrograph of pair is $\sim 7^\circ$. Viewing of stereo pairs is conveniently carried out using a lens of focal length $f \sim 15\text{cm}$ for each eye.

All the specimens examined were close to $\{111\}$ orientation and the tunnels projected onto the three $\langle 211 \rangle$ directions in this plane. Examination of the 111 stereogram (figure 4.40) shows that this condition is met if the tunnels lie either in $\langle 111 \rangle$, or $\langle 110 \rangle$ or $\langle 100 \rangle$ directions. Tunnel directions of higher index can be discounted because these would give rise to more than three directions projected onto the (111) plane and the networks would be much more complex than were observed. To decide between these possible directions a series of micrographs was taken using widely differing angles of tilt provided by the high tilt goniometer stage in the Siemens Elmiskop I. The angles between the projected tunnel directions measured on each micrograph are listed in table 4.8 against the appropriate beam direction. The beam directions were determined by analysis of the diffraction pattern relative to a foil normal of $[111]$.

Beam Direction	Measured angles		
$[123]$	70°	64°	46°
$[132]$	71°	46°	63°
$[255]$	72°	54°	54°

Table 4.8

For each beam direction the angles between tunnels were calculated assuming the tunnels lay along the $[11\bar{1}]$, $[1\bar{1}1]$ and $[\bar{1}11]$ directions. To do this the tunnel directions were first projected onto the plane normal to the beam direction by cross multiplication. For example, take the $[123]$ beam direction.

$$123 \wedge 11\bar{1} = \bar{5}4\bar{1} = \bar{a}$$

$$123 \wedge 1\bar{1}1 = 52\bar{3} = \bar{b}$$

$$123 \wedge \bar{1}11 = \bar{1}43 = \bar{c}$$

The directions $\bar{a}$, $\bar{b}$ and $\bar{c}$ are in fact the normals to the true projected

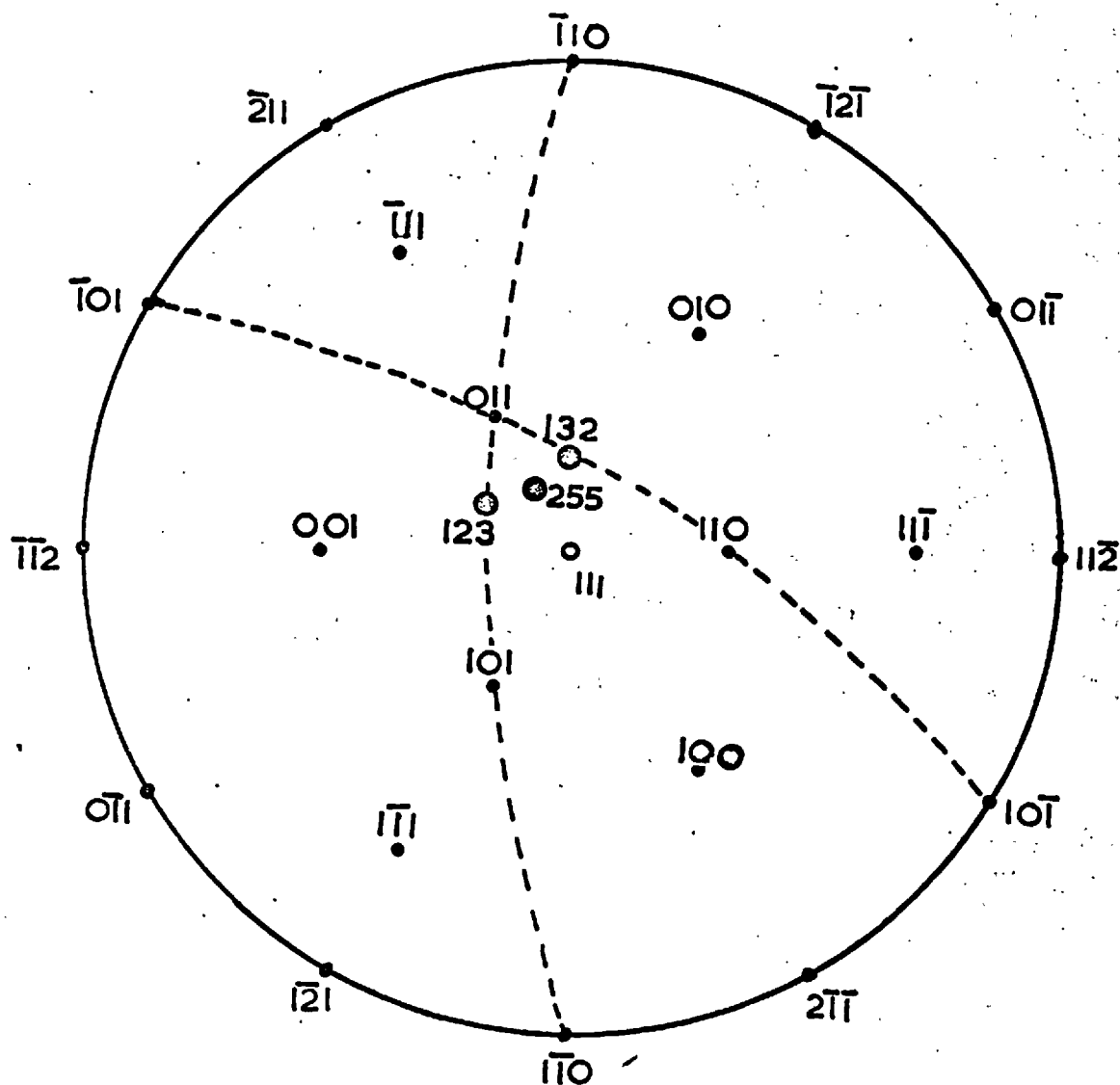


Figure 4.40 Stereogram of the (111) plane with the beam directions $[12\bar{3}]$, $[132]$ and $[255]$ marked. It can be seen that the $12\bar{3}$ and 132 points lie on the $\{111\}$ type zones which also contain the $\langle 110 \rangle$ directions. Thus for example in the case of the $[12\bar{3}]$ beam direction the two directions $[011]$ and $[101]$ appear parallel.

directions in the (123) plane. However, the relative angles between the directions would be unchanged by a further rotation through 90°

The angles between the directions $\bar{a}$, $\bar{b}$ and $\bar{c}$ were then determined using the formula,

$$\theta = \cos^{-1} \frac{\bar{a} \cdot \bar{b}}{|\bar{a}| \cdot |\bar{b}|}$$

Thus for the $[123]$ beam direction:-

$$\theta_{ab} = \cos^{-1} (14 / \sqrt{36} \times \sqrt{42}) = \cos^{-1} 0.36 = 71^\circ$$

Similarly, $\theta_{bc} = 44^\circ$ and $\theta_{ac} = 65^\circ$

The relevant angles were also calculated for the $[132]$ and $[255]$ beam directions (table 4.9)

Beam Direction	Calculated Angles		
$[123]$	71°	65°	44°
$[132]$	71°	44°	65°
$[255]$	68°	56°	56°

Table 4.9

Comparison shows that the calculated angles are within $\pm 2^\circ$ of the measured angles. Such a difference can be explained by slight deviation of the true beam direction from that indicated by the diffraction patterns.

If the tunnels lie in the directions $[110]$, $[\bar{1}01]$ and $[011]$, calculation shows that for the $[123]$ and $[\bar{1}32]$ beam directions, two of the tunnel directions would appear parallel in the micrographs. For example:-

$$123 \wedge 101 = \bar{1}11$$

$$123 \wedge 011 = \bar{1}11$$

This can also be seen from examination of the stereogram (figure 4.40)

and is clearly inconsistent with the observations listed in table 4.8. Calculations for the three $\langle 100 \rangle$ type directions show that these project normal to $[0\bar{3}2]$, $[\bar{3}01]$ and $[2\bar{1}0]$ for a $[123]$ beam direction. The calculated angles between these directions are 80° , 68° and 32° and clearly these do not correspond to the measured angles in table 4.8. It must therefore be concluded from these results that the tunnels lie exclusively along $\langle 111 \rangle$ directions.

At extinction contours, the absence of material in the tunnels gave rise to characteristic contrast. In figure 4.41a it can be seen that the contours are displaced where they are crossed by a tunnel. Figure 4.41b is a cross sectional diagram showing the relation of the tunnel at A in figure 4.41a to the top and bottom surfaces of the foil. By counting extinction contours on the micrograph it was established that the bottom of the etch pit was the equivalent of 1.5 extinction distances E_g from the unetched base of the foil. For all tunnels their projected lengths were in proportion to the depth of material below the pits.

The displacement of an extinction contour where it is crossed by a tunnel was measured as about $2/3$ of the contour separation E_g for a tunnel diameter of 0.4 μ m on the micrograph. Thus the effective thickness of the tunnel as seen by the electron beam can be written:

$$t = \frac{0.4}{\sin \theta} = \frac{2}{3} E_g. \quad \dots 1$$

Where θ is the angle between the tunnel and the normal to the foil as indicated in figure 4.41.

Also a tunnel of measured length 3 μ m penetrates a thickness of material equal to 1.5 E_g :-

$$1.5 E_g = 3 / \tan \theta. \quad \dots 2$$

Combining 1 and 2 to eliminate E_g gives a value for θ of 72.5° which is very close to the value (70.5°) of the angle between $\langle 111 \rangle$ directions.

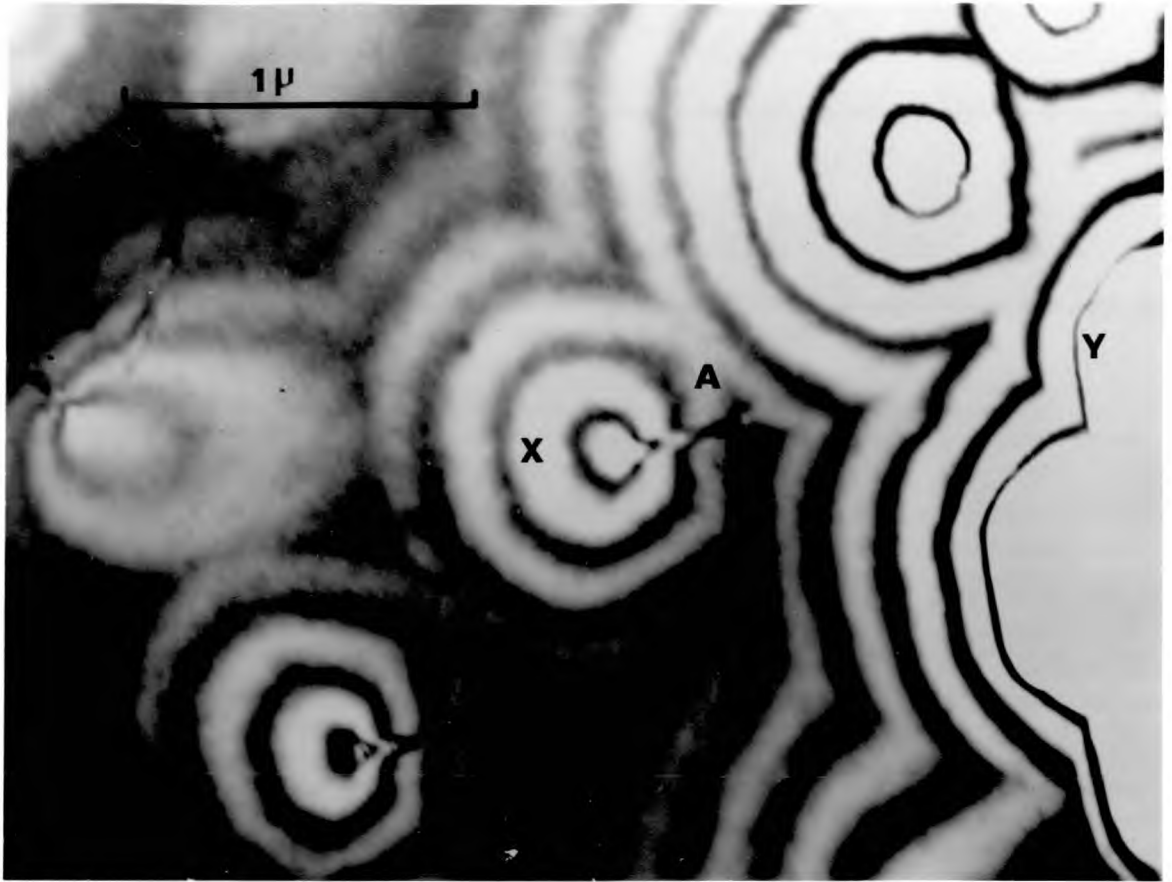


Figure 4.41a Micrograph showing the displacement of extinction (thickness) contours where crossed by a tunnel.

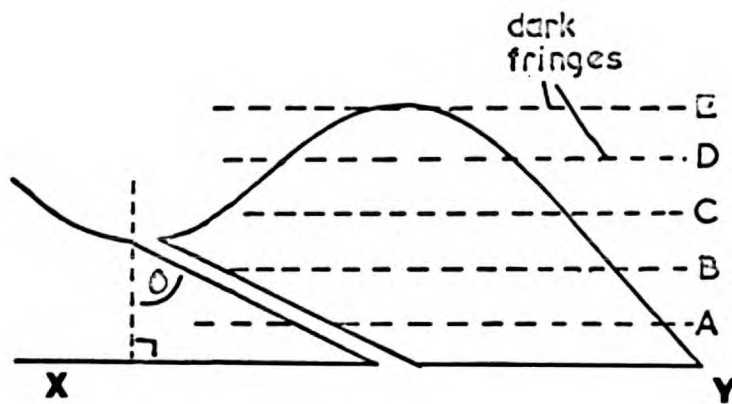


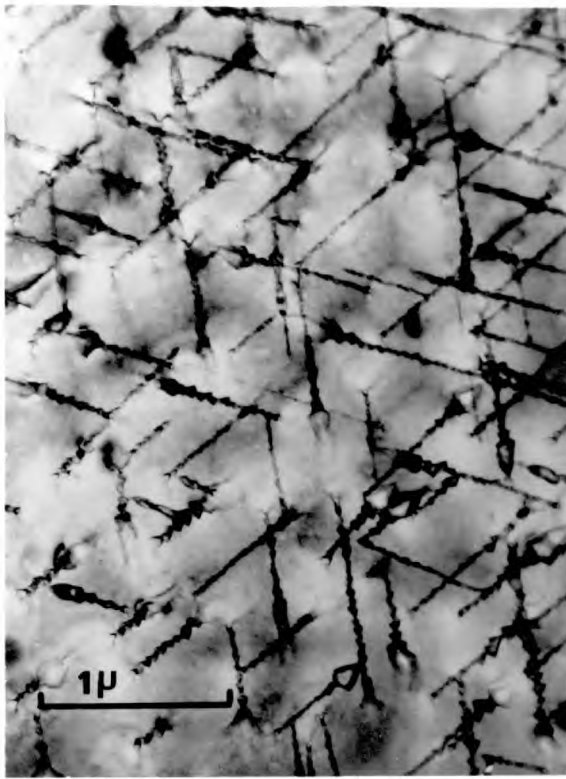
Figure 4.41b Cross sectional diagram of the tunnel marked A in the micrograph. Extinction contours are indicated where the lettered horizontal lines intersect the surface.

This therefore supports the finding that the tunnels lie in $\langle 111 \rangle$ directions and also supports the original supposition that they are in fact tunnels.

The influence of a tunnel on the position of an extinction contour can give rise to differing contrast effects as demonstrated in figure 4.42. Both these micrographs were taken in a two beam condition with a single extinction contour operating over the whole area of the micrograph. In one case (figure 4.42a) the displacement due to the tunnels shifts this to a more absorbing position and they appear dark. In the other case (figure 4.42b) the shift is to a less absorbing position and they appear bright.

Tunnels were observed in various stages of formation. In some cases the main tunnel was found to penetrate only part of the foil while the continuation was marked by a vestigial trace. An example of this can be seen in figure 4.43 at points marked A. It is interesting to contrast the crystallographic internal profiles of the tunnels shown in this micrograph with the rounder shapes exhibited in figure 4.42b. The rounded tunnels were formed in specimens which had been thinned using high applied voltages near 240 volts. The crystallographic shapes were only observed in specimens where less than 120 volts had been used. It appears therefore that at lower voltages conditions are such that some degree of preferential (crystallographic) etching can occur within the tunnels themselves.

In some specimens it was found that the tunnels lay mainly in one preferred $\langle 111 \rangle$ direction as in figure 4.42b. In some cases this was limited to just one portion of a thin foil whilst other regions had tunnels equally distributed among the three available directions. The probable explanation for this is that the preferred directions are related to the actual surface plane of the specimen at that point.



a



b

Figure 4.42 Micrographs illustrating the difference in tunnel contrast that can occur depending on whether a bright or dark extinction band is operating.

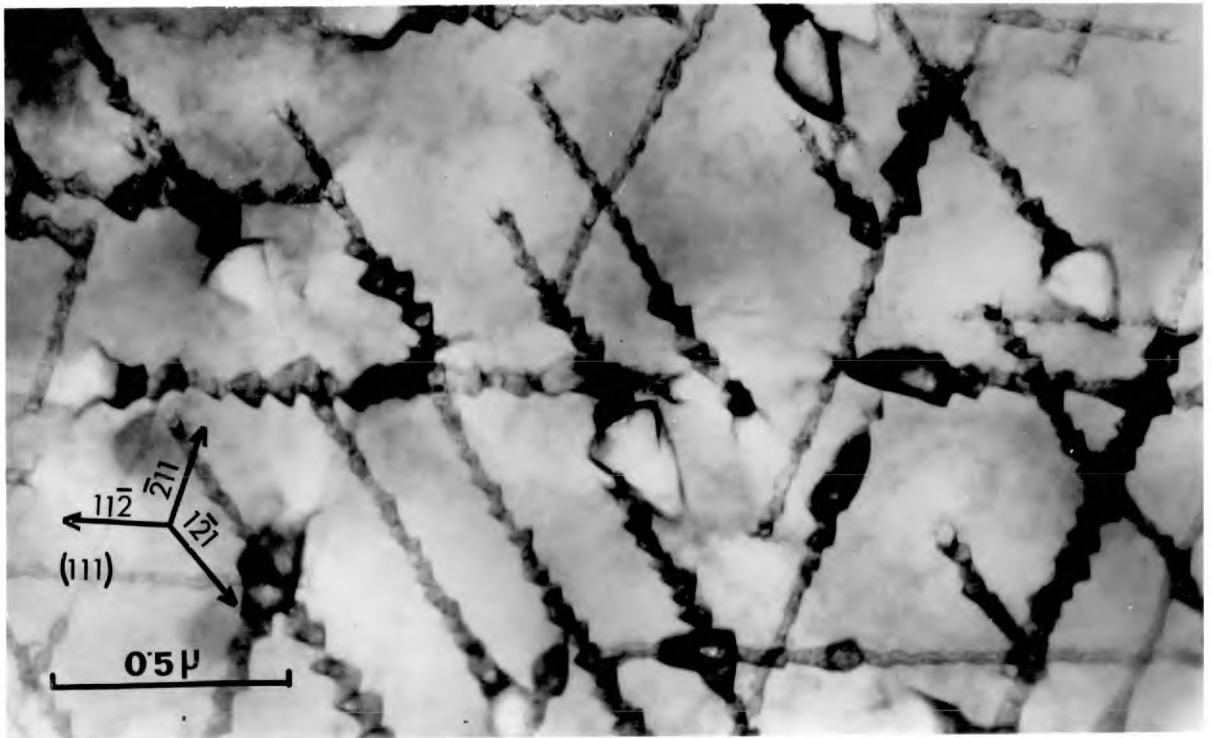


Figure 4.43 High magnification image showing the internal crystallographic profiles for tunnels formed using low voltages ($\sim 48V$) in the electropolishing process.

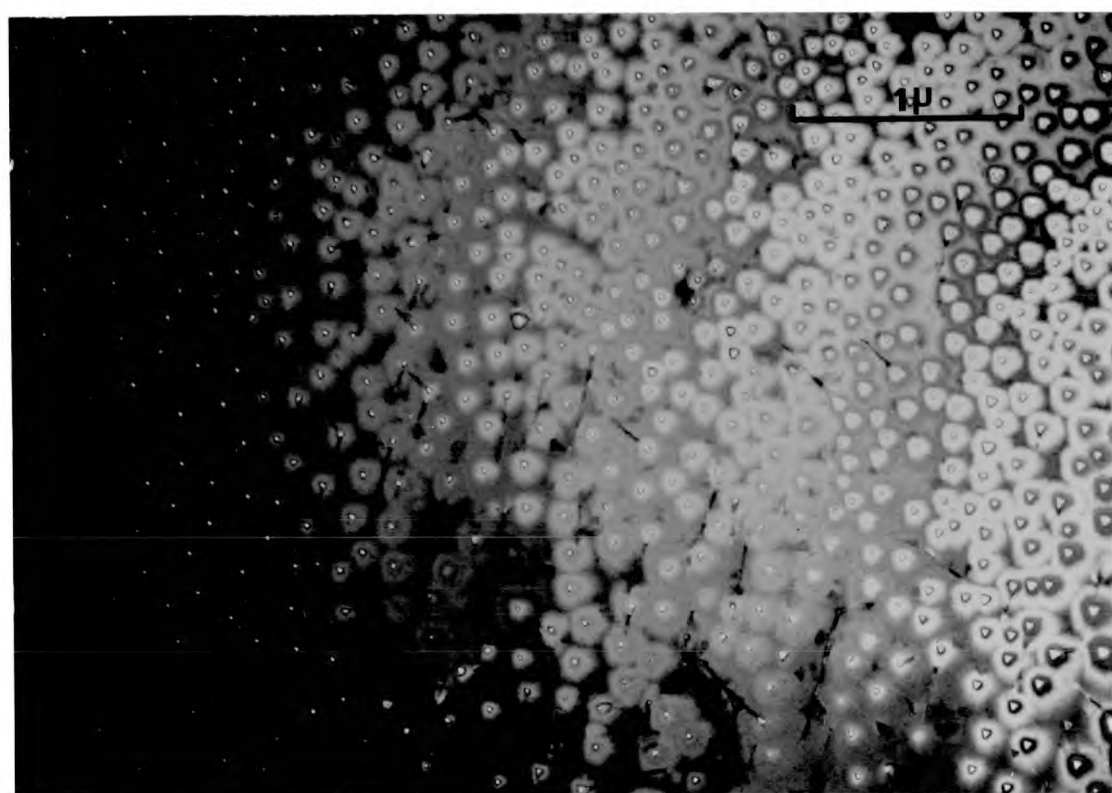
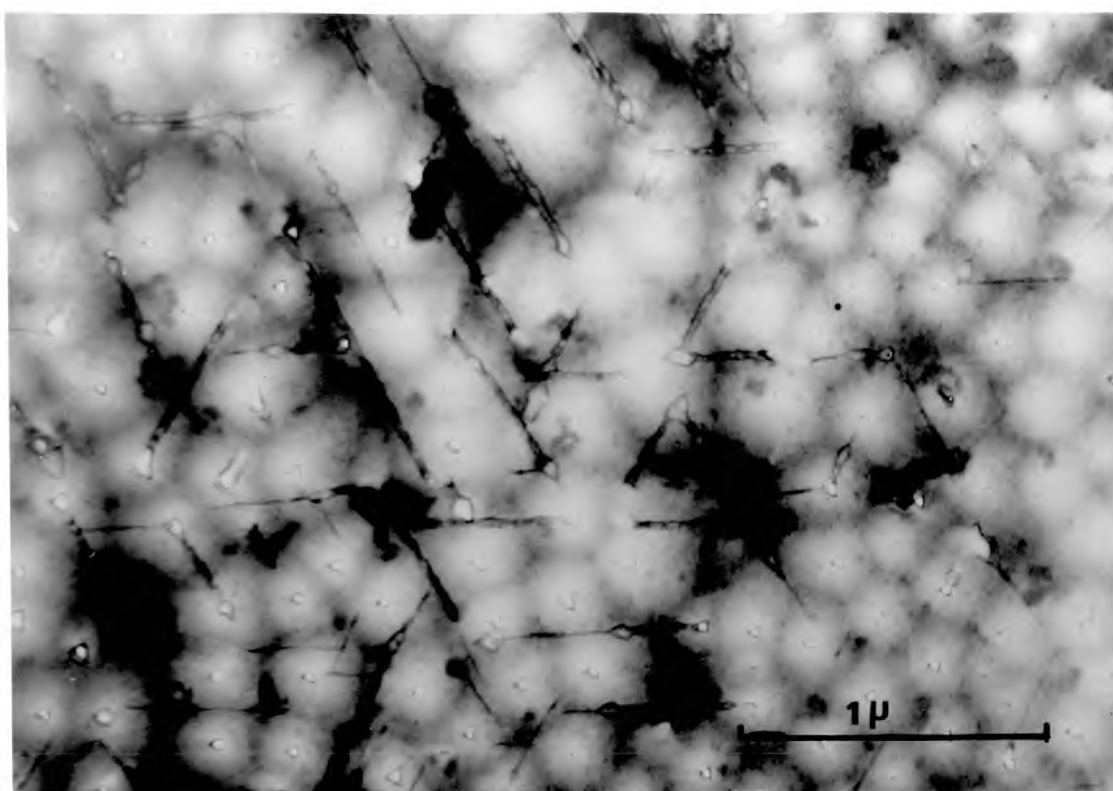


Figure 4.44 Micrographs showing the formation of tunnels in the $\langle 111 \rangle$ direction normal to the plane of the specimen. These are only formed when some etching occurred from the B or P $\{111\}$ face.

A steep sided dimple for example will present a range of different surface orientations to the reagent and some of these may be such as to encourage tunnel growth in one particular direction.

Generally specimens were thinned electrochemically only from the A or Ga $\{111\}$ face and this, as previously discussed, resulted in tunnels being formed along the three $\langle 111 \rangle$ directions lying at $70^\circ 50'$ to the specimen surface. In some cases, where leakage of reagent allowed electrochemical action to occur on the B or P $\{\overline{111}\}$ surface, additional tunnels were formed in the $\langle 111 \rangle$ direction normal to the plane of the specimen, as shown in figure 4.44a and b. This evidence suggests that tunnels are formed only in specific $\langle 111 \rangle$ polar directions in the sense of moving from a P $\{111\}$ to a Ga $\{111\}$ face.

In figure 4.44b the thickness of the foil is indicated by well defined extinction bands. Inspection of the micrograph indicates that the tunnels normal to the foil originate at shallow etch pits at the surface. In a number of cases tunnels have also been formed in the $\langle 111 \rangle$ directions at $70^\circ 50'$ to the foil surface and most of these appear associated with the same etch pits.

CHAPTER 5.

Discussion of Results.

5.1 X-ray Topography.

Although a number of specimens of GaAs were subjected to examination, satisfactory topographs were only obtained from slices of boat grown GaAs with a fairly low doping level (Figure 4.4). In material such as Zn diffused GaAs and in layers grown by vapour phase epitaxy, no anomalous transmission could be detected. This was interpreted as an indication of extremely high defect concentrations in these materials such that nearly complete absorption of the anomalously transmitted wavefield occurred. Similar results were reported by Black and Jungbluth (1967a) who found that GaAs, diffused with Zn to a depth of 50μ , was completely opaque to anomalously transmitted X-rays. In Zn doped samples grown from the melt the attenuation was much less, even at higher doping levels, and satisfactory topographs were obtainable. It appears therefore that defects induced by the Zn diffusion front are responsible for the strong absorption.

In contrast to this, Schwuttke and Rupprecht (1966), using an extinction contrast technique (Lang 1959), were able to obtain good topographs from Zn diffused GaAs. In the Te doped substrates prior to diffusion they found little evidence of dislocations but subsequent to diffusion the topographs showed up a crossed grid of long straight lines. They suggested that these lines were Lomer-Cottrell dislocations but this did not preclude the possibility that an additional network of dislocations was present and not resolved by the technique. Such a situation would be in agreement with the results of Washburn et al (1964) who found a difference of two orders of magnitude in the density of dislocations in phosphorus diffused silicon measured using X-ray topography and transmission electron microscopy. An alternative explanation is

that the observed crossed grid networks were not composed of individual dislocations but of individual slip planes each containing a number of dislocations. This effect was demonstrated by Holloway and Bobb (1968) for the case of epitaxial films of GaAs grown on Ge substrates. It may be that a similar situation can occur in Zn diffused GaAs but as yet there is no conclusive evidence to show this.

In the present work the best quality topographs were obtained from Si doped slice No. 643/2. (figure 4.4). A large number of the defects shown up in the topographs were revealed as surface scratches when the specimen was etched but no detail was observed in the X-ray topographs to correspond to dislocations revealed by etch pits in figure 4.4e. This may be a case therefore where dislocations are present yet not made visible in the topographs. In the etching process, the surface shown in figure 4.4e was etched for a longer time than that shown in figure 4.4d and consequently most of the surface damage has been removed. The etchant used was that described by Abrahams and Buicchi (1965). They produced some evidence to show that pits produced by this etch corresponded to dislocations but it was found that not all dislocations produced pits. In particular dislocations with Ga atoms edging the extra half plane (∞ dislocations) were apparently only revealed if impurity segregation had occurred. It was not established whether screw dislocations gave rise to etch pits or not.

In the topographs of figure 4.4 it is possible that the contrast due to the individual dislocations revealed by etch pits was obscured by subsurface damage. Alternatively the contrast may be blurred out if a network of dislocations, not revealed by the etch, exists with density sufficiently high to be beyond the resolution of the X-ray technique. This would be consistent with the findings of Jungebluth (1965) who found that in Czochralski grown GaAs the dislocation content was near

10^5 lines cm^{-2} and that, in anomalous transmission, individual dislocations could not be resolved due to the interaction of the strain fields. Only in material grown by the gradient freeze method was the dislocation density sufficiently low to allow direct resolution. Also Ladany et al (1969) failed to resolve individual dislocations in pulled GaP. The dislocation density was shown by an etch pit count to be 1.5×10^5 lines cm^{-2} and the network showed up as an overall grained structure, similar in nature to the background detail of figures 4.4 a, b, and c.

Certain features, prominent in the topographs of figure 4.4, were not revealed by the etch. Among these are a number of irregular blob shaped areas exhibiting high absorption. Although no positive identification was made it is likely that these were regions of impurity segregation or precipitation. In figure 4.4c a number of features of an apparent helical nature (marked S) are visible. These do not correlate explicitly with any etch pits in figure 4.4e but this does not preclude the possibility that they may be helical dislocations within the slice. Helical dislocations exhibiting similar contrast have been observed in Al by Authier et al (1965). For a dislocation of this type to be visible in the topographs when possible dislocations corresponding to etch pits are not, some enhancement of contrast, possible by decoration, may have occurred. Helical dislocations have basic edge character and so would be susceptible to decoration effects. Also they are formed from screw dislocations by a process of climb, most likely at a high temperature when vacancy diffusion can occur. Similarly impurity diffusion and segregation can also occur more easily at these temperatures. Therefore, dislocations formed at high temperatures may be more heavily decorated than those introduced by thermal stress during cooling.

The helices were only visible in topographs taken from one side of the specimen. This indicates that they were nearest to the emergent

surface in this case (figure 4.4c) and that in topographs taken from the opposite side of the specimen (figure 4.4a and b) the contrast was blurred by the Borrmann delta effect. This effect, as described in section 4.1.3, manifests itself by a spreading out of the images of features distant from the emergent face of the specimen. Measurements on the topographs showed that the observed width of surface scratches increased by about 0.2 mm as the beam penetrated a specimen thickness measured at 1.3 mm. This corresponds to an angular divergence of about 9° , not inconsistent with theory (Oldkorse and Penning 1968).

In summary, X-ray topography using anomalous transmission was adapted as a technique to be used for the examination of GaAs laser material. It was found however, that the perfection of the available specimens was not high enough for the technique to be very useful.

5.2 Inclusions in Zn diffused GaAs.

As described in the results section, various inclusions were found in the Zn diffused surfaces of a GaAs slice. Rectangular inclusions were found having strong orientation dependence with the matrix. The lines of intersection, of the interfaces with the (100) surface were found from a Laue diffraction pattern. On the (100) face the inclusions lay with their long sides along the $[011]$ direction and their short sides along $[0\bar{1}1]$. On the opposite ($\bar{1}00$) face however the orientation of the inclusions was reversed (Figure 5.1) and the long sides lay along $[0\bar{1}1]$. These lines of intersection with the (100) and ($\bar{1}00$) surfaces would be consistent with the inclusion-matrix interfaces being of type $\{111\}$.

The nature and origin of the rectangular inclusions is not fully understood. Within the resolution of the probe they were of identical composition to the matrix (99.5% GaAs, 0.5% Zn) and are thus not identifiable with any chemically independent compound of GaAs and Zn. Mechanical polishing however indicated that they were harder than the

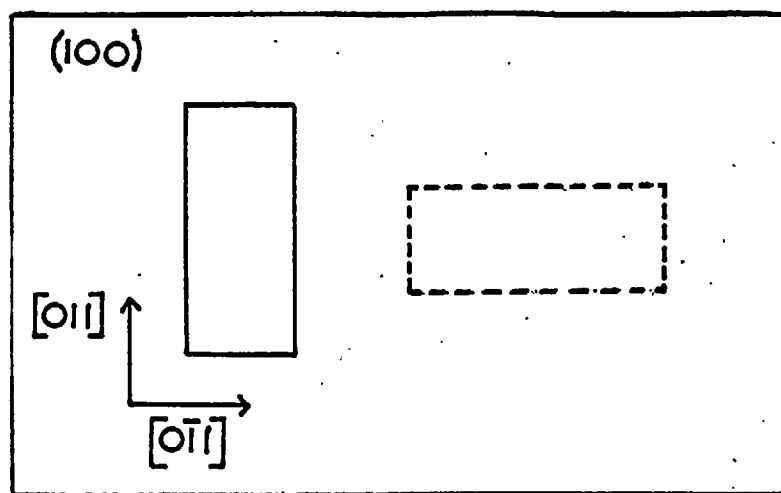


Figure 5.1 Rectangular inclusions as viewed in the $[100]$ direction. The dotted outline represents an inclusion on the far $(\bar{1}00)$ face.

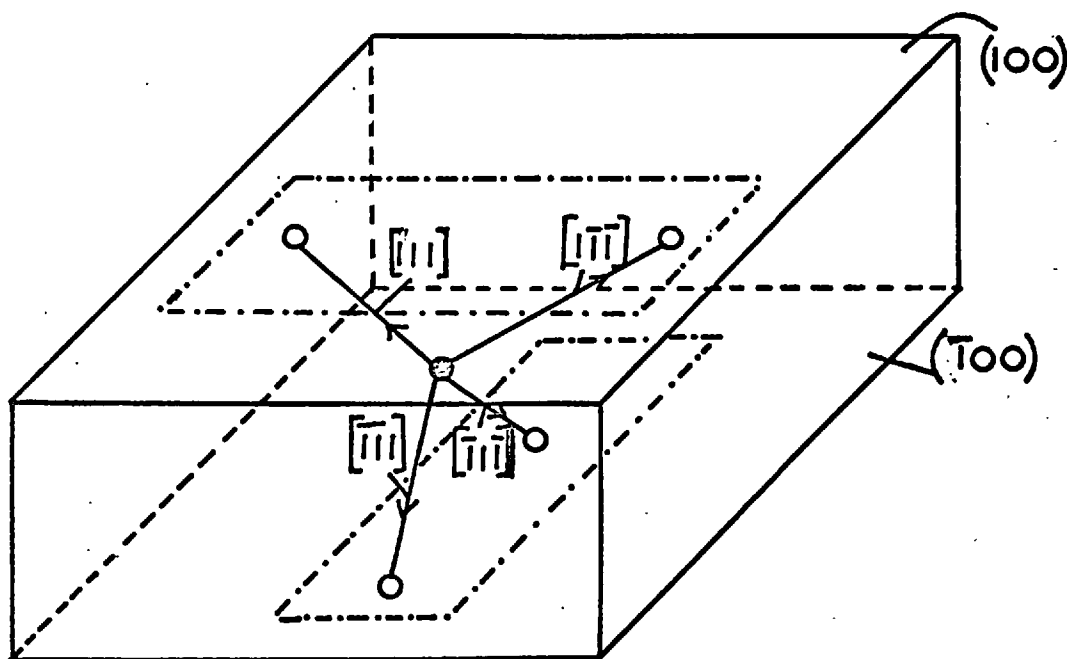


Figure 5.2 Schematic diagram showing the geometric relationship between a single atomic tetrahedron and the outlines of the inclusions on the (100) and $(\bar{1}00)$ faces.

bulk material. An increase in hardness might occur by a phase transformation whereby Zn atoms are incorporated interstitially into the host lattice in an ordered array. The additional lattice strain could increase the hardness of the material possibly in a way analogous to the martensitic hardening of steel. An additional possibility is that the inclusions are regions of twinned material formed during the Zn diffusion process. This would be consistent with the observed association with linear defects in the substrate (figure 4.6) and with the polyhedral inclusions (Zn_3As_2) because twin nuclei could originate preferentially at these defects. Rectangular inclusions have not been observed in undiffused slices so it seems certain that the presence of Zn plays a part in their formation. The inclusions were too small to establish by X-ray diffraction whether they were twinned with respect to the matrix or not.

The difference in growth habits on the (100) and $(\bar{1}00)$ surfaces could be due to polarity effects (section 2.4.1). Figure 5.2 is a schematic diagram showing the relation of a single atomic tetrahedron to the outline of the inclusions on the two surfaces. If the inclusions are bounded by $\{111\}$ faces of similar polarity, then one pair of faces, say (111) and $(\bar{1}\bar{1}\bar{1})$, would converge towards the (100) surfaces whereas the other pair, $(\bar{1}\bar{1}1)$ and $(11\bar{1})$, would diverge. If this was the case then the outline of the inclusion would alter, with interchanging of the long and short axes, as the surface was polished down. In fact no such change was observed and all faces of the inclusions were found to diverge towards the surface. This indicated that the bounding $\{111\}$ planes were of opposite polarities on the long and short sides. Thus the formation of the inclusions is probably controlled by different growth rates at surfaces of opposite polarity. In the present work the precise polar nature, Ga $\{111\}$ or As $\{\bar{1}\bar{1}\bar{1}\}$, of the individual growth

surfaces was not established. In other words the individual atoms indicated in figure 5.2 have not been identified.

The polyhedral shaped features were shown, using the electron probe, to have the composition $3\text{Zn} : 2\text{As}$. This is a strong indication that they are in fact precipitates of Zn_3As_2 . Zn_3As_2 possesses a body centred tetragonal unit cell with $a = 11.78 \text{ \AA}$, $c = 23.65 \text{ \AA}$ and a c/a ratio of 2.007 (Cole et al 1956). As there will therefore be a certain degree of lattice mismatch with GaAs ($2a = 11.307$) it follows that the interface of lowest energy, and hence the stable interface, between the precipitate and matrix will not necessarily be one of low index. Figure 5.3 shows the directions of intersection with the (100) surface for two of these precipitates. Predominantly the intersections are of type $\langle 310 \rangle$ but one of $[011]$ was observed. The lowest index planes consistent with these observations are of type $\{311\}$. These could give rise to the directions of intersection in figure 5.3 as indicated below.

Line of intersection on (100).	Possible $\{311\}$ planes.
$[011]$	$(31\bar{1})$ or $(\bar{3}11)$
$[0\bar{1}3]$	(131) or $(\bar{1}31)$
$[01\bar{3}]$	$(1\bar{3}1)$ or $(\bar{1}\bar{3}1)$
$[0\bar{3}1]$	$(11\bar{3})$ or $(\bar{1}13)$

Interfaces of type $\{331\}$ would also be consistent with the observations. Mechanical polishing indicated that the faces converged below the surface (ie the outlines decreased in size with depth) but it was not possible to positively identify the interfaces as being of $\{311\}$ or $\{331\}$ type.

A previous report of precipitation in Zn diffused GaAs was made by Black (1967) who found that Zn rich precipitates were formed at grain boundaries. As these precipitates grew at the expense of smaller precipitates in the matrix leading to denuded zones he concluded that

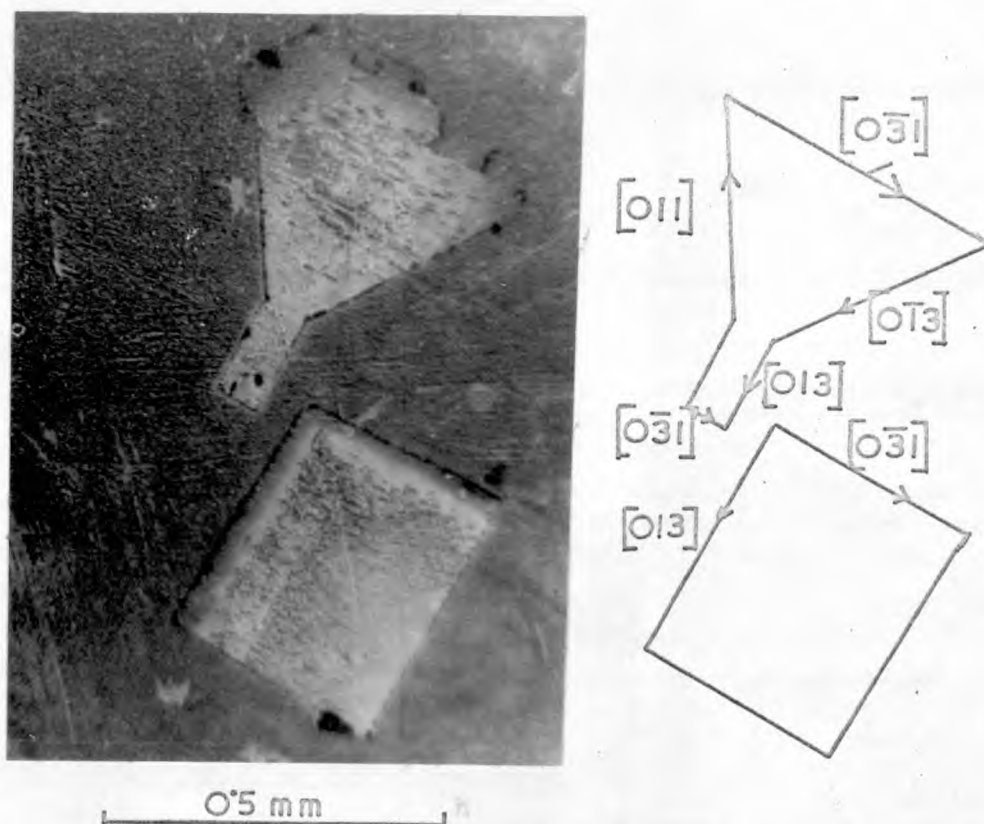


Figure 5.3 Zn_3As_2 precipitates on the (100) surface of the slice. The lines of intersection of the interfaces with the (100) surface are indicated in the diagram.

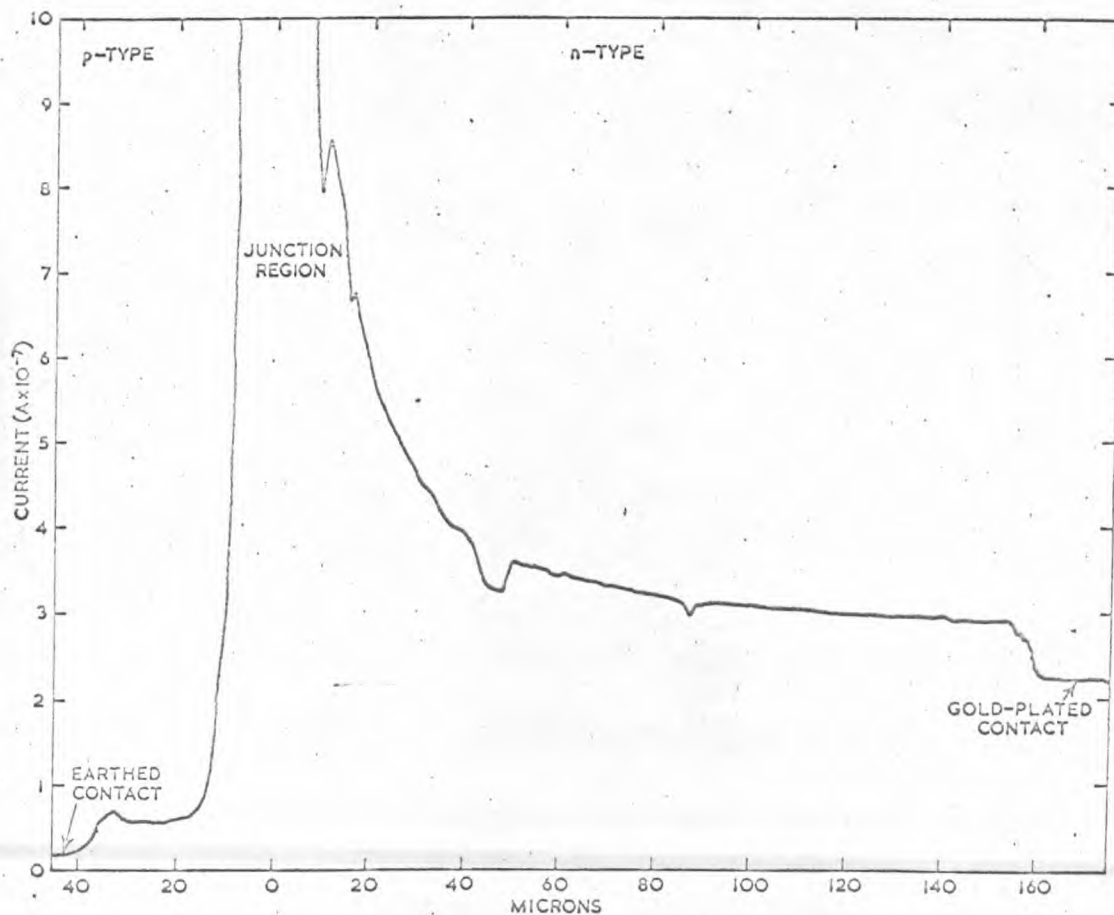


Figure 5.4 Signal strength versus distance in a line scan across a laser p-n junction.

the smaller, sub-microscopic precipitates were of similar composition. The Ga and As content of the precipitates was lower than that of the matrix but he did not specify any ratios.

Hill (1968) has observed micro-precipitates in Zn diffused GaAs by electron microscopy. Some of these precipitates were seen to have a rectangular outline with edges projecting onto the $\langle 110 \rangle$ directions when viewed in the (100) plane. It is possible that these correspond to the much larger rectangular inclusions of similar habit reported here.

Panish (1966a) reported several thermal effects on cooling GaAs - Zn mixtures from the melt (see section 2.5.4). For Zn concentrations less than about 10%, the temperatures at which these effects occur must be found by extrapolation as the thermal effects are too small to be easily detectable. At the melting point of GaAs primary crystallization commences and a second solid phase, Zn_3As_2 , appears at 860°C . At 400°C Zn_3As_2 becomes unstable and reacts with Ga to form GaAs + Zn. Thus under equilibrium conditions and for low Zn concentrations such as here, Zn_3As_2 is only stable between 860° and 400°C . The fairly rapid cooling rates subsequent to Zn diffusion represent a departure from equilibrium and it is thus possible for precipitates of Zn_3As_2 to become frozen in as in the present case.

In summary, a number of precipitates and inclusions have been observed on the surface of a GaAs Zn diffused slice. The presence of these defects may be detrimental in that they may disturb the planarity of the diffusion front. Evidence was found to suggest that imperfections present originally in the undiffused slice may act as nucleation sites in the growth of these defects. The slice examined was Zn diffused from a source of elemental Zn for 15 minutes at 1100°C . As described by Casey and Panish (1968) better results may be obtained using a source composition in which the phases Zn_3As_2 , GaAs and ZnAs_2 are in equilibrium.

5.3 Scanning Electron Microscopy.

5.3.1 Charge Collection in GaAs Laser Diodes.

Figure 5.4 shows the variation in the charge collection or junction short circuit current as the electron beam traversed across the junction. Wittry and Kyser (1965) suggested that this curve could best be represented by an equation of the form :-

$$I = A \exp (-r/L_1) + B \exp (-r/L_2)$$

Here I is the measured current, r the distance from the p-n junction, A and B are constants and the diffusion length L_2 is approximately an order of magnitude greater than L_1 . They found similar values of L_1 at electron beam voltages of both 15 and 30 kV so assumed L_1 to be the diffusion length of minority carriers. No satisfactory explanation was offered for the diffusion length L_2 . They suggested it might be due to infra-red radiation reaching the junction which would give $L_2 = \alpha^{-1}$ where α is the optical absorption coefficient. However, their measured value for L_2 of 30μ , which gives $\alpha = 300 \text{ cm}^{-1}$, did not agree with the absorption coefficient for the spectral peak of around 1500 cm^{-1} (Hill 1964).

In the present work a comparison of images taken using charge collection and cathodoluminescence (figure 4.15) shows virtually identical contrast in each case. This indicates that each type of image is formed by the same fundamental process notably the emission and detection of light. If, in the charge collection case, absorption were critical, it would be expected that shadowing would occur when the light had to penetrate regions of high absorption between the point of origin and the junction. Such regions would also have low cathodoluminescent efficiency as indicated by the results of section 4.3.2. Because no such shadowing was observed the absorption coefficient for the photon energies involved is probably fairly low. The likely explanation is

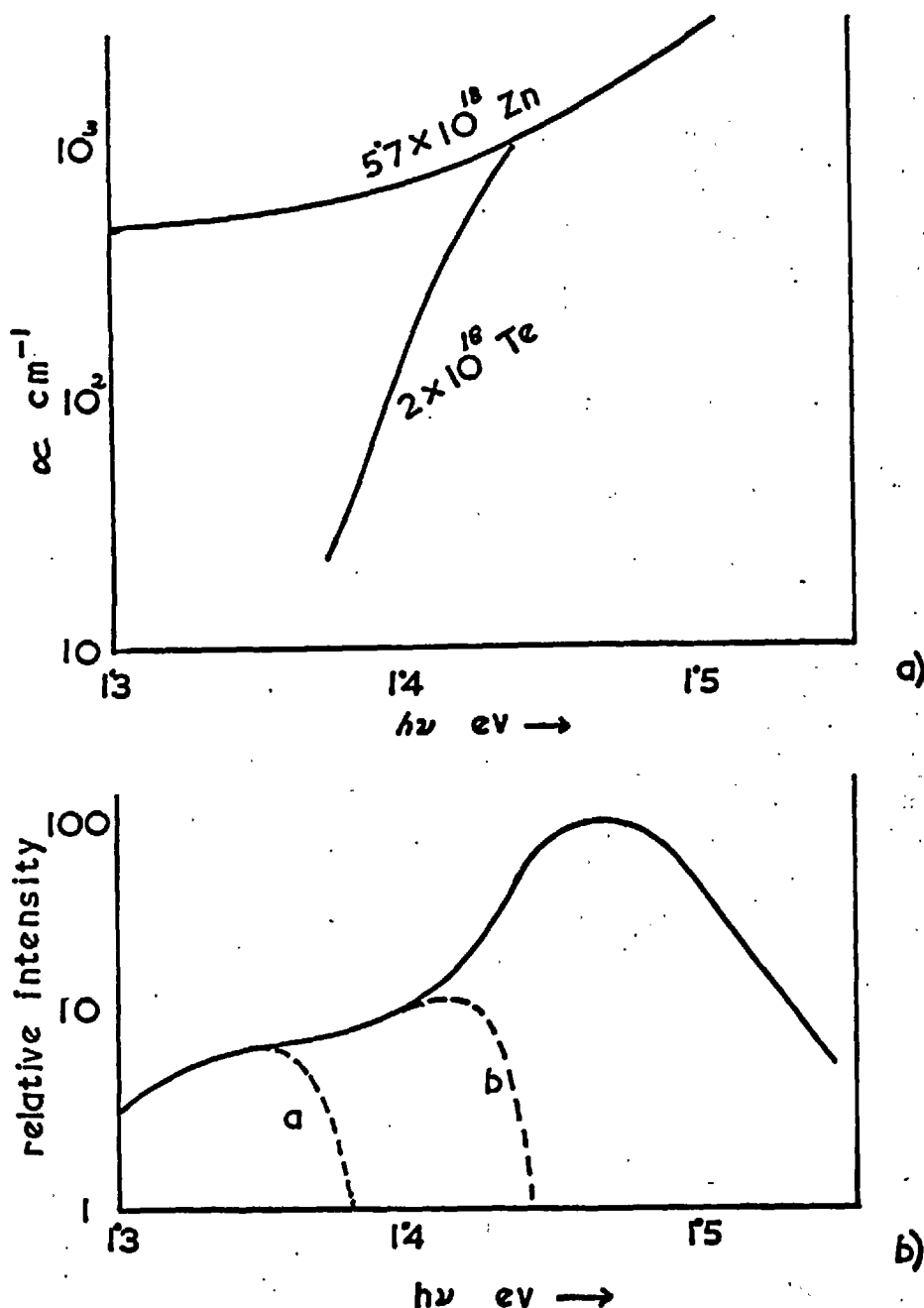


Figure 5.5 a) Optical absorption of p and n type GaAs at 300°K (after Hill 1964)
 b) Cathodoluminescence spectrum for n-type GaAs with free carrier density $N = 1.75 \times 10^{18} \text{ cm}^{-3}$ (after Casey and Kaiser 1967). The dotted curves represent the modified spectrum after absorption through a) 1 mm and b) 0.1 mm thicknesses of material.

that the initial cathodoluminescence spectrum is considerably modified by absorption before reaching the junction. Light of high photon energies will be strongly absorbed and as a result the spectral peak of the radiation reaching the junction will be shifted to a lower energy. The measured value of L_2 will thus be related to the absorption coefficient of this modified peak rather than to that of the original spectrum.

It is interesting to consider the available absorption and spectral emission data reproduced in figure 5.5. Possible modifications of the original spectra by self absorption in the n-type material are indicated in figure 5.5b. The degree of attenuation is of course dependant on the thickness of material considered but it is apparent that little absorption will occur on the low energy side of the spectrum. Examination of the modified curves shows that for the peak of curve b an absorption coefficient α of about 300 cm^{-1} is quite in order and would agree with the value of 30μ for L_2 ($L_2 = \alpha^{-1}$) measured by Wittry and Kyser (1965).

In order to be detected at the p-n junction, a considerable proportion of the incident light must be absorbed within a minority carrier diffusion length on either side of the junction plane. From figure 5.5 it can be seen that despite being little absorbed in the n-type material, the light reaching the junction will still suffer strong absorption in Zn doped material. In addition Lucovsky et al (1965) have shown that absorption coefficients in GaAs can increase by up to a factor of 10 with compensation. The junctions in this case are formed by diffusion so on the p-side the Zn doping is compensated to about $2 \times 10^{18} \text{ atoms cm}^{-2}$ with Te. Thus very high absorption coefficients are to be expected in the p-type material and also within the space charge region itself. It is this that gives the junction sufficient sensitivity to act as a

cathodoluminescence detector. For radiation emitted in the p-type material, self absorption will be very high and little will reach the junction region. For any light that does, the absorption coefficient in the junction region is low and the amount detected will probably be insignificant. In practice no long range component corresponding to L_2 could be resolved in the p-side of GaAs diodes.

An additional factor not discussed by Wittry and Kyser must be included in the analysis. This is the influence of the current flowing in the electron beam. The p-side of the specimen is connected to earth (figure 3.6) so that when the beam is incident on this part of the specimen the injected current can flow directly to earth. However, when the beam is incident on the n-side of the specimen the major part of the beam current will flow to earth through the current amplifier. This current is thus superimposed on the charge collection signal and in for example the trace of figure 5.4, was found to raise the zero level for the charge collection to about 3×10^{-7} amps. The actual value is of course determined by the beam current and by the proportion of the incident electrons that are absorbed by the specimen. The equation representing the charge collection current then becomes :-

$$I = A \exp (-r/L_1) + B \exp (-r/L_2) + C$$

where C represents the component due to the beam current.

To determine the values of L_1 and L_2 it is convenient to plot the trace logarithmically i.e. to plot $\log I$ against r . To do this it is first necessary to subtract the non-exponential component C from the expression. The value of C can be determined from the trace as a horizontal line drawn at this value is asymptotic to the curve at large values of r . As the values of L_1 and L_2 are a different order of magnitude ($L_2 \gg L_1$), for large values of r the first term in the expression for I will be negligible. In other words, the beam is so

distant from the junction that the number of charge carriers diffusing to the junction is insignificant. In this region the log plot will be of the form

$$\text{Log}_{10} I = (\text{Log}_{10} B) - r/L_2 (\text{Log}_{10} e)$$

The slope of the curve is given by

$$m = \frac{d \text{Log}_{10} I}{d r} = \frac{-\text{Log}_{10} e}{L_2}$$

and hence L_2 can be determined by measurement of m . For small values of r , i.e. with the beam incident close to the junction, the first term in the expression for I becomes predominant and then

$$\text{Log}_{10} I = (\text{Log}_{10} A) - r/L_1 (\log_{10} e)$$

$$\text{and } m = -\frac{\text{Log}_{10} e}{L_1}$$

In the trace of figure 5.4 the curve goes off scale for fairly large values of r of about $\pm 10 \mu$ and from this trace it is not possible to accurately determine the value of L_1 in the n-type material. However, by making a number of traces, as in figure 4.8, at different amplifier settings, accurate measurements of the value of I for both large and small values of r can be made.

The values obtained for L_1 and L_2 were as follows.

Diode 3434/2, Te doped, Czchrolski pulled substrate.

Trace as figure 5.4. L_1 p-type = 2.0μ .

For L_2 n-type a range of values were obtained for different values of r as predicted by the results of figure 5.5.

Value of r in μ .	25	50	90	125
L_2 in μ	20	25	32	38

Diode 2659/1. Te doped, Bridgeman grown substrate. Traces as figure 4.8. L_1 p-type = 2.3μ . L_1 n-type = 0.75μ . L_2 n-type again was dependant on r . For $r = 20 \mu$, $L_2 = 30 \mu$ and for $r = 40 \mu$, $L_2 = 45 \mu$.

The values for the constants A, B and C in the expression for I can be calculated from the trace once the values of L_1 and L_2 are known. For diode 2659/1 for example $A = 1.65 \times 10^{-4}$ amps, $B = 3.2 \times 10^{-8}$ amps and $C = 1.2 \times 10^{-7}$ amps. The values obtained for L_1 in n-type material compare with the value of the hole diffusion length $L_p = 1.2 \mu$ reported by Wittry and Kyser (1967) for n-type material with $N = 1.88 \times 10^{18} \text{ cm}^{-3}$. The carrier concentration of the material examined in the present case was known to be about $2 \times 10^{18} \text{ cm}^{-3}$ but not to a high degree of accuracy. The values obtained for L_2 are consistent with the value of 30μ reported by Wittry and Kyser (1965). As previously discussed the exact value is dependent on r (not specified by Wittry and Kyser) so no direct comparisons can be made.

Strictly, the expression for I should be modified to include a summation of the different values of L_2 for light of differing wavelengths. Then :-

$$I = A \exp(-r/L_1) + B \int f(h\nu) \exp(-r/L_2(h\nu)) d(h\nu) + C$$

Where $f(h\nu)$ is a function representing the initial spectral shape and $L_2(h\nu)$ is a function corresponding to $\propto \nu^{-1}$ for light of energy $h\nu$.

5.3.2 Charge Collection in GaP diodes.

The charge collection traces obtained from GaP diodes were much more straightforward to analyse than those from GaAs laser diodes. The principal reason for this was that the self detection of light by the p-n junction was too small to be resolved. GaP is an indirect gap semiconductor and virtually all the radiative transitions in cathodoluminescence occur between complexes within the band gap. The emitted radiation is thus of less than the band gap energy and so suffers very little absorption within the specimen. Any absorption that occurs will be via exciton complexes within the band gap; resulting minority carriers will be bound at the complexes and consequently will not be expected to

give rise to a charge collection current. Because this optical component was lacking, it was possible to express the charge collection curve in the form $I = A \exp(-r/L) + C$

It was found convenient to plot the curve logarithmically (figure 4.23b)

$$\log_{10} I - \log_{10} A = (-r/L) \log_{10} e$$

Thus $\log_{10} I$ was plotted against r (figure 4.23a) and the slope m of the straight line portion of the curve measured. The value of L was found using the expression:-

$$L = \frac{-\log_{10} e}{m} = \frac{.4343}{m}$$

The resulting measurements for L_n and L_p are listed in table 4.2.

Inspection of the log plots of figure 4.23a shows that the traces exhibit ^{near} straight line (true exponential) behaviour only in certain regions either side of the peak. If the exponential behaviour continued in the region of the peak the actual maximum of the curve would occur at a much higher value. In fact the lowering and broadening of the peak occurs partly as a result of the finite width of the depletion region but is mainly due to the finite beam diameter and the spread of primary electrons into the specimen as discussed in section 2.6.4.

In the straight line portions of the log curves, the distance from the junction is large ($2 - 5 \mu$) compared to the effective beam diameter and so the measured values for L_n and L_p will be fairly accurate. These values themselves however can only be taken as referring to the rather special conditions under which they were measured, principally, with large numbers of carriers of both types present. An additional effect which will influence the measurements is surface recombination. The penetration depth of the electrons is not very great and surface recombination can be expected to reduce the values obtained compared to those of the bulk material. Maeda et al (1969) used an optical method to measure L_n and L_p in a Zn diffused GaP diode. They obtained values

for L_n of 1.4μ and for L_p of 2.7μ . The value obtained for L_p in material with $N = 0.5 \times 10^{17} \text{ cm}^{-3}$ is roughly three times the value obtained in the present work for material with $N = 1 \times 10^{18} \text{ cm}^{-3}$.

The value obtained by Maeda et al for L_n is not directly comparable as this was for heavily compensated Zn diffused material.

Discussion of the measurements relating to both the charge collection and CL traces will be given in section 5.3.5.

5.3.3 The Detection of Cathodoluminescence.

The choice of photomultiplier for the detection of cathodoluminescence was determined ultimately by the spectral response of the photocathode. The response curves for the three photomultipliers actually used are given in figure 5.6. Also marked are the positions of the spectral peaks of the emission from GaAs and GaP at 300°K . The overall sensitivities and dark current ratings at typical operating voltages are given in table 5.1.

Photomultiplier	Cathode	Overall Voltage	Overall Sensitivity Amps/Lumen	Dark Current Amps
150CVP	S1	1800	100	5×10^{-6}
9664	S10	1050	50	1×10^{-8}
9558	S20	1500	2000	2×10^{-8}

Table 5.1 Performance data for the photomultipliers used in the detection of cathodoluminescence.

It can be seen from the figure that **only** the S1 type photocathode is sensitive to emission from GaAs. The principal disadvantage in using this type of photocathode is the high level of thermal noise associated with it. The quality of micrographs taken using the cathodoluminescence signal, was found to be very dependant on the signal to noise ratio. Fortunately GaAs exhibits highly efficient radiative recombination due to its direct band gap and in general it was possible to obtain

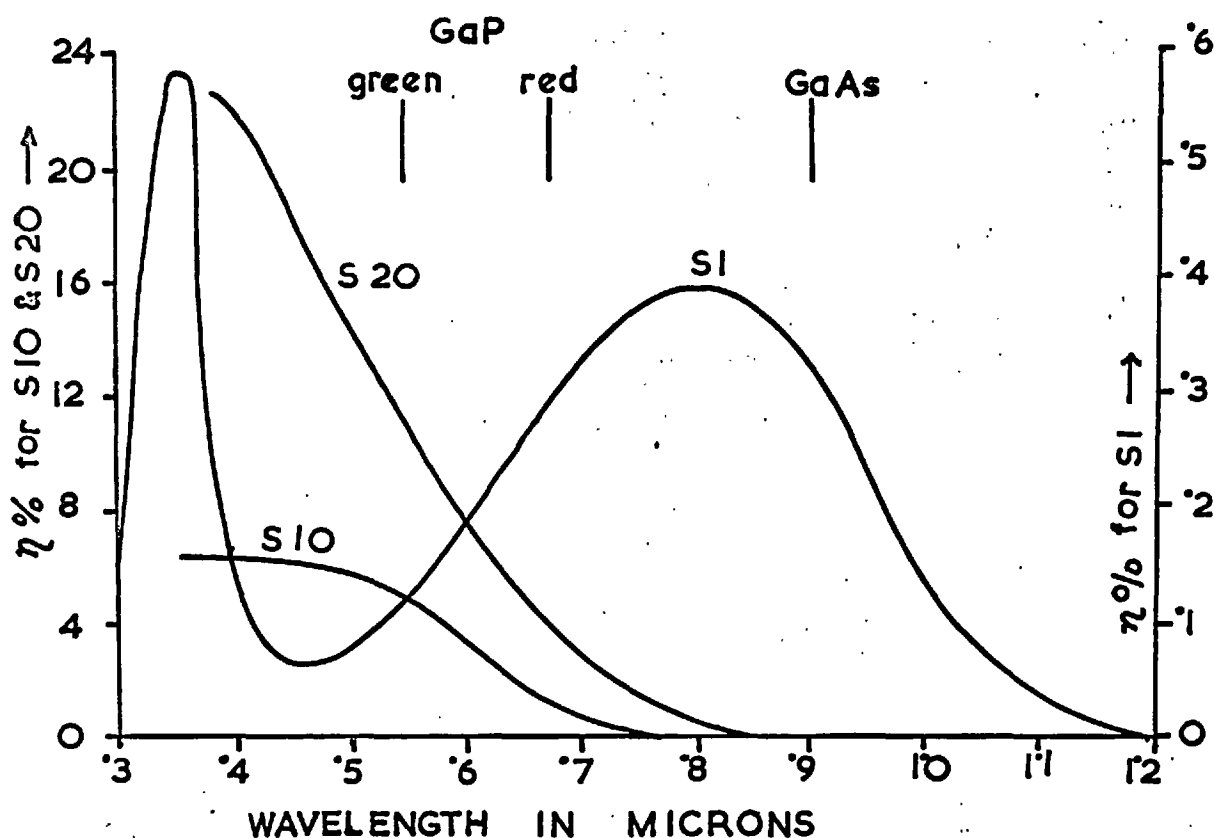


Figure 5.6 The quantum efficiencies for the three types of photocathode. The peaks of the room temperature emission from GaAs and GaP are also marked for comparison.

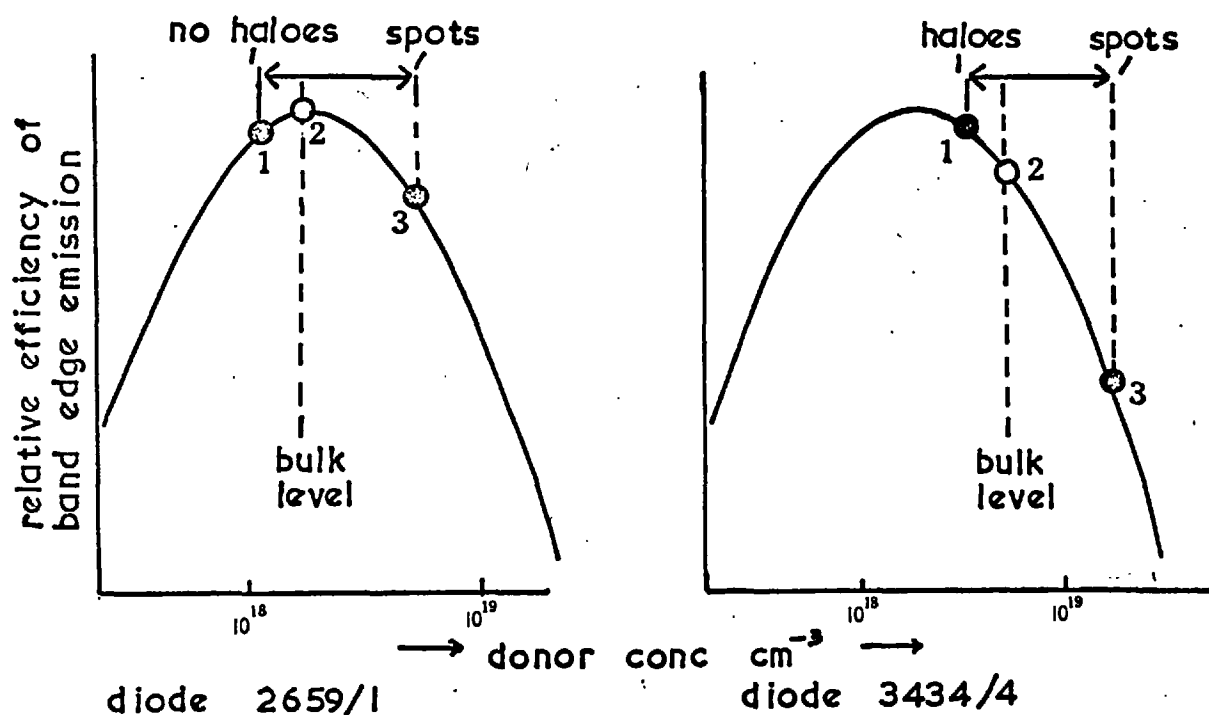


Figure 5.7 Relative efficiencies for radiative recombination in Te doped GaAs at 300°C, (after Cusano 1964). Compositions are indicated which could give rise to the observed contrast effects. Points 1, 2, and 3 in each case indicate the relative efficiencies for the depleted region, the bulk material and the dislocation spot respectively.

satisfactory micrographs. Thermal noise effects were visible in micrographs from some diodes (figure 4.13) as an overall graininess but the radiative efficiency from other diodes such as in figure 4.15 was high enough to make noise effects unnoticeable.

It was found possible to reduce thermal noise by cooling the photocathode to about -50°C . The cooling system consisted of an air pump which passed a current of air through a coil of copper tube immersed in liquid nitrogen. This cold air was then directed through a jet directly onto the photocathode face of the photomultiplier. To prevent surface condensation the air was first passed through two drying towers filled with silica gel and a quantity of silica gel was inserted into the photomultiplier case. The rate of air flow and hence the degree of cooling could be varied by using a pressure release valve situated immediately after the air pump.

Radiative recombination in GaP is a much less efficient process than in GaAs. Consequently it was found impossible to use the 150CVP photomultiplier as the noise level was found to be greater than the detected signal. Greater sensitivity was provided by the photomultipliers of type 9558 and 9664 which had much lower noise levels. Type 9664 was used in the preliminary examinations with the electron probe where the built in optical system provided a convenient and efficient method of channelling the light to the photocathode. For use in the S.E.M., where a line of sight system was used, the 9558, with its greater sensitivity, was found more suitable. The spectral cut off of both these photomultipliers was at too low a wavelength to enable them to be of use in the examination of GaAs.

5.3.4 Cathodoluminescence in Te Doped GaAs.

It is interesting to compare the results from the two diodes numbered 3434/4 and 2659/1. The former was Czochralski grown and the

junction formed by Zn diffusion at 850°C with As overpressure for 7½ hours. The latter was Bridgman grown and Zn diffused at 1100°C for 15 minutes with no As overpressure. In both diodes, growth striations were observed in infra-red transmission but only in diode 3434/4 were they visible in cathodoluminescence (figure 4.14). Also the dark spots associated with segregation effects appeared with different contrast in either case. In diode 3434/4 white haloes were observed around the spots (figure 4.13) but these were absent in diode 2659/1 (figure 4.15).

These results can be attributed to differences in the overall Te concentrations in the bulk material. The results of Cusano (1964) indicate that as the Te concentration in GaAs is increased, the relative energy efficiency of the band edge emission increases to a maximum and then decreases. At 300°K this peak occurs at donor concentrations of about $2 \times 10^{18} \text{ cm}^{-3}$, similar to those quoted by S.E.R.L. for the diodes under examination.

Figure 5.7 shows radiative efficiency data obtained by Cusano for Te doped material. Possible donor concentrations in the region of the segregation spots are indicated for each diode. In both cases the segregation results in a decrease in CL efficiency at the centre of the spots. If, initially, the donor concentration corresponded to a point of the curve with a negative slope, as indicated in figure 5.7b, the depletion of the surrounding region leads to an increase in CL efficiency. This would explain the appearance of haloes in diode 3434/4 (figure 4.13). If, however, the initial composition corresponded to a point near the peak of the curve (figure 5.7a) little change would be observed in the CL intensity from the depleted region and no haloes would be observed as in diode 2659/1 (figure 4.15).

Striations represent a regular increase and decrease in donor concentration. If in diode 2659/1 the composition was exactly on the

peak the variations in CL efficiency might not be detected. In optical transmission however, the absorption edge displays no such peak and small variations in donor concentration can give rise to contrast. The image converter tube used to observe striations had a spectral response similar to that of the S1 type photocathode (figure 5.6). The infra-red film used to record the striations (figure 4.14) was only sensitive to wavelengths from 8000 to 10000 Å and to allow adequate transmission in this range the specimen was cooled to liquid nitrogen temperature.

It is interesting to compare the results of Casey (1967). He examined bulk undiffused Te doped GaAs and observed white haloed spots for free electron concentrations N from 2×10^{17} to $8 \times 10^{18} \text{ cm}^{-3}$. The haloes reached a maximum diameter of about 100μ for material with $N = 2.5 \times 10^{18} \text{ cm}^{-3}$. The presence of growth striations in all these floating-zone grown samples means that the free electron concentration must vary across the area of examination and thus limit the accuracy of the results. There is however general agreement with the above analysis and data of figure 5.7.

Using the A-B etchant Casey found that etch pits formed at the spots and he attributed these to dislocations. When the same etchant was used on diode 3434/4 in the present work etch pits were also found at the spots. These however were rounded pits (figure 4.12c) and did not have the well defined crystallographic shapes normally expected of dislocation etch pits. Furthermore the pits showed up distinctly even in regions of heavy subsurface damage where large numbers of dislocations had been introduced. This indicates that the formation of these etch pits may be a direct result of Te segregation rather than the presence of simple dislocations. Laister and Jenkins (1968) reported clusters of Te precipitates lying on $\{111\}$ planes in GaAs. They found

that these faulted regions were of similar size to the dark spots observed in cathodoluminescence by Wittry and Kyser (1964). They suggested that a depleted zone would be formed in the capture area of the faults and that this would give rise to similar images of dark spots with light haloes. Their results also indicate however, that faults of this nature are only important in material for which $N > 10^{18} \text{ cm}^{-3}$ and a similar conclusion can be drawn from the work of Meieran (1965). Casey however observed spots at $N = 2 \times 10^{17} \text{ cm}^{-3}$ and these differed in nature from those observed at high doping only by virtue of the extent of the haloes. It would thus appear that these spots are not associated with clusters of Te precipitates and that Te segregation at edge dislocations is a much more likely explanation. More conclusive evidence comes from the work of Iizuka (1968b) who examined Te doped GaAs using X-ray topography. In material with $N = 6.4 \times 10^{18} \text{ cm}^{-3}$ the topographs showed a fine dispersion of precipitates throughout the material with regions depleted of precipitates in the vicinity of dislocations. These precipitates are probably similar to those found by Meieran (1965) using the electron microscope and which occurred in addition to the precipitates giving stacking fault type contrast as observed by Laister and Jenkins. It is the presence of precipitates such as these which Cusano suggested gave rise to the decrease in CL efficiency for $N > 2 \times 10^{18} \text{ cm}^{-3}$. At high doping levels ($> 10^{18} \text{ cm}^{-3}$) however, clusters of planar precipitates, as observed by Laister and Jenkins, may occur and could give rise to contrast very similar to that attributed to Te segregation at dislocations.

5.3.5 Cathodoluminescence in GaP.

It was found that detail shown up in the CL images of GaP diodes varied considerably when different photomultipliers were used. In particular, the visibility of striations present in Zn - O doped material

of diodes Nos L 136 and L 129 was more intense when observed using the S 10 type photocathode than using the S 20 type (figure 4.17). The S 10 photocathode is not sensitive to wavelengths greater than about 0.75μ (see figure 5.6) and this cut off is close to the red emission peak of Zn - O doped GaP. The photocathode will therefore be very sensitive to any minor fluctuations in the position of the spectral peak which may occur across the striations. Striations have not been observed in diodes grown by the process of double liquid epitaxy. It thus appears that they may be limited to diodes in which a Zn - O doped liquid epitaxial layer is grown directly onto a pulled substrate. In this case it is possible that the striations are grown in to the material as a result of impurity striations being initially present in the substrate.

In a typical diode the ratio of the CL intensity from the p and n type material as detected by the S 20 type photocathode was found to be about 2.3 : 1. When corrected for the photocathode response using the data reproduced in figure 5.6, this became 9 : 1 in terms of emitted intensity.

Comparison of the superimposed CL and charge collection line scan traces, as described in section 4.4.3, showed that a finite displacement existed between the centres of the junctions indicated by the two types of trace (see figure 4.22). To understand the true significance of these observations, it is necessary to consider the fundamental relationship existing between the two types of trace. The charge collection trace represents, in effect, the distribution of minority carriers about the point of incidence of the electron beam. The height of each point on the trace is proportional to the number of carriers reaching the p-n junction. The CL trace, on the other hand, is representative of the number of carriers that recombine radiatively times a factor to correct

for the differing photomultiplier response to radiative radiation from n and p type material.

Consider the electron beam incident on the p-type material at a distance r away from an abrupt p-n junction. A number of minority carriers will diffuse to the p-n junction and drift across the space charge region giving rise to the charge collection current. These will then be injected into the n-type material as low energy majority carriers and will not take part in radiative recombination. Also a number of majority carriers (holes) will diffuse to the p-n junction and a small proportion of these will penetrate the space charge region to the n-type material where they can recombine radiatively. Thus the radiative recombination will have two components, the main one due to recombination in the p-type material, but a small component due to recombination in the n-type material. The proportion of minority carriers reaching the p-n junction will be given by an expression similar to that used to describe the charge collection curve. If this expression is denoted as $F_p(r)$ and the number of electron hole pairs produced per second by the beam is N_0 , then $N_0 F_p(r)$ minority carriers/second will reach the p-n junction. If it is assumed that these carriers then take no part in radiative recombination, then the number remaining which may recombine radiatively is $N_0(1 - F_p(r))$. Similarly, the number of majority carriers which diffuse to and across the space charge region can be described by an expression $G_p(r)$. Then the total radiative intensity I will be given by

$$I_{(p\text{-type})} = N_0 \{ \eta_p (1 - F_p(r)) + \eta_n G_p(r) \}$$

where η_p and η_n are the radiative efficiencies in the p and n-type material. The CL traces show that levels of constant intensity I_p and I_n are reached either side of the junction. By definition $I_p \propto N_0 \eta_p$ and $I_n \propto N_0 \eta_n$ but are also dependent on the photomultiplier response. In terms of I_p and I_n , the intensity I close to the junction is given by

$$I_{(p\text{-type})} = I_p(1 - F_p(r)) + I_n G_p(r)$$

and a similar expression exists for the beam incident on the n-side of the junction

$$I_{(n\text{-type})} = I_n(1 - F_n(r)) + I_p G_n(r)$$

When the beam is incident on the junction itself, equal numbers of carriers of either type will be generated in the n-type and p-type material either side. The net intensity will then be given by

$$\begin{aligned} I_{jn} &= (I_{(p\text{-type})} + I_{(n\text{-type})}) / 2 \\ &= (1 - K) (I_n + I_p) / 2 \end{aligned}$$

Where $K = F_p(o) + F_n(o) - G_p(o) - G_n(o)$

In terms of the charge collection trace, the value of K is the ratio of the measured peak height at the junction to a theoretical peak height obtained by extrapolating the straight line regions of the logarithmic plot (figure 4.23a). In the determination of this theoretical height it would be necessary to make allowance for the fact that the carriers are generated in a region of finite size beneath the beam. When the beam is distant from the junction, it can be approximated to a point source for carrier diffusion to the junction. This point however, will be displaced towards the junction as carriers in this position will have a shorter distance to diffuse. The net effect is an artificial broadening of the trace which would lead to an artificially high value of the extrapolated peak height.

In GaP diodes, the intensity I_p is greater than the corresponding value I_n . Thus as a further simplification I_n was put equal to zero.

Then

$$\begin{aligned} I_{(p\text{-type})} &= I_p (1 - F_p(r)) \\ I_{(n\text{-type})} &= I_p G_n(r) \\ I_{jn} &= (1 - K) I_p / 2. \end{aligned}$$

Inspection of these expressions shows quite reasonable agreement with the line scans obtained in practice. Firstly consider the beam incident

on the p-type material and scanning towards the p-n junction. The initial drop in CL intensity will occur at the same point that minority carriers first reach the junction. Thus the initial drop in the CL curve should correspond exactly to the point at which the charge collection trace begins to increase. This behaviour was observed in every diode examined. In contrast to this, when the beam approaches the junction from the n-type material, the initial increase in CL intensity will occur only when sufficient injection of carriers into the p-type material occurs by diffusion against the field of the p-n junction. Thus, as observed in practice, the initial increase in CL intensity is displaced towards the p-type material compared with the charge collection profile.

With the beam incident on the p-n junction itself the intensity is simply a function of K . The value of K as already discussed will depend on the distribution of generated carriers beneath the beam. The value of K must be finite and therefore I_{jn} will be less than $I_p/2$. The value of r corresponding to $I = I_p/2$, and used to define the position of the CL junction, will thus be displaced into the p-type material.

In GaAs diodes, Wittry and Kyser (1965) found that the CL trace exhibited a dip in intensity as the beam crossed the junction itself. In GaAs, radiative recombination is a more efficient process than in GaP (see section 2.1.2) and as a result the values of I_n and I_p are of similar orders of magnitude. This means that it is not possible to approximate the smallest of these, I_p , to zero. A loss of carriers by the charge collection process can therefore lead to a local drop in intensity at the p-n junction below the mean level I_p .

The analysis so far has considered abrupt junctions where the distributions of Zn - O recombination centres, donors and acceptors exhibit step functions at the interface. This is an ideal situation

unlikely to be attained in practice. In the growth of the liquid epitaxial Zn - O doped layer some degree of melt back of the substrate is employed and incomplete mixing could result in a distribution of n-type impurities on the p-side of the junction, giving rise to a competing and less efficient radiative recombination mechanism. Of the dopants used, Zn, O, and Te, Zn has the much higher thermal diffusion coefficient as it diffuses interstitially (Chang and Pearson 1964). Thus it can be expected that during the growth, as the material cools from about 1150°C , some Zn diffusion will occur into the n-type material and this may lead to a depletion of the Zn - O recombination centres on the p-side of the junction. Both this and the presence of n-type impurities in the same region would tend to increase the displacement between the junction positions, measured using the charge collection and CL techniques. An additional loss mechanism may be the presence of non-radiative centres associated with the growth interface.

Electroluminescence in GaP diodes has been shown to originate on the p-side of the junction (Gershenson et al 1966). For maximum efficiency carriers must recombine in a region with the optimum concentration of radiative Zn - O complexes and with a minimum of competing, non-radiative centres. These conditions are also those which, as described above, can decrease the separation between the charge collection and CL junctions. Thus, this separation is a good guide to device efficiency. That this is true in practice can be seen from the results of table 4.2 and has also been demonstrated for a large number of diodes by Calverly and Wight (1970).

An additional factor is that to obtain good injection of carriers into the p-type material, little recombination should occur in the space charge region. As described in section 2, recombination within the space charge region gives a value of $\beta = 2$ in the expression for the I - V characteristics, $I = I_0 \exp qV / \beta kT$, and for recombination outside

the junction, as is required, $\beta = 1$. The scatter in the measured values of β (table 4.2) was too great to enable any correlation to be obtained with device efficiency. This scatter and the fact that some values of β were obtained outside the theoretical limits (i.e. $\beta > 2$) suggests that in some cases gross defects such as Ga inclusions may have been present at the p-n junctions. It appears, from the evidence of Shih et al (1968) and others, that in red emitting diodes β is lowest for diodes with the highest quantum efficiencies. The value of β may be increased if excess recombination centres exist within the space charge region. Such an increase could be caused by the presence of non-radiative centres associated with the growth interface as mentioned above. Ladany (1969) found that the efficiency of diodes was increased if the Zn - O doped layer was compensated by the addition of Te but no satisfactory explanation was offered for this behaviour. In Zn diffused GaAs diodes Lasher and Stern (1964) showed that efficient carrier injection into the compensated p-type region, where recombination occurs, might be due to a process where electrons can tunnel at constant energy between states in the donor impurity band. If a process of this type can occur in compensated GaP diodes then any reduction in luminescent efficiency caused by the presence of n-type impurities on the p-side of the junction may be more than offset by an increased injection efficiency. Ladany found that the diode efficiency reached a peak when about 7×10^{-3} At % Te was added to the p melt. The degree of compensation attained in the diodes examined in this work depends on the amount of mixing that occurred subsequent to the melt back of the n-type substrate during growth. This is a factor that can undergo considerable variation between different growth runs, being particularly dependent on the degree of melt back, and also on the initial rate of cooling. It is possible that wide variations in efficiency between different diodes may be caused in this way.

A half width was defined and measured for

both the CL and charge collection traces as described in section 4.4.3. The values obtained are listed in table 4.2. In general it was found that the two half widths measured for each diode were of a similar order. In some diodes the charge collection half width was slightly larger than the CL half width but in others the reverse was true. No correlation was obtained between either the size or ratio between the half widths and diode efficiency. From the preceeding discussion it can be seen that the half widths will be a function of the size of the carrier generation region beneath the beam. This size will depend on the degree of focusing of the electron beam and also may be influenced by such variables as the beam current and voltage. The beam voltage was the same for each diode examined (30 kV) but variations in the current and in the size of the focused spot may have occurred. The half width of the CL trace may be broadened if a concentration gradient of recombination centres exists on the p-side of the junction and may thus be expected to exhibit a relationship with device efficiency. However, it was found that the shift between the CL and electrical junctions was a more reliable measurement, being less dependent on the size of the carrier generation region, and a consistant relationship between this and device efficiency has been established.

5.4 Transmission Electron Microscopy of GaP.

5.4.1 Thinning.

When opaque substances such as GaAs or Si are being thinned for electron microscopy they become transparent to visible light, appearing orange to the eye, when at a suitable thickness is reached. When an automatic thinning system is used, it is this light which is detected by the photomultiplier. GaP however, is transparent to certain regions of the spectrum to which both the photomultiplier and the human eye are sensitive. Absorption edges of GaAs and GaP are shown in figure 5.8

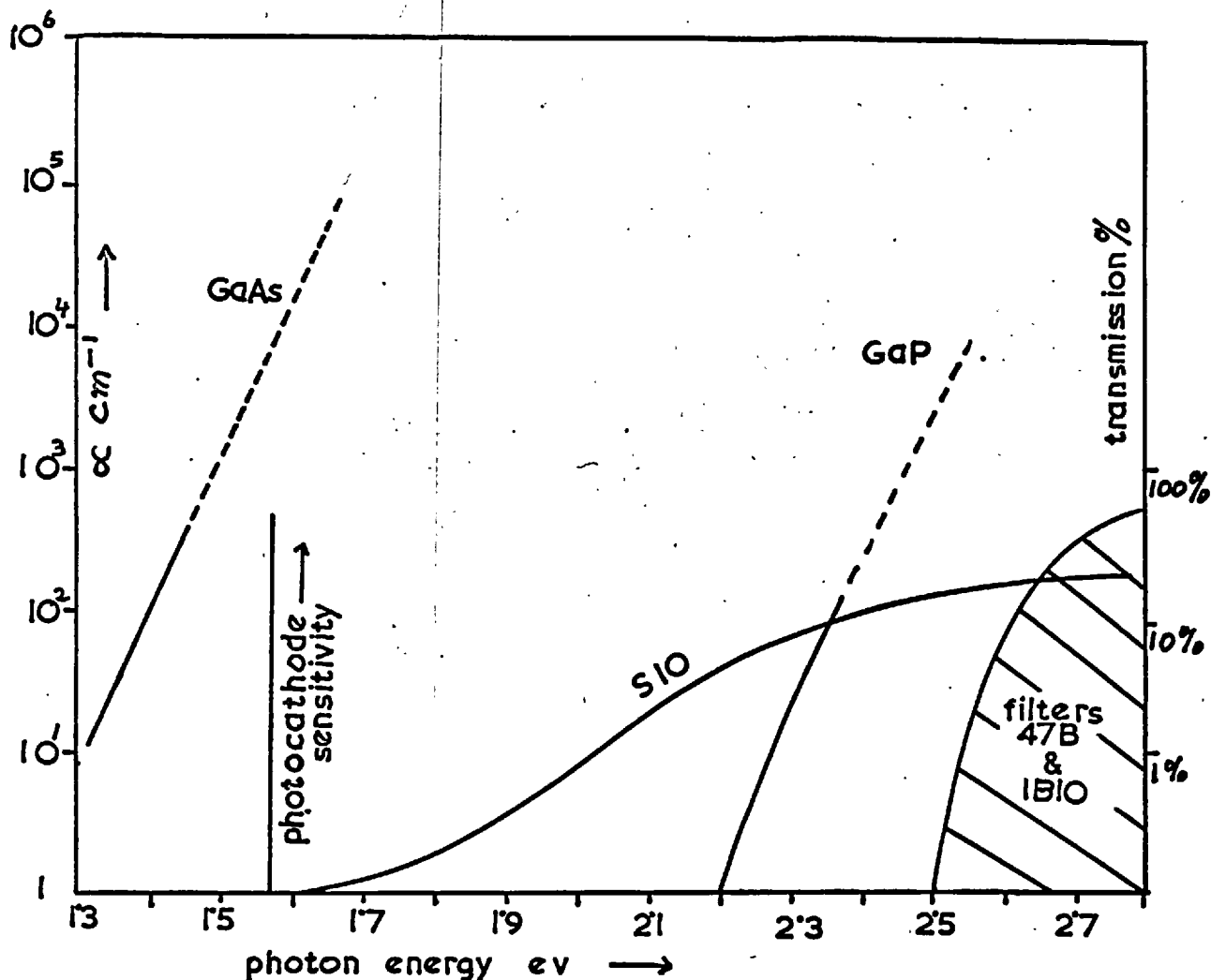


Figure 5.8 Diagram showing the relation of the absorption edges of GaAs and GaP to the spectral response curve for the S10 type photomultiplier used in the automatic thinning process. The transmission curve for the 47B type filter used when thinning GaP is also shown. It can be seen that in each case the minimum photon energy detectable has an absorption coefficient of about 10^{-4} cm^{-1} in the material in question.

together with the spectral response curve of the S 10 type photocathode used in the photomultiplier. It is apparent that the photomultiplier is completely insensitive to wavelengths of light transmitted by a thick specimen of GaAs. However, a specimen of thickness near $5000 \text{ \AA}^0$ may transmit sufficient light of high enough energy to be detected and this is also a suitable thickness for electron microscopy.

As an order of magnitude calculation suppose that the photomultiplier triggers the solenoid when 1% of the light incident on the specimen is transmitted. Ignoring reflection, the transmitted intensity I is given by the expression:-

$$I = I_0 \exp(-\alpha t)$$

Where I_0 is the intensity of the incident light, α is the linear absorption coefficient and t the specimen thickness. In this case $I / I_0 = .01 = \exp(-\alpha t)$. This gives $\alpha t = 4.6$.

For $t = 5000 \text{ \AA}^0$, $\alpha = 9.2 \times 10^4 \text{ cm}^{-1}$

Thus a wavelength of light with a linear absorption coefficient near 10^5 cm^{-1} will be transmitted through a thin specimen with sufficient intensity to trigger the detection system.

In practice a range of wavelengths and absorption coefficients are involved but the calculation serves to illustrate the principle. Extrapolation of the absorption data for n-type GaAs with free carrier concentration $2 \times 10^{18} \text{ cm}^{-3}$, reproduced in figure 5.8, shows that a wavelength of about 0.75μ ($h\nu = 1.65 \text{ eV}$) corresponds to a value of α of 10^5 cm^{-1} . This corresponds to light of a reddish orange colour just detectable by the photomultiplier.

The absorption edge of GaP lies at a much lower wavelength than that of GaAs. Even a thick specimen will transmit visible light with very little absorption. For automatic thinning it was necessary to use optical filters to cut out the portion of the transmitted spectrum to

which the photomultiplier was sensitive. Ideally an interference filter would provide a suitable narrow band width for which α has a value near 10^{-5} cm^{-1} . A satisfactory and cheaper alternative was found using Kodak Wratten filter no. 47B in conjunction with a Chance Pilkington OB10 absorption filter to remove the infra-red component. The combined region of transmission is illustrated by the shaded area in figure 5.8. The two filters were positioned close to the photomultiplier rather than at the illumination source so as to minimise the effects of any extraneous light.

5.4.2 Defects in Vapour Phase Grown GaP.

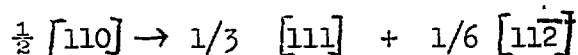
Comparison of the electron microscope results for material grown by the three different basic processes shows that the heaviest concentrations of defects occur in material grown by vapour phase epitaxy. Typically the dislocation density in the vapour grown layers was between $10^7 - 10^8$ lines / cm^2 compared to densities of about $10^5 - 10^6$ lines / cm^2 in pulled material. In n-type liquid epitaxial layers the dislocation density was too low to be measured using the electron microscope but in the Zn-O doped material the density was estimated at about 10^5 lines / cm^2 . Vapour phase material does not make efficient electroluminescent diodes and this may be because the defects introduce a large number of non-radiative centres into the material (see section 2.4.2). It has been suggested that the origin of the dislocations in vapour phase grown material is attributable to the lattice and thermal expansion mismatch between GaP and the GaAs substrate (Saul 1968, 1969). Abrahams et al (1969) working with $\text{GaAs}_{1-x}\text{P}_x$ layers on GaAs found evidence that the principal factor was the lattice mismatch. They reported sets of inclined dislocations projecting upwards through the epitaxial layer and originating from the misfit dislocations at the interface. In the present work it was found that both the dislocation and stacking

fault density increased with doping. In doped material, impurity atoms may segregate to dislocations with the production of a Cottrell atmosphere and / or precipitation. Pinning of the 'grown in' dislocations by this mechanism may lead to increased dislocation multiplication as the material cools down. In other words, in doped material more dislocations may be introduced by virtue of the differences in thermal expansion coefficient than in undoped material. The increased density of stacking faults that occur when the material is doped can be explained if the stacking fault energy is reduced by Suzuki segregation. A discussion of this and other impurity segregation phenomena is given by Suzuki (1957). Suzuki segregation occurs because the equilibrium concentration of impurities in the strip of hexagonal material associated with a stacking fault is different to that in the bulk material. Segregation of impurities either to or away from the fault occurs in such a way that the stacking fault energy γ is reduced. If the total energy of the fault remains constant the reduction in γ can result in an increase in the fault area by further separation of the bounding partials. It is also possible that a reduction in γ will occur on atomic planes closely adjacent to the stacking fault. Dislocations on these planes will thus require less energy to dissociate into further stacking faults lying parallel to and overlapping the original fault. Examples of overlapping fault structures are clearly seen in figures 4.28 and 4.31. The preferential etching effects observed in the vicinity of faults (figure 4.24) are consistent with a localised increase in the concentration of impurity atoms.

In epitaxial layers of Silicon, Booker (1964) showed that stacking faults could arise from nucleation centres on the substrate and propagate through the layer. This generally resulted in the tetrahedral type of stacking fault although in some cases only one side of the fault was propagated. In vapour grown GaP the linear type of stacking fault was very common whereas only a few isolated faults of the tetrahedral variety

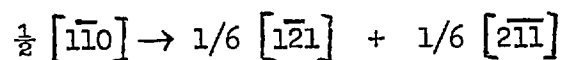
were found. To explain the predominance of the linear type of fault there are two possibilities. Either only one side of tetrahedral faults nucleated at the substrate interface propagates through the layer or else the faults are formed independently by dissociation of dislocations. In either case Suzuki segregation would be influential. If the faults are all initiated at the substrate interface and propagate through the epitaxial layer then the width of the faults at the surface of the layer should be the same. In general this was found not to be the case and it is concluded that the majority of faults in this material were formed either by dissociation of dislocations or else possibly by nucleation at defects, such as precipitates, within the epitaxial layer.

Analysis of the dislocations associated with the faults in figure 4.28 showed that the majority were Schockley partials but that in some cases the bounding dislocations were Frank partials. The presence of the latter suggests that stacking faults, lying for example in a (111) plane, may form by dislocation dissociation with the reaction



Total Frank + Shockley

In this case the Frank partial will be sessile and any expansion of the fault will occur by motion of the Schockley partial. Faults bounded by two Schockley partials could also form by a reaction of the type:



All the faults observed were intrinsic in nature. This compares with the work of Abrahams and Tietjen (1969) who observed intrinsic faults bounded by Schockley partials in $\text{GaAs}_{1-x}\text{Px}$ alloys. Similarly in their work, faults were only observed when the epitaxial layers were doped.

5.4.3 Defects in Pulled and Liquid Epitaxial GaP.

One of the objects of this examination was to try and establish the precise nature of the defects responsible for the difference in etching

characteristics between pulled and liquid epitaxial GaP, and also why diodes grown by diodes formed by the growth of a single Zn - O doped layer directly onto a pulled n-type substrate are very inefficient. In general, the pulled material, etched using the procedure described by Saul (1968), shows a number of characteristic dislocation etch pits. However a much more dense array of smaller etch pits is also generally found to be present. These pits which do not occur in liquid epitaxial material are not fully explained. An example of the different etching behaviour can be seen in figure 5.9 which is a micrograph of the etched surface of a GaP diode. The upper part of the micrograph shows the liquid epitaxial layer whilst the darker region below is the etched surface of the pulled substrate. It will be noted that defects in the pulled substrate do not appear to have grown into the epitaxial layer.

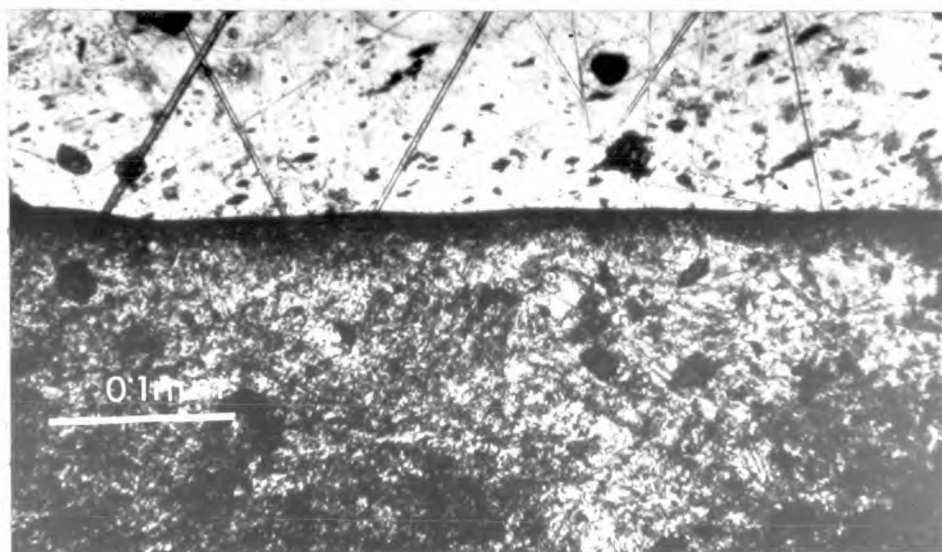


Figure 5.9 The etched surface of a GaP diode showing the different etching characteristics of pulled and liquid epitaxially grown material.

The electron microscope study of the present work did not detect any defects peculiar to the pulled material to which this etching characteristic might be attributed. One possible explanation is that the

etching characteristics of pulled material are influenced by a lack of stoichiometry. This would not be detectable using the electron microscope if no clustering or ordering of the point defects occurred but could lead to changes in the chemical and physical properties of the material. In particular the presence of Ga vacancies might be expected to encourage the formation of the $V_{Ga} + Te_3$ type of complex described by Vieland and Kudman (1963). It is not possible to be specific as to whether Ga or P vacancies are likely to predominate as little is known about the existence region of GaP and in any case this would be critical on the equilibrium established between the partial pressure of phosphorus vapour over the melt and the growing material.

However, it is possible that this partial pressure may be increased due to the vapour being in contact with portions of the melt at temperatures much higher than the melting point and this could result in excess phosphorus being incorporated into the growing crystal. It has been reported, in fact, that some Ga is often found remaining in the crucible after the crystal has been pulled (Bass 1969). Ga vacancies, if present in the substrate, could act as sinks for Zn diffusion from the epitaxially overgrown Zn - O doped layer. It is possible that this could deplete the radiative centres of Zn and so lead to inefficient diodes. This would be consistent also with the measurements of table 4.2 for diodes L 136 and L 129 and with the results of Calverly and Wight (1970) which show very large separations of the charge collection and CL junctions in these diodes.

In layers grown by liquid epitaxy from a Ga melt, any stoichiometry variations will be on the Ga rich side of the existence region. Thus in a diode grown by double epitaxy, no excess of Ga vacancies is likely to be present near the p-n junction. The possible presence of excess P vacancies in this material may influence device efficiency but this has not yet been established.

The very low defect concentration found in GaP grown by liquid epitaxy is in accordance with the high electroluminescent efficiencies found in this type of diode. The lack of dislocations, despite the high doping levels, is indicative of very low thermal stresses during growth. Precipitation may well be the limiting factor in determining the ratio of radiative to non-radiative centres which is critical to luminescent efficiency. Ladany (1969) showed that diode efficiencies could be increased by optimisation of the amount of Zn and O added to the p melt. When excess dopants were added above this optimum, the efficiency of the diodes decreased. It is likely that this drop off in efficiency is due to the introduction of competing non-radiative centres possibly in the form of precipitates. It would appear from the evidence of the electron micrographs (sections 4.5.2 and 4.5.3) that precipitation, in the form of complexes the order of $40 \text{ \AA}^0$ in diameter, is present in all Te and S doped samples with free carrier concentrations near $1 \times 10^{18} \text{ cm}^{-3}$. Some evidence of what may be precipitation has also been found in Zn - O doped specimens (figure 4.37). Precipitates of a comparable nature have been observed in n-type GaAs by Kressel et al (1968), Meiran (1965) and Abrahams et al (1967) and have been identified by electron diffraction and Moire fringe spacings to be of the Ga_2Se_3 and Ga_2Te_3 type. In the present work the precipitate density was too low to enable any positive identification to be made but it is likely that the precipitates are of a similar type. Precipitation in Zn - O doped GaP is not so well understood. Observations of precipitates in Zn doped GaP (Gershenzon and Mikulyak 1962) and Zn diffused GaAs (Black and Jungbluth 1967b, and Hill 1968) may not be comparable as the precipitates were much larger in size than those observed in the present work.

5.4.4 Electrochemical Polishing of GaP.

The presence of electrochemical corrosion tunnels has not previously been reported in GaP. Tunnels have however, been observed in certain other materials under a variety of circumstances.

Westwood and Rubin (1962) investigated the growth and dissolution of L_1F crystals in aqueous solutions containing long chain fatty acids. Both positive and negative whiskers could be formed using super saturated and undersaturated solutions containing identical concentrations of stearic acid. It was thus possible to equate the formation of tunnels with a reversal of crystal growth. It was suggested that the fatty acids acted as step poisons and were less concentrated at the base of the tunnels than at the surface. The maximum depth of the tunnels was 200μ and their diameter between 1 and 2μ .

Swann (1969) described a mechanism of corrosion tunneling applicable to the dissolution of Cu_3Au in ferric chloride solution. Electron microscope studies showed that a passive layer of gold was formed on the tunnel walls. A theory was developed to explain the longitudinal rather than lateral growth of the tunnels. This showed that passivation of the tunnel walls would occur at a critical radius found by equating the number of gold atoms in the tunnel with the number of copper surface sites on the tunnel walls. This radius was found to be $2/3$ of the maximum radius of the hemispherical pit at the base of the tunnel. Thus the tunnel walls become passivated before the base and the tunnels grow longitudinally.

The formation of etch tunnels in L_1F and in Cu_3Au thus depends on passivation of the tunnel walls in preference to the base of the tunnels. This unfortunately does not compare with the state of affairs existing in the case of GaP. Here the formation of the tunnels appears to be purely an electrochemical phenomenon ^{on} and no passivation, as such, is likely to occur. X

In the present work, no relation was found between the formation of tunnels and any observed defects originally present in the material. It is certain that they do not follow lines of dislocations as they formed in material in which the dislocation density was too small to be resolved. Furthermore, dislocations tend to lie along $\langle 110 \rangle$ directions whereas the tunnels were invariably formed along $\langle 111 \rangle$ directions. The observed density of tunnels was found to vary between about 10^6 to 10^8 tunnels / cm^2 and this density was found to increase with the electropolishing voltage used. It therefore seems certain that the tunnels are formed as a result of electrochemical reaction occurring at the semiconductor-electrolyte interface.

It has been shown (Turner 1960) that in a semiconductor electron holes are required to carry out anodic reactions. In etching holes are presumably necessary to break the covalent bond between surface and underlying atoms. The rate of the reaction may be determined by the number of holes continuously available at the surface. Holes consumed may be replaced by diffusion from the bulk or by generation of electron hole pairs in the surface region. The surface of an n-type semiconductor becomes depleted of holes at a relatively low current density thus limiting the anodic reaction rate. This depletion produces a space charge region which increases in width as the applied voltage is increased. When the voltage is raised to a critical value, breakdown of this space charge region can occur. Then holes diffusing from the semiconductor bulk are accelerated to kinetic energies sufficient to produce hole multiplication. This breakdown does not take place uniformly over the surface but occurs first at defects scattered through the single crystal and non-uniform pitting results. It is suggested that this effect may be fundamental in the formation of tunnels in GaP. The voltages actually used were between 120 and 240 volts, and probably sufficient to

give rise to avalanche breakdown. If a series of pits were formed by virtue of such breakdown it is possible that they may propagate as tunnels by virtue of the high field region associated with small radius points. This could lead to a state of continuous avalanche breakdown at the apices of the tunnels. The holes formed by this process would give rise to preferential dissolution at the ends of the tunnels which as a result would propagate longitudinally. This process however is not limited solely to GaP and if it applied unconditionally to all semiconductors the formation of tunnels would be a common phenomenon. ^{or} Clearly this is not so and some property of GaP must be particularly conducive to tunnel formation.

It is well known that polarity effects exist in the III-V compounds (Barber and Heasell 1965). In particular the Ga $\{111\}$ and P $\{\bar{1}\bar{1}\bar{1}\}$ surfaces of GaP exhibit markedly different etching and polishing characteristics. The P $\{\bar{1}\bar{1}\bar{1}\}$ surfaces show a much greater rate of dissolution than the Ga $\{111\}$ surfaces which are more noble or less chemically reactive. A comparison was made of tunnels formed from the P $\{\bar{1}\bar{1}\bar{1}\}$ surface (figure 4.44) with those formed from the Ga $\{111\}$ surface (figure 4.39). This showed that the tunnels were invariably formed in a $\langle 111 \rangle$ direction parallel to the covalent bonds in the sense of moving from a phosphorus to a gallium atom. Thus, polarity effects appear to limit the tunnels to formation in directions normal to the P $\{\bar{1}\bar{1}\bar{1}\}$ planes in the sense of moving into the material. It is concluded that the tunnels in GaP are probably initiated and propagated as a result of the local injection of holes, subject to constraints imposed by the polar nature of the $\langle 111 \rangle$ directions. It is noted that these directions are such that the base of the tunnels can always be of greater reactivity than the walls. This is analogous to the effects of passivation in L_1F and Cu_3Au .

CHAPTER 6

Summary and Conclusions.

GaAs laser diodes, GaP red electroluminescent lamps and the materials used in their construction have been examined using a range of different techniques. Initially, at the request of the sponsors (S.E.R.L. Baldock), the work comprised an investigation into defects in GaAs material supplied by them.

Zn diffused GaAs laser diodes were examined in an adapted electron probe microanalyser using the charge collection and cathodoluminescence modes. In the n-side of diodes doped with Te, a number of dark spots and lines, sometimes with white haloes, were observed using both techniques. The spots exhibited a one to one correspondence with pits subsequently formed by etching. The evidence from this work and from similar work done concurrently by other authors suggests that these features are attributable to impurity segregation effects at dislocations. It was demonstrated that the p-n junction can, in certain circumstances, act as an efficient detector for cathodoluminescence emitted in the n-type material. Line scans were made of the charge collection signal across the p-n junction and it was shown that to a good approximation these curves could be represented by the sum of two exponentials, one apparently dependent on the minority carrier diffusion length and the other on the net optical absorption coefficient. It was shown that this net optical absorption coefficient was a function of the distance between the p-n junction and the point of incidence of the electron beam. It was demonstrated that growth striations made visible using infra-red transmission, could in some cases be displayed using cathodoluminescence.

To examine defects present in large slices of GaAs a camera was constructed to take X-ray topographs using the principle of anomalous transmission. Not all specimens were found suitable for examination by

this technique. In particular, ~~in Zn diffused slices of GaAs, no anomalous~~ transmission could be detected. Presumably this was due to very heavy defect concentrations associated with the diffusion front. The best topographs were obtained from undiffused slices of boat grown GaAs. No features were observed in the topographs to correspond to pits formed subsequently by etching but conversely some features, probably due to precipitation within the slice, were revealed by the topographs alone. A number of features possibly representing helical dislocations appeared in the topographs but no overall dislocation network was resolved. This may be due to the defect density of the available specimens being so high that interaction of strain fields occurred.

Defects induced in a GaAs slice by Zn diffusion were examined optically and by electron probe microanalysis. Microanalysis indicated that precipitates of Zn_3As_2 were present but other inclusions, rectangular in profile, were observed with a composition similar to that of the matrix. Some of these appeared to nucleate at defects present in the undiffused slice and it was demonstrated that the observed growth habit was related to the polar nature of the GaAs structure.

At the request of the sponsors the research program was turned to GaP. Again scanning electron beam techniques proved useful and diodes were examined in the electron probe and in a scanning electron microscope also modified to detect cathodoluminescence. It was found that variations in cathodoluminescence efficiency could occur at inclusions in pulled GaP and, by using microanalysis, could be related to the chemical composition of the material. The use of cathodoluminescence also showed that striations could be formed in Zn-O doped layers grown by liquid epitaxy. Line scans of the charge collection current and cathodoluminescence intensity across the p-n junction were examined for a number of diodes. The distance separating the centres of the two types of trace was found to be largest in diodes of low efficiency and vice-versa.

An expression was derived to show the relation between the two types of trace. Measurements were made of the minority carrier diffusion lengths and the I-V characteristics of the diodes were investigated.

Transmission electron microscopy was used to examine GaP. An automatic jet thinning technique was developed using chlorine - methanol as the reagent. Optical filters were incorporated into the system to limit the light to wavelengths detectable by the photomultiplier only when the specimen thickness was 1μ or less. Only the P $\{\overline{111}\}$ faces could be polished using chemical means alone and an electrochemical technique was developed to enable specimens to be thinned from the Ga $\{111\}$ faces. It was found that a result of the electrochemical reaction was the formation of dense networks of tunnels which penetrated the specimen along polar $\langle 111 \rangle$ directions. A large number of specimens grown by different processes were examined. It was found that dislocations and stacking faults were present in the greatest concentration in GaP grown by vapour phase epitaxy and that the concentration increased with doping. Analysis was made of stacking faults, all of which were found to be intrinsic, and of the associated dislocations. The defect content of pulled material was found to be higher than that of layers grown by liquid phase epitaxy but in all specimens with free carrier concentrations $N > 1 \times 10^{18} \text{ cm}^{-3}$ evidence was found to suggest that precipitation of impurities had taken place.

It has been shown that the segregation and precipitation of impurities and the reaction of impurities with crystal defects can be of great importance in GaP and GaAs. The work has demonstrated the importance of using a number of different techniques for the observation of imperfections and inhomogeneities. Different techniques were found to resolve different types of defect. Techniques sensitive to the optical properties of defects have been found to be important in relating the quality of the material to device performance. In principle the

results can be used to improve growth techniques in a way beneficial to device yield and efficiency.

LIST OF REFERENCES

- Abrahams M.S. & Buiocchi C.J. (1965) J. Appl. Phys. 36 2855.
 (1966) *ibid* 37 1973.
 (1967) J. Phys. Chem. Sol. 28 927.
- Abrahams M.S., Buiocchi C.J. & Tietjen J.J. (1967) J. Appl. Phys. 38 760.
- Abrahams M.S., Weisberg L.R., Buiocchi C.J. & Blanco J. (1969) J. Matls. Sci. 4 223.
- Abrahams M.S. & Tietjen J.J. (1969) J. Phys. Chem. Sol. 30 2491.
- Albers W. & Haas C. (1969) Philips Tech Rev. 30 pages 82, 107 & 142.
- Amelinckx S. (1964) Sol State Physics. Suppl. 6.
- Authier A., Rogers C.B., & Lang A.R. (1965) Phil. Mag. 8 12 117.
- Bailey L.G. (1967) Trans. Met. Soc. AIME. 239 310.
- Barber H.D. & Heasell E.L. (1965) J. Phys. Chem. Sol. 26 1561.
- Barth H. & Hoseman R. (1958) Z. Naturforsch. 13a 792.
- Bass S.J. & Oliver P.E. (1966) in "Gallium Arsenide: 1966 Symposium Proceedings", Inst. Phys. & Phys Soc. London 1967.
- Bass S.J. & Oliver P.E. (1968) J. Crystal Growth 3 286.
- Bass S.J. (1969) S.E.R.L. Baldock. Private Communication.
- Bell R.L. Latkowski R. & Willoughby A.F.W. (1965) J. Matls. Sci. 1 66.
- Bell R.L. & Willoughby A.F.W. (1970) *ibid* 5 198.
- Biederman E. & Brack K. (1966) J. Electrochem. Soc. 113 108.
- Black J.F. (1967) *ibid* 114 1292.
- Black J.F. & Jungbluth E.D. (1967a) *ibid* 114 181
 (1967b) *ibid* 114 188.
- Booker G.R. (1964) Disc. Far. Soc. 38 298.
- Borrmann G., Hartwig W. & Irmeler H. (1958) Z. Naturforsch. 13a 423.
- Braunstein R., Pankove J.I. & Nelson H. (1963) Appl. Phys. letts. 3 31.
- Broom R.F., Barrie R. & Ross I.M. (1958) "Semiconductors and Phosphors".
 Proc Int Coll. at Garmisch Partenkirchen.
 Interscience N.Y. P 453.
- Broom R.F. Gooch C.H., Hilsum C. & Oliver D.J. (1963) Nature 198 368.
- Buiocchi C.J. (1967) J. Appl. Phys. 38 1980.
- Burns G. & Nathan M.I. (1963) I.B.M. J. Res & Dev 7 72.
 (1964) Proc IEEE 52 770.

- Burstein E. (1954) Phys. Rev 93 632.
- Calverly A. & Wight D.R. (1970) Sol. St. Elec. 13 382.
- Carlson R.O. (1967) J. Appl. Phys 38 661.
- Casella R.C. (1963) Ibid 34 1703
- Casey H.C. (1967) J. Electrochem. Soc. 114 153.
- Casey H.C. & Kaiser R.H. (1967) ibid 114 149.
- Casey H.C. & Panish M.B. (1968) Trans. Met. Soc. AIME 242 406.
- Chang L.L. & Pearson G.L. (1964) J. Appl. Phys. 35 1960.
- Chedzey H.A. & Hurle D.T.J. (1966) Nature 210 933.
- Cole H., Chambers F.W. & Dunn D.M. (1956) Acta. Cryst. 2 685.
- Cole G.S. & Winegard W.C. (1965) J. Inst. Metals. 7 153.
- Cullity B.D. (1956) Elements of X-ray Diffraction, Addison Wesley.
- Cunnell F.A. & Gooch C.H. (1960) J. Phys. Chem. 64 127.
- Cusano D.A. (1964) Sol. St. Comm. 2 353.
- Cuthbert J.D. Henry C.H. & Dean P.J. (1968) Phys. Rev. 170 739.
- Czaja W. (1966) J. Appl. Phys. 37 4236.
- Czaja W. & Patel J.R. (1965) ibid 36 1476.
- Dash W.C. (1956) ibid 27 1195.
- Dean P.J. & Thomas D.G. (1966) Phys. Rev. 150 690.
- Dean P.J., Gershenzon M. & Kaminsky G. (1967) J. Appl. Phys. 38 5332.
- Dousmanis G.C., Nelson H. & Staebler D.L. (1964) Appl. Phys. Letts. 5174.
- Elliott R.J. (1957) Phys. Rev. 108 1384.
- Epstein A.S. (1969) Sol. St. Elec. 12 485.
- Figielski T. (1964) Phys. Stat. Sol. 6 429.
- Foster L.M., Plaskett T.S. & Scardefield J.E. (1966) I.B.M. J. Res. & Dev 10 114.
- Fuller C.S. & Allison H.W. (1962) J. Electrochem. Soc. 109 880.
- Gatos H.C., Finn M.C. & Levine M.C. (1961) J. Appl. Phys. 32 1174.
- Geiseke G. (1966) in 'Semiconductors and Semimetals' Eds Willardson R.K. & Beer A.C. Academic Press, N.Y. 2 63.

- Gershenson M. & Mikulyak R.M. (1964) J. Appl. Phys. 35 2132.
- Gershenson M. (1966) Luminescence of Inorganic Solids. Ed. Goldberg P. Academic Press N.Y. P 603-684.
- Gershenson M., Logan R.A. & Nelson D.F. (1966) Phys. Rev. 149 580.
- Gippius A.A. & Vavilov V.S. (1963) Sov. Phys. Sol. State. 4 1777.
(1965) *ibid* 6 1873.
- Goldstein B. (1961) Phys. Rev. 121 1305.
- Gooch C.H. (1969) S.E.R.L. Tech. J. 19 10.1.
- Grimmeiss H.G., Rabenau A. & Koelmans H. (1961) J. Appl. Phys. Suppl. 32 2123.
- Haasen P. (1957) Acta Met. 5 598.
- Hall R.N. (1959) Proc. IEE. 106 923.
- Hall R.N. (1963) Sol. St. Elec. 6 405.
- Hall R.N., Fenner G.E., Kingsley J.D., Soltys T.J. & Carlson R.O. (1962) Phys. Rev. letts. 4 361.
- Haynes J.R. (1960) Phys. Rev. letts. 4 361.
- Heine V. (1966) Phys. Rev. 146 568.
- Henry C.H., Dean P.J. & Cuthbert J.D. (1968) *ibid* 166 754.
- Hill D.E. (1964) *ibid* 133 A866
- Hill M.J., Holt D.B. & Unvala B.A. (1968) J. Sci. Inst. Series 2 1 301.
- Hill M.J. & Holt D.B. (1968) J. Matls. Sci. 3 244.
- Hill M.J. (1968) Private communication.
- Hirsch P.B., Howie A., Pashley D.W., Whelan M.J. & Nicholson R.B. (1965) Electron Microscopy of Thin Crystals, Butterfields.
- Holloway H. & Bobb L.C. (1968) J. Appl. Phys. 39 2467.
- Holonyak N. & Bevacqua S.F. (1962) Appl. Phys. letts. 1 82.
- Holt D.B. (1960) J. Appl. Phys. 31 2231.
(1962) J. Phys. Chem. Sol. 23 1353.
(1966) *ibid* 27 1053.
- Holt D.B. & Chase B.D. (1968) J. Matls Sci. 3 178.
- Hornstra J. (1958) *ibid* 5 129.
- Howie A. & Whelan M.J. (1962) Proc. Roy. Soc. A267 206.
- Hurle D.T.J. (1966) Phil. Mag. 13 305.

- Iizuka T. (1968a) Jap. J. Appl. Phys. 7 485.
 (1968b) *ibid* 7 490.
- Jonscher A.K. & Boyle M.H. (1966) in "Gallium Arsenide: 1966 Symposium Proceedings", Inst. Phys. & Phys. Soc. London 1967, 78.
- Jungbluth E.D. (1965) J. Electrochem Soc. 112 580.
- Keyes R.W. (1963) Proc. IEEE (Corresp) 20 602.
- Kressel H. & Ladany I. (1968) J. Appl. Phys. 39 5339.
- Kressel H., Hawrylo F.Z., Abrahams M.S. & Buiocchi C.J. (1968) *ibid* 39 5139.
- Kressel H., Nelson H., McFarlane S.H., Abrahams M.S., LeFur P. & Buiocchi C.J. (1969) *ibid* 40 3587.
- Kudman I. & Vieland L.J. (1963) J. Phys. Chem Sol. 24 967.
- Kyser D.F. & Wittry D.B. (1966) The Electron Microprobe, Eds. McKinley T.D., Heinrick K.F.J., & Wittry D.B. Wiley N.Y. p. 691.
- Ladany I. (1969) J. Electrochem Soc. 116 993.
- Ladany I., McFarlane S.H. & Bass S.J. (1969) J. Appl. Phys. 40 4984.
- Laister D. & Jenkins G.M. (1968) J. Matls. Sci. 3 584.
- Lang A.R. (1958) J. Appl. Phys. 29 527
 (1959) *ibid* 30 1748.
- Lasher G. & Sterne F. (1964) Phys. Rev. 133 A553.
- Levene S.H. (1966) M.Sc Thesis, Imperial College, London.
- Logan R.A., White H.G. & Trumbore F.A. (1967) Appl. Phys. letts. 10 206.
- Longini R.L. (1963) Sol. St. Elec. 5 1548.
- Lorenz M.R. & Pilkuhn M.H. (1966) J. Appl. Phys. 37 4094.
- Lorenz M.R., Pettit G.D., & Taylor R.C. (1968) Phys. Rev. 171 876.
- Lucovsky G. & Varga A.J. (1964) J. Appl. Phys. 35 3419.
- Lucovsky G., Varga A.J. & Schwarz R.F. (1965) Sol. St. Comm. 3, 9.
- Maeda K., Kasami A., Toyama M. & Wakamatsu N. (1969) Jap. J. Appl. Phys 8 65.
- Meiran E.S. (1965) J. Appl. Phys. 36 2544.
- Morgan T.N. Welber B. & Bhargava R.N. (1968) Phys. Rev. 166 751.
- Morizane K., Witt A.F. & Gatos H.C. (1966) J. Electrochem. Soc. 113 51.

- Muller Von. A. & Wilhelm M. (1964) Z. Naturforsch 19 254.
- Nathan M.I. (1966) Proc IEEE 54 1276.
- Nathan M.I., Dumke W.P., Burns G., Dill F.H. & Lasher G.J. (1962)
Appl. Phys. letts. 1 62.
- Nelson H. (1963) RCA Rev. 24 206.
- Oatley C.W. ^{Myron and Pease} (1965) Adv. in Electronics & Electron Phys. 21 181. X
- Okkerse B. & Penning P. (1968) Philips Tech Rev. 29 114.
- Panish M.B. (1966a) J. Phys. Chem. Soc. 27 291.
(1966b) J. Electrochem. Soc. 113 224.
(1967a) ibid 114 91.
(1967b) ibid 114 1161.
- Panish M.B., Queisser H.J., Derick L. & Sumski S. (1966) Sol. St. Elec.
9 311.
- Pilkuhn M.H. & Rupprecht H. (1964) Trans. Met. Soc. AIME 230 296
(1967) J. Appl. Phys. 38 5.
- Plaskett T.E., Blum S.E. & Foster L.M. (1967) J. Electrochem. Soc. 114
1303.
- Quist T.M., Rediker R.H., Keyes R.J., Krag W.E., Lax B., McWhorter A.L.
& Zeigler H.Z. (1962) Appl. Phys. letts
1 91.
- Sah C.T., Noyce N. & Shockley W. (1957) Proc. IRE 45 1228.
- Saul R.H. (1968) J. Electrochem Soc. 115 1184.
(1969) J. Appl. Phys. 40 3273.
- Schottke G. (1966) J. Phys. Chem. Sol. 27 1721.
- Schwuttke G.H. (1962) J. Appl. Phys. 33 2760.
- Schwuttke G.H. & Queisser H.J. (1962) ibid 33 1540.
- Schwuttke G.H. & Rupprecht H. (1966) ibid 37 197.
- Shaw D.A. & Thornton P.R. (1968) J. Matls Sci. 3 507.
- Shih K.K., Lorenz M.R. & Foster L.M. (1968) J. Appl. Phys. 39 2747.
- Shockley W. (1949) Bell Syst. Tech. J. 28 435.
- Stringfellow G.B. & Greene P.E. (1969) J. Appl. Phys. 40 502.
- Sturge M.D. (1962) Phys. Rev. 127 768.
- Sulway D.V., Kyaw H., Thornton P.R. (1967) Sol. St. Elec. 10 545.
- Suzuki H. (1957) in 'Dislocations and Mechanical Properties of Crystals.'
Wiley N.Y. page 361.
- Swann P.R. (1969) Corrosion 25 147.

- Taylor R.C., Woods J.F. & Lorenz M.R. (1968) J. Appl. Phys. 39 5404.
- Thomas D.G., Gershenzon M. & Trumbore F.A. (1964) Phys. Rev. 133 A269.
- Thomas D.G. & Hopfield J.J. (1966) *ibid* 150 680.
- Thomas D.G., Gershenzon M. & Hopfield J.J. (1963) *ibid* 131 2397.
- Thornton P.R. (1967) The Physics of Electroluminescent Devices E & F.N. Spon. London 1967.
- Thornton P.R. (1968) Scanning Electron Microscopy. Chapman & Hall.
- Thurmond C.D. (1965) J. Phys. Chem. Sol. 26 785.
- Trumbore F.A., White H.G., Kowalchik M., Logan R.A. & Luke C.L. (1965) J. Electrochem Soc. 112 782.
- Turner D.R. (1960) in 'Surface Chemistry of Metals and Semiconductors'. Ed Gatos H.C. Wiley & Sons N.Y. P.285.
- Turner W.J. & Reese W.E. (1964) J. Appl. Phys. 35 350.
- Venables J.D. & Broudy R.M. (1958) *ibid* 29 1025.
- Vieland L.J. & Kudman I. (1963) J. Phys. Chem. Sol. 24 437.
- Washburn J., Thomas G. & Queisser H.J. (1964) J. Appl. Phys. 35 1909.
- Weisberg L.R. & Blank F.A. (1963) Phys. Rev. 131 1548.
- Weissman S. (1968) in 'Fifty Years of Progress in Metallographic Techniques' ASTM STP 430 P. 141.
- Welker H. (1952) Z. Naturforsch 7a 744.
- Westwood A.R.C. & Rubin H. (1962) J. Appl. Phys. 33 2001.
- Whelan M.J. & Hirsch P.B. (1957) Phil. Mag. 2 1121 & 1303.
- White J. G. & Roth W.C. (1959) J. Appl. Phys. 30 946.
- Wight D.R. (1970) S.E.R.L. Baldock, Private communication.
- Willardson R.K. & Goering H.L. (1962) Eds. Compound Semiconductors, Vol. 1. Preparation of III-V Compounds Reinhold.
- Williams E.W. & Blacknall D.M. (1967) Trans. AIME. 239 387.
- Wittry D.B. & Kyser D.F. (1964) J. Appl. Phys. 35 2439.
(1965) *Ibid* 36 1387.
(1967) *ibid* 38 375.
- Wittry D.B. (1966) Appl. Phys. letts. 8 142.
- Wolff G.A., Kech^K P.H. & Broder J.D. (1954) Phys. Rev. 94 753.
- Ziegler G. & Henkel H. (1965) Z. Angew. Phys. 19 401.

Acknowledgements.

The author would like to thank Professor J.G. Ball for providing research facilities and the Ministry of Defence (Navy) for financial support.

Thanks are due to Dr. D.B. Holt for his continued interest, advice and criticism throughout the course of this work and to S.E.R.L. Baldock for the provision of specimens.

The author is grateful for the helpful assistance offered by his colleagues at Imperial College and the many informal discussions which resulted. Thanks are also due to Mrs. G. Murray for the typing.