

THE EPITAXIAL GROWTH OF GALLIUM ARSENIDE
ON A SEMI-INSULATING GALLIUM ARSENIDE SUBSTRATE

by

JOHN HALL DOWNIE. B.Sc.

Thesis presented for the Degree of M.Sc. in the
Faculty of Science, Edinburgh University.

September, 1969.



Summary

The present need for ultra-high purity, high resistivity gallium arsenide for use in such microwave devices as the Gunn diode has stimulated the work for this report.

A review of the development of epitaxial processes to this end is given with particular emphasis on quartz as a source of impurity in the deposited layer. The design of a cold wall, resistance strip heated reactor is described and the difficulty with which epitaxy was achieved is analysed.

The work described also includes an analysis of substrate preparation methods and an appendix is given describing various electrical evaluation techniques for an epitaxial layer including a proposed varactor diode structure for identifying carrier concentration.

ACKNOWLEDGEMENTS

The author wishes to thank J. Weaver for suggesting the topic and for his continued and constructive interest throughout the project; Ferranti Ltd. in general and the individuals of the Valve Department in particular for the support which made this work possible; the author's wife for her help in preparation of this report; and finally Professor Farvis for his useful guidance.

INDEX

Chapter 1. Introduction

1.1	The development of gallium arsenide as a semi-conductor for microwave devices.	1
1.2	Gallium arsenide epitaxy	5
1.3	Growth methods for epitaxial gallium arsenide	8
1.4	Comparison of reported growth results.	14
1.5	Reactor impurities.	15
1.6	Other growth methods.	16
1.7	Design of a reactor.	17
1.8	Epitaxial film evaluation.	18
1.9	Evaluation of crystallinity.	18
1.10	Determination of film thickness	18
1.11	Resistivity measurement.	19
1.12	Hall mobility measurement.	20
1.13	Carrier concentration measurement.	20
1.14	Ohmic contacts.	21
1.15	Substrate preparation	21

Chapter 2. Design of Apparatus

2.1	Reactor design	24
2.2	Heater design	26
2.3	Framework	28
2.4	Flow system and hydrogen purification	29
2.5	Gallium source	32
2.6	Temperature control	33
2.7	Safety precautions	35
2.8	Reactant materials	36

Index (Cont'd.)

Chapter 3 Substrate Preparation

3.1 Mechanical polishing.	37
3.2 Chemical polishing	38
3.3 Substrate cleaning	42

Chapter 4 Attempted Growth Experiments

4.1 Initial growth experiments.	44
4.2 Examination of etching rate to detect the approach of growth conditions.	47
4.3 Systematic growth runs.	48
4.4 Modified runs.	50
4.5 Analysis of reactor deposits.	51
4.6 Growth runs with re-positioned heaters.	53

Chapter 5. Chemical Reactions

5.1 Reported reactions	57
5.2 Probable deposition reactions.	59
5.3 The effect of the substrate on growth.	60
5.4 Vapour etching.	61

Chapter 6. Growth and Etching in the Reactor

6.1 Convection problems.	63
6.2 Vapour liquid solid growth.	66
6.3 Needle growth.	68

Chapter 7. Conclusion 70

Appendix

A1. Ohmic contacts.	72
A2. Resistivity and Hall mobility.	74
A3. Carrier concentration.	77

References	84
------------	----

Chapter 1

Introduction

1.1 The general tendency in the electronics industry towards higher frequency power handling capabilities of devices and equipment has been the main driving force behind the development of semiconducting materials. The first theory based research on such materials, (using Wilson's energy band model) was on germanium; work on silicon soon followed. Research was extended to compounds in the hope of obtaining even better electrical properties, their semiconducting nature having been known since Faraday's early work on the non-metallic conduction of silver sulphide.

The properties which at first were sought were those which would give better transistor action. For high frequency operation a high charge carrier mobility resulting in fast electron or hole transit within a device is necessary, as also is low dielectric constant. A wide energy band gap allows greater operating temperatures and hence higher power handling capabilities. A further desirable property - consistent device operation down to low temperatures - is desirable but information about impurity activation energies is difficult to obtain and at first, though recognised, little work was done on this aspect.

A wide range of materials was considered. Jenny¹ in 1958 gave an excellent comparison of the characteristics of many semiconductors including, for example, the elements silicon, germanium and /

and diamond, the binary compounds gallium arsenide, indium antimonide and silicon carbide, the ternary compounds silver thallium telluride and the organic compound anthracene, with respect not only to their semiconducting properties but to their thermal and mechanical stabilities, and their technological difficulties in preparation, purification and crystal growth. Though each class of compound semiconductors contains a wide range of energy band gaps, each has a characteristic mobility range.

It soon became clear that as well as the Group IV elements, germanium and silicon, the III-V elements had desirable properties and of these gallium arsenide stood out clearly as having the best characteristics for transistor action. The III-V compounds crystallize in the zinc-blende structure which is geometrically identical to the diamond structure of germanium and silicon. The atoms of each component element are contained in their own face-centered cubic sub-lattices. This similarity in lattice structure between gallium arsenide and germanium is significant when comparing them as semiconductors.

One of the best such comparisons is given by Sze and Irvin² who compare resistivity, mobility and impurity levels in gallium arsenide at 300°K.

	Mobility at 300°K $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$			Energy gap between valence and conduction band at 300°K (eV)
	n-type	p-type		
Ge	4.7×10^3	2×10^3	drift mobility	0.67
Si	2×10^3	6×10^6	"	1.12
GaAs	7×10^3	3.8×10^2	Hall mobility	1.43

Table 1

It should be noted, however, that the Hall mobility given tends to be a 'state of the art' figure for material purity. For gallium arsenide the highest reported room temperature mobility of $9,700 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$ has been achieved by Conrad³⁵ in epitaxially grown films with a donor impurity concentration of less than 10^{15} cm^{-3} .

Since the initial comparative work on these semiconductors the electronics industry has progressed considerably, with simple oxide passivation and epitaxial growth of silicon achieving remarkably good planar transistors. Various difficulties of gallium arsenide bipolar transistors, especially doping problems have hindered their development, but other devices are now being made to use the high mobility, wide energy band gaps and low-temperature conductivity of gallium arsenide. These include varactors, Schottky-barrier diodes and high frequency field effect devices.

Since /

Since work started on gallium arsenide a number of new and important bulk effect phenomena have been discovered which have given rise to a whole new and important range of devices, including injection lasers, light emitting diodes, bulk effect microwave power sources, negative resistance amplifiers and bulk effect integrated circuits. Almost all of these devices have been introduced with a view to obtaining higher frequency and higher power equipment. The production of high purity gallium arsenide for use in bulk effect microwave devices was the aim of the work for this report.

The bulk effect phenomena occurs due to the presence of two energy minima, separated by only 0.36 eV, in the conduction band of gallium arsenide. The application of a high external electric field causes electrons in the lower minima, where they have high mobility, to enter the higher minima where their effective mass increases with a corresponding large reduction in mobility. The material, therefore, exhibits the negative resistance proposed by Ridley and Watkins⁴ in 1961. The effect was first shown by Gunn⁵ in 1964 who applied electric fields in excess of $3,000\text{Vcm}^{-1}$ to achieve negative resistance resulting in microwave oscillations.

A high resistivity must be exhibited by the gallium arsenide to obtain sufficiently high electric fields for this effect to occur. Such material may be obtained by having a low impurity carrier concentration or by compensating shallow donors with deep trapping levels. The latter would be unsuitable because of its low mobility /

mobility and thermal instability due to ionisation of the deep levels at elevated temperatures.

Gallium arsenide epitaxy

1.2 Though purification occurs by impurity segregation when bulk crystals of gallium arsenide are grown at the melting point (1238°C), the considerably lower temperatures at which thin single crystals may be formed are potentially capable of permitting higher purity. A number of papers on the production of gallium arsenide suitable for microwave devices has been written. Wolfe⁷ and Tietjen⁸ described the material production for Gunn devices and microwave diodes respectively. Semiconductor devices which operate at microwave frequencies generally have small physical dimensions and the best such devices are now being formed in these thin films.

In this report such a film grown onto and orientated with a single crystal substrate will be referred to as an 'epitaxial' film following common semiconductor terminology although many researchers such as Joyce⁹ prefer the word 'autoepitaxy' when referring to a film on a substrate of the same material.

Electrical properties of the substrate should be such that they either provide low contact resistance to the film or take no part in the electrical operation of the device (depending on its design). Fortunately gallium arsenide displays, as well as a semiconducting nature, a semi-insulating nature, achieved by producing deep acceptor levels near the centre of the band gap which compensate shallow donor levels. Few of these acceptors ionise (to give low mobility holes) at room temperature and thus an /

an excellent substrate material is obtained. The mechanism was first proposed by Allen¹⁰ in 1960 and since then iron, oxygen, chromium, copper and selenium have been found to produce deep trapping levels and in particular chromium which forms a level 0.64 eV from the conduction band, has been shown by Cronin and Haisty¹⁴ to produce good stable semi-insulating gallium arsenide. Hoyt and Haisty¹⁵ have produced such material by means of iron doping. Resistivities at room temperature are at least 10^8 ohms-cm with mobilities between 200 and 2,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. King, Wasse and Sandbank⁶ have assessed such materials and Bailey¹¹ has reviewed key developments in the preparation of group III-V semiconductors with particular emphasis on epitaxial gallium arsenide grown on semi-insulating gallium arsenide substrates.

One important benefit of experimental epitaxial growth of p or n type material on semi-insulating substrates is that many electrical measurements, designed to characterise the epitaxial layer, are simply made and are virtually unaffected by the substrate's presence. The use of these substrates for the isolation of integrated circuits has been shown by Mehal, Haisty and Shaw¹². Manasevit¹³ has used other insulating substrates such as spinel, sapphire, beryllia and thorium oxide though the gallium arsenide grown on them exhibited poor crystalline quality due to the considerable lattice mismatches involved. This report therefore will deal with epitaxial growth of high purity gallium arsenide on a semi-insulating gallium arsenide substrate.

There /

There are a number of important properties and features required of an epitaxial film and of the process by which it is made.

A high degree of crystallinity is necessary since semiconductor crystal imperfections (defects) may act as shallow energy levels or even as trapping centres for charge carriers. Joyce⁹ has suggested that the upper limit in quality achieved by vapour phase gallium arsenide growth is being imposed by defects such as vacancies, di-vacancies and vacancy pairs, rather than by the presence of impurity atoms. Poor crystal structure may also cause fast and uneven diffusion of impurities or their precipitation at the defect boundaries. The measurement of structural quality is usually given as a number of defects per unit area of the crystal surface.

The number of impurity atoms should be as low as possible unless specific dopants are to be added to modify the electrical properties of the material. Group II elements may replace gallium atoms to form acceptor levels in the energy gap and group VI elements may replace arsenic atoms to form donor levels. In addition, group IV elements such as silicon may substitute for either gallium or arsenic. The presence of even small amounts of these impurity atoms has a considerable effect on the electrical conduction of the crystal. Measure of their number is given in parts per million of the semiconductor's atoms or in terms of the electrical effect as charge carrier concentration in number of carriers per unit volume.

Largely /

Largely related to this is the need for material with a specific Hall mobility (given in $\text{cm}^2\text{V}^{-1}\text{S}^{-1}$) and a specific resistivity (ohms-cm). Such control may be achieved by including in the system a means of introducing dopant atoms.

Epitaxial film thickness must also be controllable in the growth process especially for microwave devices in which performance depends on their dimensional accuracy.

For bulk effect devices such as Gunn diodes a high Hall mobility and high resistivity are both required and reproducible control of these properties is an absolute necessity. Though the production of microwave varactors and certain types of ohmic contacts requires doping facilities it was decided to omit them from the basic experimental system as non-essentials.

1.3 Growth Methods for Epitaxial Gallium Arsenide

The wide variety of techniques used in producing gallium arsenide may be divided into two main groups.

Liquid phase method

The first of these is growth from the liquid state. In this method gallium arsenide is dissolved in a molten metal at an elevated temperature (600°C to 900°C) in an atmosphere of argon or hydrogen. A gallium arsenide substrate is immersed in the solution and the temperature slowly reduced. An epitaxial layer forms covered by a tenacious layer of the original metal solvent which must be removed while it is still molten.

For heavily doped abrupt p-n junctions this technique has been /

been used with success by Nelson¹⁶ who employed tin as the metal solvent. Kang and Greene³ used gallium metal as the solvent and by careful choice of reactor materials achieved very high purity layers: $9,500 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$ being obtained for room temperature Hall mobility. Bolger, Franks, Gordon and Whittaker¹⁷ used the same technique for doped layers, with the selenium dopant dissolved in the solvent. The high purity is attributed to segregation of impurities into the melt.

The principal disadvantage of the technique is that control of the process, especially over the thickness of the layer, is poor. For thick epitaxial layers the method is fast and shows definite promise.

Vapour phase method

The second technique, and the one which is the concern of this report, is growth from the vapour phase.

Arsenic, either in its vapour phase or in the form of a volatile compound, and a volatile gallium compound are transported to the surface of the substrate. Chemical reactions, possibly catalyzed by the substrate, cause the formation of gallium arsenide at the substrate.

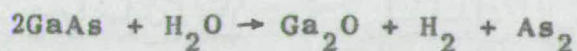
The main problem of the technique is that there are no suitable compounds of gallium which are gaseous at room temperature and pressure and in practice either the oxide or halide is used.

Oxide Transport Methods

Lawley¹⁸ has used the oxide transport method and has tabulated the effects of a variety of growth control parameters.

The /

The films produced showed good crystalline quality but required substrate temperatures of about 1,050°C. These high temperatures led to outdiffusion of the substrate impurities with harmful results on the control of the film's electrical properties. In an earlier paper Gottlieb and Corboy¹⁹ described the reactions in their system based on the chemistry of gallium oxides investigated by Cochran and Foster²⁰. Purified hydrogen containing water vapour is passed over a pure single crystal gallium arsenide source. N-type dopants such as selenium and tellurium may be transferred from source to substrate but silicon and the p-type dopants such as zinc and cadmium are not. The reaction suggested is :-



It occurs at the heated source and is reversed at the substrate which has a slightly lower temperature. So far, this system has not produced epitaxial material with sufficiently good electrical quality, the minimum donor impurity achieved is between 2×10^{15} and $5 \times 10^{15} \text{ cm}^{-3}$ with a corresponding Hall mobility of $7,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. No papers have shown the possibility of oxygen doping of the grown film in this method but it should be remembered that the presence of oxygen in gallium arsenide leads to deep energy levels which cause a decrease in the mobility of the material. Methods using halide transport have been shown to be very sensitive to oxygen causing poor crystal structure.

Halide Vapour Transport Methods

The halide (usually chloride) vapour transport methods have /

have many variations. The gallium is transferred in the system as a halide, obtained either externally by bubbling a transporting gas through gallium trichloride liquid or by reacting a chloride with a gallium source in the reactor. Zuegel²¹ has established the gallium-chlorine and gallium-arsenide-chlorine system thermo-dynamic equilibria and the temperature dependence of the corresponding equilibria constants.

Arsenic, which is volatile at atmospheric pressure at temperatures above 604°C is obtained externally by bubbling a transport gas through liquid arsenic trichloride, or by using a solid source of elemental arsenic within the reactor. In many practical systems more than one of these sources may be used at the same time. Goldsmith and Oshinsky²² and Rubenstein and Myers²³ used purified hydrogen bubbled through heated gallium trichloride which had been purified by the techniques developed by Kern.²⁴ The hydrogen was passed over high purity gallium (prepared to six nines purity by the techniques of Goldsmith, Mayer and Vieland²⁵) in an oven heated reactor containing five nines pure elemental arsenic and the substrates. Undoped layers grown gave carrier concentrations in the low 10^{16} cm^{-3} range. They also reports the growth of 'hillocks' on the surface of the material and attributes this to leakage of oxygen into the system. A leak of 10^{-4} standard cm^3 of air per second reduced the growth rate to zero.

A system using gallium trichloride was decided against in this work for two main reasons. The vapour pressure of gallium trichloride is much lower than that of arsenic trichloride. A gas /

gas saturator together with all the vapour supply lines to the reactor would, therefore, have to be heated to a much greater temperature. This would have added considerable complications. Furthermore, the workers who have employed hydrogen chloride or arsenic trichloride as the source of the available chlorine for reaction with gallium in the reactor have achieved much better results with regard to electrical properties, perhaps because arsenic trichloride is available with higher purity than gallium trichloride.

Tietjen and Amick¹⁸ used hydrogen chloride in a hydrogen carrier gas passed over heated gallium in the reactor. Arsine gas was admitted to the system where it dissociated (to arsenic and hydrogen) the arsenic reacting with the gallium chloride to form epitaxial gallium arsenide on the substrate. Layers with a room temperature Hall mobility of $5,100 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$ were obtained in this manner. Though the method has a number of advantages, such as ease of doping and the production of good tertiary alloy semiconductors, it appears to be limited by the purity of the arsine gas available, the authors having detected the presence of nitrogen, argon, carbon dioxide and oxygen - additional argument against the use of arsine is its extremely high toxicity, toxic level being given as 0.05 parts per million by volume.²⁷

What seems to be the most promising system was pioneered in this country by Effer.²⁸ In this, hydrogen carrier gas is bubbled through arsenic trichloride liquid at about room temperature. These /

These enter the reactor where the high temperature (more than 600°C) causes the reduction of the arsenic trichloride by hydrogen to hydrogen chloride and arsenic. The arsenic vapour is completely absorbed by the gallium source until saturation occurs at 2.25% arsenic (Hall²⁹). When the melt becomes saturated a skin of gallium arsenide forms over the surface with the possibility of beneficial impurity segregation. At this stage free arsenic may condense beyond the gallium source. The substrates are then inserted into the furnace and epitaxial growth begins. Effer achieved pure gallium arsenide with a mobility of $8,000 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. Many other workers have used this technique with variations such as further addition of hydrogen chloride from an external source and the introduction of elemental arsenic in bulk form. Eddolls, Knight and Wilson³⁰ used Effer's method to produce pure material for bulk effect devices. Good control over layer thickness was obtained but with inadequate control of electrical properties. They also investigated sources of impurity within the system and concluded that further attention should be paid to the purity of reagents and substrates. They used five nines pure arsenic trichloride, six nines pure gallium and palladium diffused hydrogen. Shaw^{31,32} extended considerably the knowledge of this system by intensive investigation of the effect of different temperatures within the furnace (especially the substrate temperature) and the effects of different substrate orientations. He showed the effects of outdiffusion of a doped (low resistivity) substrate on the impurity profile /

profile of the grown layer and showed that the electrical properties appear to be a function of the gallium to arsenic ratio in the vapour phase and not the absolute concentration values.

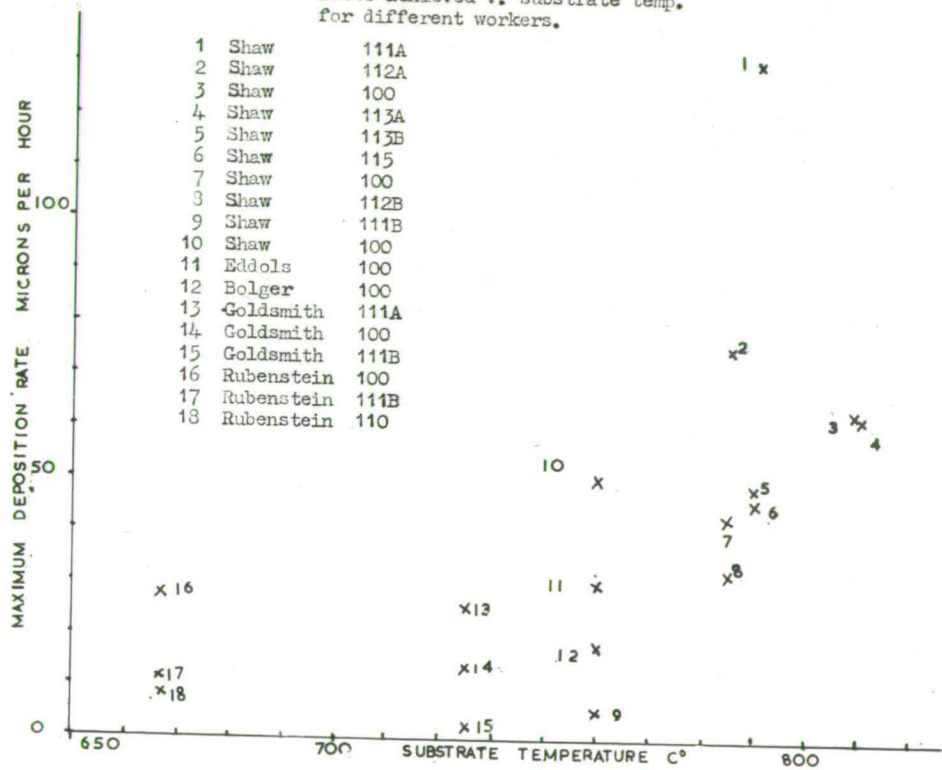
1.4 Comparison of Reported Growth Results

There is a wide variation of reported results from the different workers. It was thought worthwhile to compare the different experimental results with respect to the effects of substrate orientations, flow rates and temperatures, on growth rates. The work of Shaw^{31,32}, Bolger¹⁷, Eddols³⁰, Goldsmith and Oshinsky²² and Rubenstein and Myers²³ is compared here in table 2 and Fig. 1.

Of particular note is that in Shaw's system there is a great difference between the A and B 111 faces whereas Rubenstein and Myers found both orientations to give about the same growth rates. Bolger and Eddols use basically the same system with similar results. The following table indicates some of the different systems and conditions used.

	Source of Ga	Temp.	Source of As	Flow rates Lit/min.	Concentrations (atmospheres)
Shaw	Ga metal	875°C	As metal	0.383	PoGaCl 7.9 x 10 ⁻³ PoAs ₄ 3.7 x 10 ⁻³
Eddols	Ga metal	800°C	AsCl ₃	0.05	PoAsCl ₃ 10 x 10 ³
Goldsmith & Oshinsky	Ga metal & GaCl ₃	750°C	As metal 425°C	0.550	PoGaCl ₃ 2 x 10 ⁻³
Bolger et al	Ga metal charged with As	800°C	AsCl ₃	0.25	PoAsCl ₃ 6.6 x 10 ⁻³
Rubenstein & Myers	GaCl ₃		As metal 450°C	0.2	PoAs ₄ 1.5 x 10 ⁻³ PoGaCl ₃ 5.54 x 10 ⁻³

fig. 1 A comparison of maximum deposition rates achieved v. substrate temp. for different workers.



Shaw also showed that different gallium to arsenic ratios in the vapour phase had a considerable influence on the Hall mobility of the grown layer as well as on the growth rate.

Moest³³ also showed that substrate impurity concentration affects the impurity profile of the epitaxial film. Williams³⁴ investigated the effects of structural defects in epitaxial gallium arsenide grown by halide transport, showing how they varied with various substrate orientations and different growth conditions. He found the surprising result that dislocation density of the epitaxial layer was about half that of the substrate. Very high purity layers were produced by Conrad³⁵ using this method. He achieved room temperature Hall mobilities of $9,700 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$.

1.5 Reactor Impurities

Since the most significant feature of any one epitaxial reactor is its ability to produce pure epitaxial layers, it is important to look for the possible sources of impurity, to identify the impurities and if possible to eliminate them. Eddols³⁰ found evidence to suggest an acceptor impurity, perhaps copper, was diffused from some substrates but did not agree that, as Edmond³⁶ found, there was copper diffusion from the quartzware. Most of the published work on epitaxial gallium arsenide does not identify the impurity or impurities present in 'undoped' layers. Ekstrom and Weisberg³⁷ showed the main contaminants in bulk single crystal gallium arsenide to be silicon, copper and to a much lesser extent magnesium. Gansauge and Hoffmeister³⁸ made radiotracer measurements of copper contamination in gallium arsenide originating from quartz /

quartz. Silicon contamination originating from quartz was shown by Stearns and McNeely³⁹. They examined the effects on gallium arsenide of silica and boron nitride boats and indicate the impurity electron concentration and actual silicon concentration by emission spectroscopy. The amphoteric nature of silicon in gallium arsenide has been shown by Spitzer and Allerd⁴⁰ who investigated its distribution between the lattice sites.

Taylor⁴¹ shows that it is possible to use argon as the carrier gas instead of hydrogen in the arsenic trichloride and gallium system and suggests that this may reduce the likelihood of silicon contamination of gallium arsenide caused by possible hydrogen reduction of quartz. Other reasons for the use of argon include the minimisation of density differential between the carrier and the reacting species and the elimination of at least one reaction in the system. He compares the argon and hydrogen systems and shows that he obtained similar electrical properties in layers produced with both carrier gases. It was also found that maximum growth rates occurred at temperatures some 50°C lower than in the hydrogen carrier system. Taylor concludes that, should a very high purity reactor be built, the argon system may potentially give better material. One important disadvantage is the difficulty with which argon is prepared at high purities.

1.6 Other Growth Methods

At this point it is worth briefly looking at the other forms of epitaxial gallium arsenide growth which have been tried. A hybrid /

hybrid of the above mentioned techniques consists of depositing a layer of metal on the substrate. This metal acts as a 'solvent' for gallium; the arsenic is transported to the surface in a normal vapour phase reactor. Crystal growth occurs by nucleation from the substrate surface when the solvent has become saturated with the constituents. Barns and Ellis⁴² used this technique to produce long 'whisker' crystals from the substrate by employing gold, gallium, platinum and palladium as solvents. The resulting needles had a very high degree of crystal perfection and, though purity was not investigated, could have uses in some devices where 'bulk material' of very small dimensions is required.

Light, Hall and Gareth⁴³ have used a flash evaporation technique for growing thick semi-insulating gallium arsenide films. They produced a 40 micron thick chromium doped film by flash evaporating a mixture of chromium doped gallium arsenide powder together with excess arsenic. The degree of crystal perfection and growth control was low with this technique and it was not considered as suitable at this stage for microwave devices.

No sealed tube reactors have been reported in the available literature, probably because of the difficulties of gallium transport.

1.7 Design of a Reactor

With all the above evidence in mind it was decided to construct a vapour phase flow system using hydrogen gas saturated with arsenic trichloride. An arsenic saturated gallium source would be situated in the reactor and as far as possible all sources of impurities would be reduced or eliminated.

1.8 /

1.8 Epitaxial Film Evaluation

An essential part of the work on materials preparation is the assessment and evaluation of materials produced. As has been shown already crystal perfection, film thickness, resistivity, Hall mobility and carrier concentration all need careful control and hence there must be a means of measuring these.

1.9 Evaluation of crystallinity

X-ray diffraction and electron beam diffraction are both widely used techniques in demonstrating crystalline perfection. The necessary specimen thinning for these studies has been demonstrated by Biedermann and Brack.⁴⁴ In addition to these techniques there are the methods which display crystal defects by means of special selective chemical etches. These are often applied to assess the substrate prior to growth with particular emphasis on the depth and extent of damage caused by substrate preparation. Williams³⁴ showed the use of different selective etch solutions on different crystal orientations.

1.10 Determination of Film Thickness

The most commonly employed technique of film thickness measurement is to bevel-lap and polish the substrate and then to etch or 'decorate' the bevel. Usually there are widely differing doping levels between film and substrate and the position of the interface may be seen and measured by optical microscopy. Infra-red spectrometry, as employed by Hilton and Jones⁴⁵ makes use of the difference in reflectance levels to give an indication of thickness. Capacitance versus voltage measurements of reverse biased /

biased Schottky barrier diodes may also indicate film thickness by examination of the way in which the depletion region spreads. Here too the measurement depends on a discontinuity of doping levels in the material.

All these methods show only the 'electrical' thickness of the layer and, due to diffusion of doping impurities during the growth process, this value may not indicate the actual physical thickness of the layer. Neither would they show the depth if there was a similar doping level in both the layer and the substrate. For normal device production, however, ^{only} the electrical film thickness ~~only~~ is important and there usually exists a wide doping level difference. In the case of materials study where the actual growth rate is required there is only one reliable guide to actual film thickness. This has so far been used only in silicon epitaxy but may well have its parallel in gallium arsenide work.

Most stacking faults that appear on the surface of the grown layer have their origin at the substrate/film interface. Merely measurement of the surface dimensions of these faults, whose geometry is predictable, gives the exact position of the true interface. Other actual thickness measurement techniques include mechanical weighing and the direct mechanical measurement of the new thickness after prolonged runs.

1.11 Resistivity Measurement

Direct measurement of the resistivity of gallium arsenide is usually carried out by the methods of Van der Pauw⁴⁶ in which a disc of arbitrary shape with four contacts alloyed (but not necessarily /

necessarily ohmic) to the/perimeter is used. It cannot be employed, however, where substrates of the same conductivity type as the epitaxial layer are utilised and in this case pilot substrates must be used. The 'four point probe' technique is not normally used because of very high reverse resistance of gallium arsenide to point contact junctions. The reverse bias characteristics of a point contact diode at breakdown are, however, employed in a three point probe technique described by Norwood.⁴⁷ The analysis of the point contact diode at reverse bias breakdown is not yet fully understood and the resistivity given by this method must be calibrated by some other means. It has a considerable advantage over the Van der Pauw method in that it is virtually non-destructive and the evaluation of the epitaxial layers is unaffected by the substrate's presence.

1.12 Hall Mobility Measurement

Hall mobility may also be obtained from Van der Pauw's method, and this appears to be the technique most used by workers on gallium arsenide. The more usual Hall bar method employed for Hall mobility measurement in other semiconductors is unsuitable due to poor contact found between gallium arsenide and 'mechanical' contacts.

1.13 Carrier Concentration Measurement

Carrier concentration measurement is usually achieved by measuring the relationship between capacitance and applied voltage in a reverse biased Schottky diode. A typical apparatus has been described by Schlickman.⁴⁸ The limitations imposed by this system on accuracy of carrier concentration determination in gallium arsenide /

arsenide Schottky diodes are indicated by Smith.⁴⁹ There are also problems in the formation of suitable ohmic contacts when the substrate is semi-insulating material. Fortunately the interdependence of resistivity, carrier concentration and Hall mobility permit non-direct measurement of at least one of these parameters.

1.14 Ohmic Contacts

Closely connected with some of the above measurements is the need for good ohmic contacts. Microwave devices such as the Gunn oscillator are also dependent on the ability to produce good ohmic contacts. Though such contacts are achieved without great difficulty on the lower resistivity samples of gallium arsenide (such as the evaporated silver contact described by Schmidt⁵⁰) there are considerable problems when high resistivity material is involved. Since Gunn diodes require such material there has been extensive recent research into this problem. Salow and Grobe⁵¹ have shown that although pure tin contacts are free from mechanical stress they have low thermal stability. Gold/germanium eutectic contacts give non-uniform interfaces and so these workers used a 1:1 alloy of tin and gold/germanium eutectic to give good ohmic contacts for their Gunn oscillators.

An increasing amount of interest is being centred on the system where an epitaxial layer of low resistivity gallium arsenide is deposited onto the high resistivity material in the ^{intended} contact area before applying the metal contact.

1.15 Substrate Preparation

Another very important feature of epitaxial growth work

is in the preparation of the substrate prior to growth. Epitaxial growth requires a substrate surface of high crystalline perfection. The normal sawing and lapping of crystal ingots leaves considerable depth of damage and this must be removed to achieve ordered growth. Jones and Hilton⁵² have used infra-red techniques to demonstrate that mechanical polishing leaves damage below the surface of gallium arsenide to a depth of at least that of the polishing particle size.

Chemical polishing etch techniques are therefore employed to remove this damage. There has been a variety of chemical polishing etchants used on gallium arsenide. Reisman and Rohr⁵³ have achieved a polish on all crystalline orientations of gallium arsenide with a solution of sodium hypochlorite as a source of available chlorine. They used an apparatus where the etchant was fed onto a rotating polishing cloth against which was held the substrate. Sullivan and Kolb⁵⁴ used a similar polishing machine with dissolved bromine in methanol as the etchant. They obtained high quality polishes on all faces especially when high pressures were applied between the substrate and the cloth.

Other etch solutions for polishing have been tried. Lowen⁵⁵ used sulphuric acid, hydrogen fluoride, hydrogen peroxide and water which gave polishing on all but the 111A faces. Packard⁵⁶ described the features required of a polishing etch solution for gallium arsenide; oxidative properties, high solubility and high viscosity. On this basis he suggested a mixture of hydrochloric /

hydrochloric acid, nitric acid, glycerol and glycol, but did not make clear the effects on the 111A face, generally considered as the most difficult to polish. Both Lowen and Packard's etches were used without polishing pads.

Chapter 2

Design of the Apparatus.2.1 Reactor design

As stated in the introduction, the aim of this work was to produce high purity epitaxial gallium arsenide by the vapour phase transport of arsenic and gallium chloride. Bearing in mind the evidence showing contamination of gallium arsenide from quartz boats, especially contamination by the inherent silicon, it was reasoned that further purity could be gained in the reactor by the omission of heated quartz walls. Any possibility of the hydrogen reduction of quartz, such as suggested by Taylor,⁴¹ would thus be eliminated. As a transparent, thermally stable and easily workable material quartz is very useful in reactor construction. It was, therefore, decided to use quartz, but to keep its temperature down to a few tens of degrees centigrade.

A number of ways of achieving the required high temperatures, for transport and deposition reactions to take place, was considered. These included the use of an r.f. furnace and graphite susceptor, infra-red radiation heating using the materials themselves as susceptors, and resistance strip heating.

The r.f. generator technique looked very attractive; temperature can be controlled accurately and there is great simplicity within the reactor. It was decided against, however, since two independently controllable heaters would be required which would involve considerable expense.

The /

The infra-red technique has been used in epitaxy by Gottlieb and Corboy¹⁹ and is marked by simplicity, cheapness and the possibility of purity. Unfortunately gallium arsenide is fairly transparent to infra-red radiation and gallium is highly reflecting so neither would act as good susceptors. There are considerable problems in the arrangement of optical systems to transmit power to any appreciably sized body, especially through cooled quartz walls.

The resistance strip heating method has been used in the simpler silicon epitaxy growth reactor with some success. In this system a strip of material such as graphite is clamped between two cooled conductors and a large electrical current is passed through it. The power source for this is several orders of magnitude cheaper than an r.f. furnace, is easily controlled and brings no additional high temperature contaminants into the system. For these reasons the strip heating system was chosen.

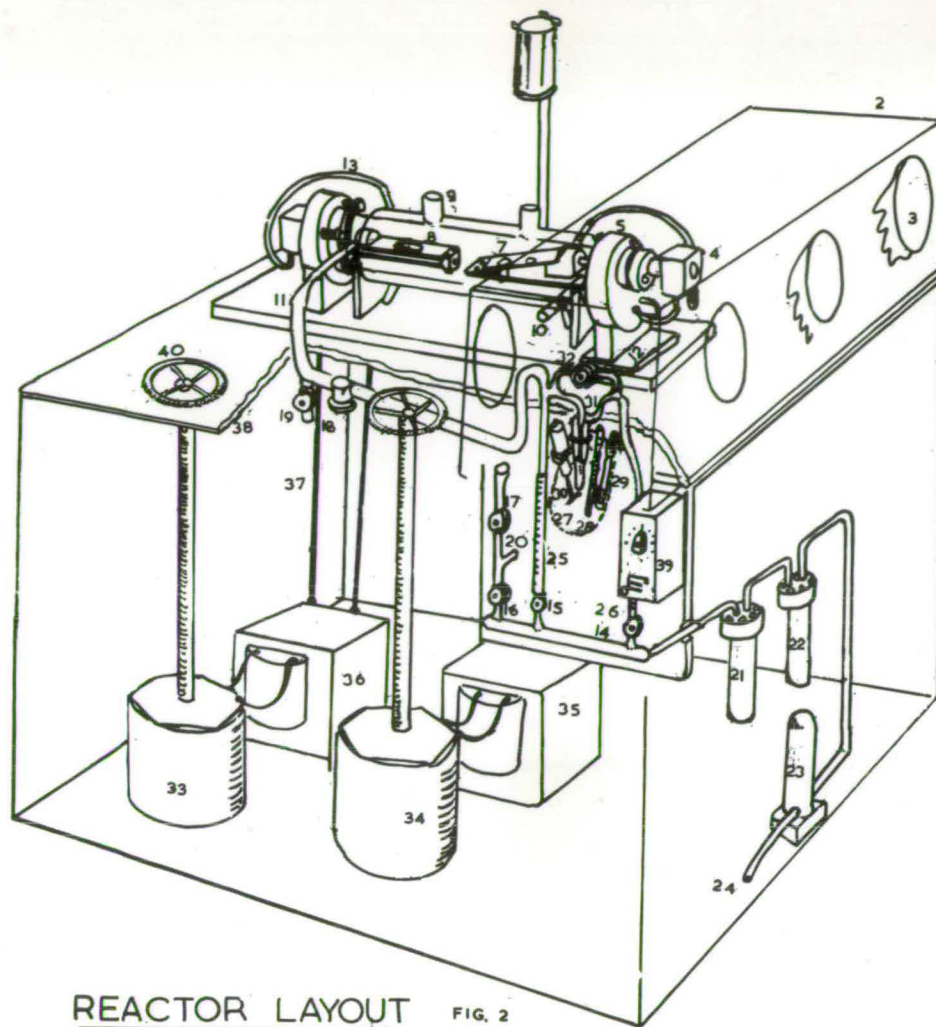
To reduce the possibility of even the smallest gas leaks into the system it was decided to make all possible gas line joints by fusing glass to glass. For necessary wall cooling a water jacket was provided with two small optical windows, at some distance from the centre of the tube, to enable temperature measurement and unrestricted observation of the high temperature regions. Two inlet and two outlet pipes for the cooling water were added to the water jacket. Access to the inside of the tube for the materials and the electrical conductors was provided by leaving both ends open. /

open. Water cooled end-pieces and heater supports (Fig. 2,3) were constructed with provision for clamping to the standard 2 inch B.S. buttress ends of the reactor. An inlet and an exhaust pipe were added, the inlet pipe being directed with its orifice pointing towards the end of the reactor. It was hoped that this would give a more turbulent flow down the reactor tube thus aiding an even distribution of the reactants in the vapour phase. The entire reactor tube, together with optical windows, water jacket, buttress ends and access tubing was made of quartz by Wesley Coe Ltd. of Cambridge.

2.2 Heater design

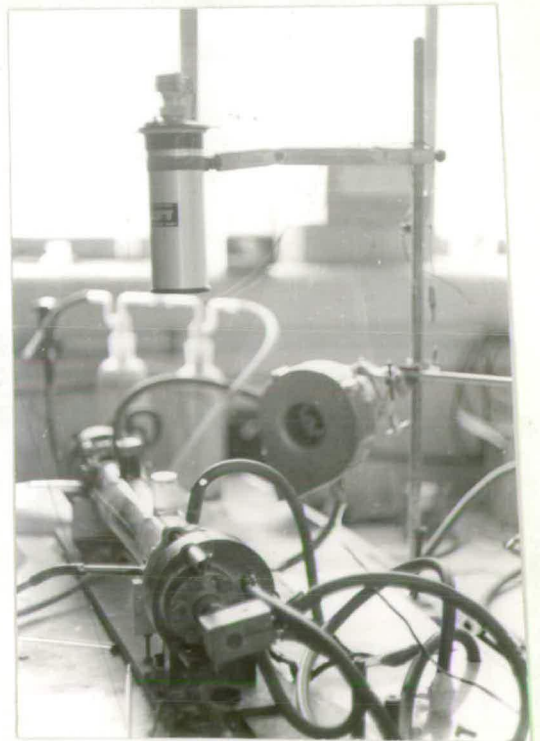
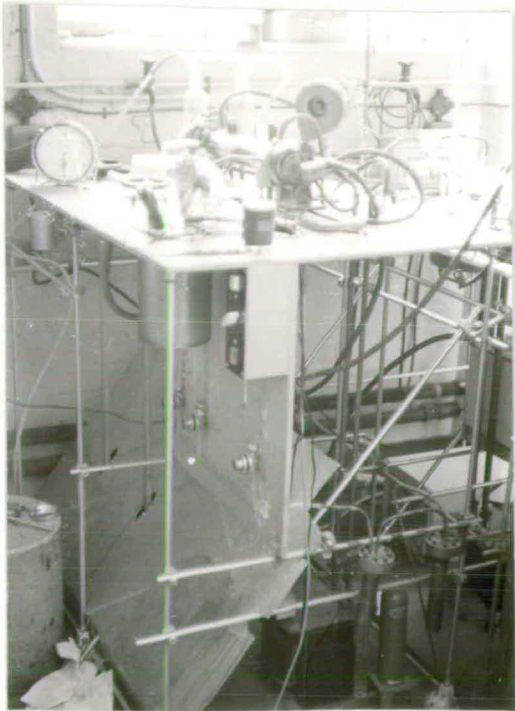
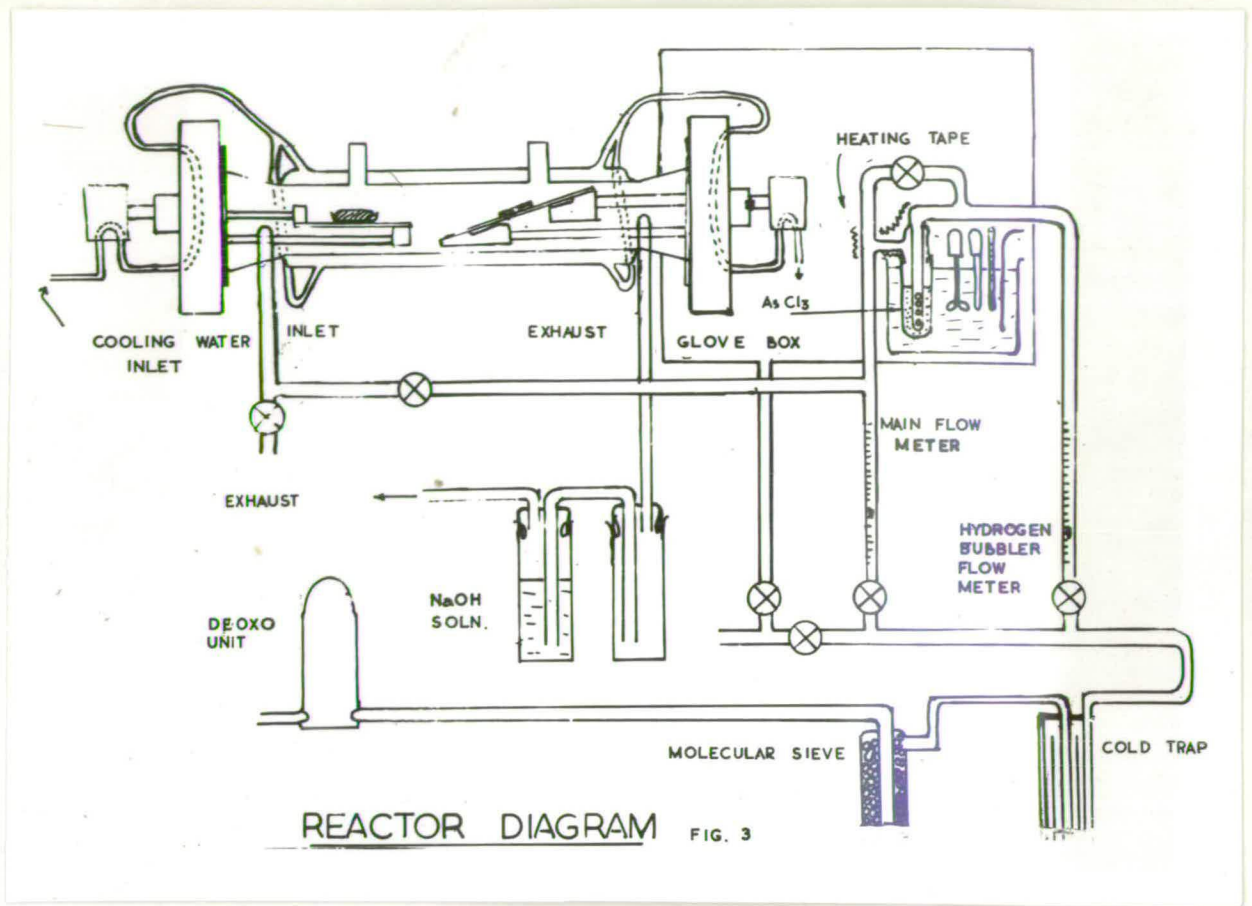
Careful consideration was given to the choice of the heater material. It would be of no advantage if, in removing the possible contaminating presence of high temperature quartz, a worse source of impurity in the form of poor strip heater material was added. Fortunately, high density graphite, with an ash content less than 5 parts per million (le Carbone (Great Britain) Ltd., type PT 586F8) was available. This material may be further purified for use in the reactor by baking in bromine vapour so that all impurities with volatile halides are removed. Heaters capable of dissipating up to about 4 kilowatts had been found to achieve temperatures of more than 1,000°C in the similar silicon reactor.

Four /



REACTOR LAYOUT FIG. 2

- | | |
|--|---|
| 1. Land pyrometer | 21. Cold trap |
| 2. Glove box | 22. Molecular sieve |
| 3. Glove port | 23. Platinum catalyst tower |
| 4. Water cooled electrode block | 24. Hydrogen inlet |
| 5. Brass end piece | 25. Hydrogen main flow meter |
| 6. Electrode | 26. Hydrogen bubbler flow meter |
| 7. Substrate heater | 27. Controlled temperature bath |
| 8. Gallium heater | 28. Thermometer |
| 9. Optical window | 29. Immersion heater |
| 10. Exhaust pipe (to Dreschel bottles) | 30. Stirrer |
| 11. Pyrex / quartz seal (to inlet) | 31. Bubbler |
| 12. Loading trolley | 32. Bubbler bypass tap |
| 13. Water cooling pipes | 33. Source heater Variac |
| 14. Hydrogen bubbler tap | 34. Substrate heater Variac |
| 15. Hydrogen main flow | 35. Voltage reduction transformer |
| 16. Argon inlet tap | 36. Voltage reduction transformer |
| 17. Glove box flushing tap | 37. Copper conductors for heater supply |
| 18. Reactor isolation tap | 38. Diagrammatic cuttaway |
| 19. Vacuum connection tap | 39. Temperature controller |
| 20. Argon inlet pipe | 40. Variac control handle |



Reactor Apparatus Fig.4

Four hundred amp, ten volt output transformers were available at short notice from Messrs. Savage, Transformers Ltd. with control being supplied by Variacs. This system was designed with the possibility of adding electronic control by thyristors should the need arise. Two heaters were required since individual control of the gallium source temperature and the substrate temperature was needed. Temperatures up to $1,000^{\circ}\text{C}$ have been reported for the gallium source with temperatures up to 850°C for the substrate heater (during etching). Inch wide strip heaters, 0.06 inch thick and of convenient length were designed to give a resistance of about 0.03 ohms.

The substrate heater was given a slope since there was some evidence of uneven layer growth (that is, tapering from the source end) in the silicon system. The amount of tilt was dictated by the mechanical limitations imposed by a practical layout. To ensure that the substrate would remain in position on the heater 0.005 inch deep recesses were milled into the surface. Since the end blocks of the heater could achieve high temperatures they too were constructed of the high density graphite as were the clamping screws. Molybdenum rods were chosen as the conductors since they provide very good conduction at high temperatures, they are relatively unaffected by the hydrogen chloride gas even at elevated temperatures, and molybdenum atoms do not readily act as electrically active impurities in the gallium arsenide crystal lattice. These conductors were water cooled at their ends to prevent their reaching very high temperatures whilst conducting heat energy away from the graphite heaters.

The water cooled reactor ends were constructed of brass since their temperature was to be kept down to room temperature or below. For ease of construction both ends were made identically.

A ceramic insulated copper 'lead through' (Ferranti Ltd.) was welded to a stainless steel flange and the flange clamped to the brass end-piece. To ensure that this joint was gas tight a piece of 0.020 inch diameter gold wire was welded into an 'O' ring and compressed between flange and end-piece until it provided only 0.005 inch separation. This provided the conductor for each heater with the brass end-piece forming the other conductor. The molybdenum rods were screw cut at the ends and tapped into the brass and copper of the lead through. To the external end of the lead through was clamped a water cooled copper block. Double sided p.t.f.e. gaskets with compressible composition separators acted as gaskets between the ground quartz buttresses and the brass end-pieces. 'Quickfit' cast metal clamps with graphitised composition seatings between clamp and quartz held the reactor tube to the brass ends under considerable pressure.

2.3 Framework

The whole tube was mounted non-rigidly in 'Sindanio' supports on a brass base plate. The end-piece supporting the substrate heater was mounted on a small wheeled trolley to allow smooth movement to and from the reactor tube. This was decided as necessary to ensure that the position of the substrates did not change during their introduction into the reactor. The other end-piece supporting the gallium heater was bolted to a brass block screwed to the base plate since access to this was thought

to be infrequently needed. A frame for the whole apparatus was made from half-inch aluminium rod and clamps sold as 'Kemiframe'. The reactor assembly was mounted on a 'Sindanio' top and the heavy transformers and Variacs were screwed to a thick plywood base on which the whole apparatus was mounted. Extensions to the Variac control handles allowed heater control with direct observation of the heaters. To one side of the assembly was attached a 'Sindanio' panel to which the gas flow meters were attached.

2.4 Flow System

To provide concentration controlled transport by the hydrogen gas stream with the volatile liquid arsenic trichloride it was decided to bubble a small portion of the gas stream through the liquid so as to achieve complete saturation. This would then be diluted with a controlled amount of the main stream of hydrogen. Based on the work of previous researchers a dilution of about 1 part of arsenic trichloride vapour in 100 parts of hydrogen vapour (by volume) would be a suitable 'mean' around which to design the flow system. To achieve a constant degree of saturation of the gas stream it was decided to slightly elevate the temperature (above room temperature) of a gas saturator containing liquid arsenic trichloride. For this purpose a temperature controlled bath was employed consisting of a wide mouthed Dewar flask, a small immersion heater controlled by a 'Griffin' thermostat, a thermometer and a small electrically powered stirrer. The liquid chosen for the bath was glycerol which is not very volatile at /

at moderate temperatures. To achieve an overall concentration of arsenic trichloride of 1 part in 100 of hydrogen it was decided to saturate 1/10 of the hydrogen with arsenic trichloride such that there was 1 part of the chlorine in 10 parts of hydrogen. At atmospheric pressure (760 Torr) the temperature at which arsenic trichloride has a vapour pressure of 76 Torr is 65.0°C. This, therefore, was the temperature chosen for the glycerol bath. To prevent condensation of the chloride in the flow lines up to the point where mixing with the mainstream of hydrogen was to occur an 'Electrothermal' heating tape (designed to give temperatures in excess of 65°C) was wound round them. The heating tape and the stirring motor were powered by means of mains driven transformers. No heating was necessary in points beyond this since condensation of the arsenic trichloride would not occur at 1 part per hundred unless the temperature fell below the vapour pressure at 7.6 Torr (18°C).

Two flow meters were, therefore, needed and so graduated but uncalibrated 'Rotameter' meters were employed. These were accurately calibrated for hydrogen in the laboratory by timing the passage of a soap film (made with dilute Teepol) along a horizontal tube of known volume for a variety of flow rates. 'Springham' greaseless stopcocks were used to control the flow of gases through the system. An inlet, to allow the introduction of argon gas for flushing the reactor when cool, was included and a wide bore tube was also added to the flow system near the reactor to provide a means of evacuation so that leak testing could /

could be carried out. For this a vacuum pump and vacuum gauge were attached, the reactor vessel pumped down (exhaust and flow meters being sealed off) and acetone sprayed over all joints. Any sudden rise of pressure would have indicated a leakage point.

To connect the flow system, which was formed with pyrex glass, to the quartz inlet tube of the reactor a graded glass seal was used. The hydrogen purification consisted of a 'catalytic Deoxo Purifier' which converts any oxygen present to water. This was followed by a copper cylinder containing 13x molecular sieve. A second copper cylinder followed this. It contained a series of nested copper tubes acting as a labyrinth which could be immersed in liquid air to condense any remaining water vapour. Both these copper cylinders were constructed with removable brass covers which were clamped to matching brass ends brazed to the copperwork. As with the reactor end-pieces, a compressed gold wire 'O' ring provided a gas tight seal. For connection from hydrogen cylinder to Deoxo unit to copper vessels, copper tubing was employed. A 'Pyrex' to 'Kovar' glass /metal seal joined the purification system to the gas flow and metering system. No argon purification was thought necessary since fairly high purity argon was available and argon flushing would not be used at high temperature except in cases of emergency.

Exhaust gases from the reactor were passed through two Dreschel bottles and expelled by plastic tubing to a position external to the laboratory and about ten feet above the ground level. /

level. The first Dreschel bottle was connected by its short tube to the exhaust stub on the reactor by a plastic pipe. Its long tube was connected to the long tube of the second bottle which contained concentrated sodium hydroxide solution. This arrangement caused the chemical stripping of any possible arsenous compounds which otherwise could have proved dangerous when discharged to the atmosphere. Any 'sucking back' of the sodium hydroxide solution into the reactor by sudden cooling was prevented by the reversed position of the first bottle.

2.5 Gallium source

Though it was to be a subject of experimentation the initial choice of gallium source crucible material was made between quartz, vitreous carbon, high density graphite and alumina. Quartz was ruled out for the same reasons as were the hot walled reactor systems, that is, the possibility of inherent quartz impurity. Vitreous carbon is very pure and has a high quality surface which could be useful but was at first decided against since no boats were available with suitable dimensions and a flat bottom. This material has high conductivity along the directions of its smooth faces and thus it would allow the molten gallium to 'short out' the heater. High purity graphite was ruled out for the same reason, that is, to get good thermal contact there would be good electrical contact. Alumina of high purity was available in very thin sheets. It would not seem to be an unstable material at high temperatures in the atmosphere likely to exist in the reactor so it was chosen to support the gallium. To prevent the molten gallium from /

from running off the heater a thin wall of high density graphite was laid on the alumina.

2.6 Temperature control

Most reports indicate that very accurate temperature control and measurement are necessary. Such temperatures as would be encountered in the reactor are often measured by platinum/platinum rhodium thermocouples. Unfortunately the hydrogen chloride atmosphere readily attacks platinum and its alloys. Such a thermocouple has been seen to volatilise in a few seconds in a similar environment. The problems of imbedding thermocouples in the heaters include the difficulty of isolating them electrically in such a limited space. Even then, this would only give a measure of heater temperature and not of the actual substrate or gallium source.

For these reasons optical pyrometry was decided on. Two systems were tried and in fact used in conjunction. The most sensitive measure was by means of a Land pyrometer which consists of a semiconductor p n junction where an image of the region whose temperature is to be measured is focused. A digital voltmeter measures the current output of the junction which is connected across a 500 ohm resistor for the purpose. The optical windows on the reactor tube permitted optical access to the heaters. This system was calibrated in a hydrogen atmosphere by means of a platinum/platinum rhodium thermocouple imbedded in a retaining wall of the gallium source 'boat'.

The /

The same calibration system was employed for the second optical measurement device. This consisted of a hot filament pyrometer in which the colour of a heated filament of wire is visually matched with that of the heated body. The current to produce this colour in the filament is monitored by an ammeter calibrated in degrees of temperature. Since this calibration is intended for black body radiators it was necessary to use the thermocouple method. This second pyrometer was used in experiments for approximate temperature settings. For fine adjustments, however, the more rapidly responding and accurate Land pyrometer was used.

Calibrations for surface of heater, gallium surface, crucible surface and surface of substrate were compared. Unfortunately the only measurement of repeatable accuracy was that of the heater surface. The gallium surface changed its reflectivity considerably as it was 'charged' with arsenic prior to growth. Calibration of crucible surface temperature is of some use but its visible area is very restricted by the area of the gallium. The temperature measurement of the gallium source is usually reported as being less critical than that of the substrate. The main problem of measuring the gallium arsenide surface temperature is caused by the use of very small substrate areas. This may be overcome by reducing the viewing area of the pyrometer, but at the expense of sensitivity. It is also important to take into consideration the frequency at which the radiation is received by the cell. Jona and Wendt⁵⁷ reported the effects of different surface finishes /

finishes (on both sides) and angles of view of a gallium arsenide wafer measured at infra-red frequencies where gallium arsenide may become transparent. In both cases (source and substrate) it appears that temperature measurement is best made by looking at the surface of the heaters with calibration to predict the temperature drop between the heater and the heated body.

2.7 Safety Precautions

A large 'Perspex' glove box was constructed to fit over the access end of the reactor and also to enclose the heating bath, and arsenic trichloride bubbler. This served two purposes. Since volatile arsenic compounds are extremely toxic the loading of the arsenic trichloride bubbler could be performed without hazard. The box also served as a clean area when the reactor end was removed. Four arm-length rubber gloves allowed complete freedom of work inside the box and an inlet pipe was attached so that, during substrate loading and unloading, an argon atmosphere could be provided. An airlock for introducing substrates to the box was not added, one glove being partially removed for a very brief period to permit this facility.

A further hazard introduced by such epitaxial reactors is presented by possible explosion during operation. If a tube in part of the flow system had broken whilst the heaters were running in a hydrogen atmosphere there could have been a dangerous hydrogen/air mixture formed. For this reason a face mask was always worn whilst operating the reactor. An additional precaution applied /

applied from time to time was the detection of arsenic or its compounds around the reactor end joints and on surfaces near the equipment. This was done by wiping the surface with a filter paper and detecting any arsenic by the 'Gutzeit' test. In this test arsenic-free zinc was dissolved in dilute sulphuric acid to produce nascent hydrogen. The contaminated filter paper was added to the acid and another filter paper, soaked in silver nitrate was held at the mouth of the test tube. The presence of arsenic was indicated by a yellow to black precipitate of silver on this filter paper. The test is very sensitive qualitatively but it was necessary to carry it out in a fume hood because of the formation of arsine gas during the reaction.

2.8 Reactant Materials

The materials necessary for the growth of high purity gallium arsenide must themselves be extremely pure. Hydrogen, obtained from the British Oxygen Co. Ltd. was purified as described above. The laboratory purification of arsenic trichloride is complex, involving fractional distillation technique, so an external source was sought. Koch-Light Laboratories Ltd. supply 99.999% pure arsenic trichloride and 99.999% pure gallium and their materials were therefore used. Semi-insulating substrates with (111) orientation were originally chosen for their availability. These and subsequent substrates were obtained from M.C.P. Electronics Ltd.

Chapter 3

Substrate Preparation3.1 Mechanical polishing

Initial substrate preparation included progressive mechanical lapping and polishing until a mirror finish was achieved. Substrates were attached with dental wax to a stainless steel or alumina block, excess wax being removed with chloroform, and lapped using Centriforce Abrasive BM304. A good surface for working on was found to be a photographic glass plate with the gelatine removed. De-ionised water was employed as the lubricant. Some care was necessary in removing all the waste material produced during lapping since it could prove toxic. Mechanical polishing was effected by using the abrasive as for lapping but supported against a soft surface. Lens tissue was found preferable for this purpose to Selvyt cloth or the emulsion side of photographic paper since it appeared to suffer less from the mechanical action of the very hard substrate edges.

A series of water soluble oil-based diamond polishing compounds was then tried. The coarsest of these, with a grit size of 1 micron, gave a rapid polishing on all the above polishing pads, the oil base acting as a lubricant. Fresh lens tissue, which is supplied in an extremely 'clean' state (that is there are no appreciably abrasive particles present), was found to be the most successful polishing pad when used with the diamond polish. The oil base in the polish acted as an adhesive between the double thickness tissue and a sheet of flat glass and prevented the tissue moving under the polishing action. This operation was repeated using /

using $\frac{1}{2}$ micron diamond polish on a fresh lens tissue followed by a final polish with $\frac{1}{4}$ micron diamond on yet another tissue. The surface produced looked quite smooth under the optical microscope with a 5460 \AA interferometer. It was subsequently found that, for optical smoothness, the 1 micron diamond polish gave as good a surface as did the progressive polish. Absolute cleanliness had to be maintained with all traces of abrasive being removed by washing.

The mechanical lapping and polishing stages must be carried out with great care since gallium arsenide is a very friable and brittle material. There is a constant danger of the edges crumbling due to uneven pressure and fragments may cause extensive damage to the polished surface. For this reason a simple polishing jig was made of stainless steel in which the specimen was waxed to the central plunger and was held square to the polishing surface by the cylindrical assembly. Though it was superseded by a polishing machine it was found very useful for bringing the surfaces of a number of very small specimens into a common plane.

3.2 Chemical polishing

At first a series of immersion polishing etches were attempted on 111 orientated substrates. As expected from the literature the gallium rich face (111 or A face) rapidly formed etch pits but even the arsenic rich face ($\bar{1}\bar{1}\bar{1}$ or B face) attained only an unsatisfactory polish.

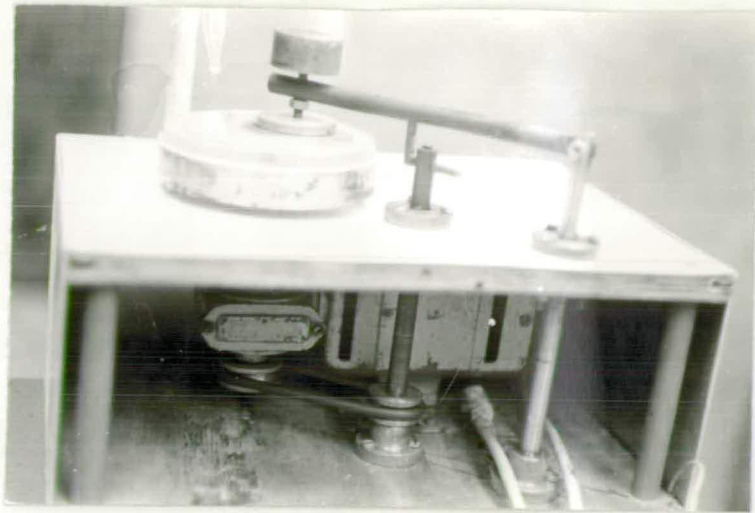
It was therefore decided that if any useful polishing technique was to be achieved a polishing machine should be constructed.

A /

A simple machine was made as shown in Fig. 5. A 'Parvalux' f.h.p. electric motor with a built in reduction gear drove directly a gold plated brass polishing wheel. A sheet of glass plate was bonded to the top of this wheel. A pulley drive was taken from the motor shaft to a shaft bearing an eccentric pin. This pin moved in a slot on the polishing arm and caused it to oscillate. By making the pulleys a slightly different diameter it was ensured that the polishing head and the wheel made a large number of individual cycles before repeating their joint cycle of motion. This allowed even wear of the polishing pad and even distribution of the etch solution. The pads obtained were the 'Hyprocel Pellon' type from Messrs. Engis Ltd. All shafts were made of stainless steel, pulleys and bearings of brass. The polishing top was made of formica topped plywood and an aluminium cover encased the apparatus. A clamp was made to hold a short burette for the etch solutions. The polishing table rotated about 60 r.p.m.

Both sodium hypochlorite and bromine methanol polishes were tried on the polishing machine. Initial tests showed that both achieved reasonable polishes on the $\bar{1}\bar{1}\bar{1}$ face but caused some shallow pitting on the 111 face. Sodium hypochlorite was much faster than the bromine when both were in concentrations recommended by the relevant papers.^{53,54} Because of the volatile nature of the bromine etch a much faster flow onto the surface was necessary. The recommended pressure on the specimen, in excess of 200 gm/cm^{-2} tended to cause very rapid wear of the polishing disc.

It /



Polishing Machine
Fig.5

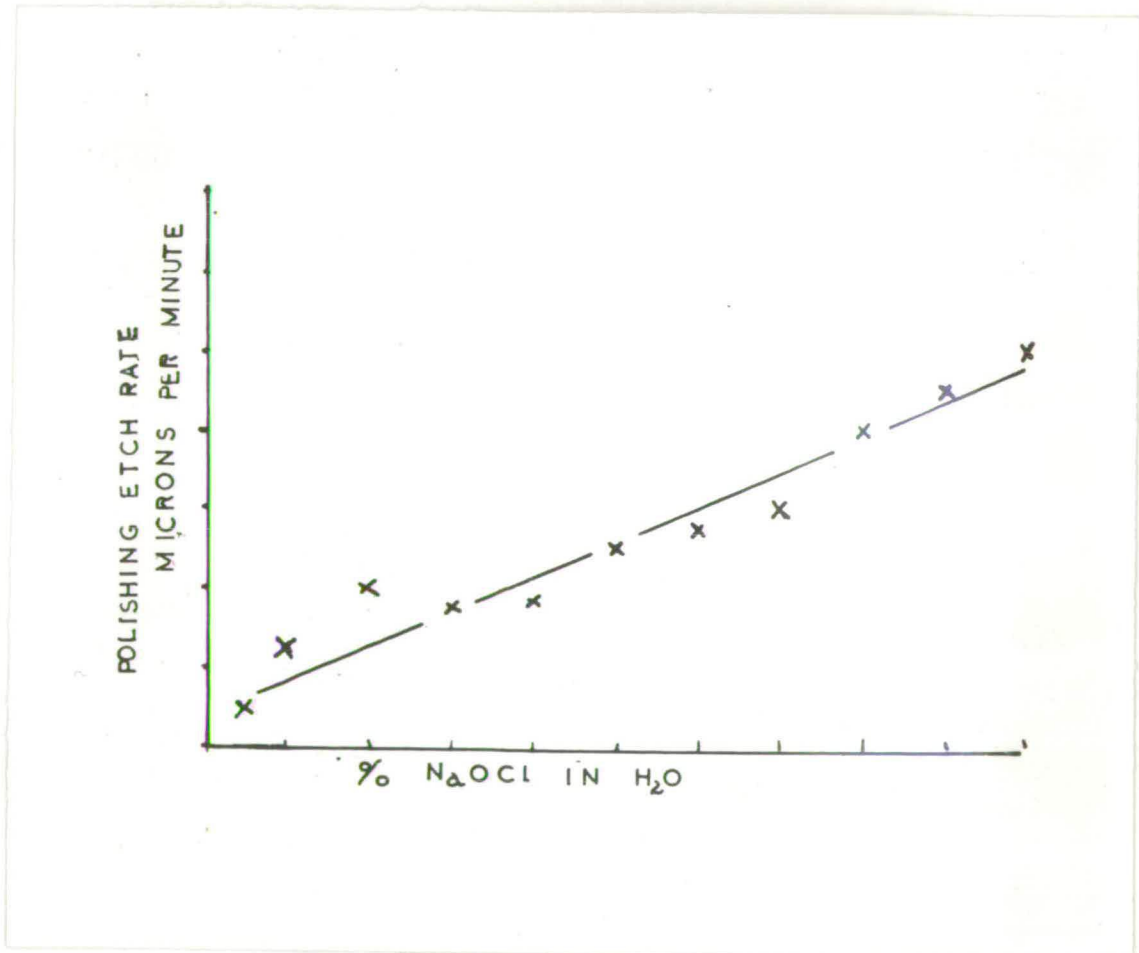


Fig.6

It was therefore decided to concentrate on polishing with the sodium hypochlorite. To find if there was any optimum concentration for polishing (below the concentration of the available solution) polishing rate was plotted against concentration as shown in Fig. 6. In this experiment the sample face was 111 B orientated semi-insulating gallium arsenide. A 50 gm weight was added giving a load of 39.7 gm cm^{-2} . The polishing solution was applied at the rate of $10 \text{ cm}^3 \text{ min}^{-1}$ by allowing a continuous stream of drops to flow over the pad. The thinning of the specimen was measured by micrometer. As the concentration decreased there was an increased tendency for the typical arsenic black stain to appear on the surface. Since there was no significant maximum etch rate the highest concentration was used in subsequent work. The sodium hypochlorite solution available was of nominally 15% available chlorine content. This was, however, analysed by liberating iodine from a potassium iodide solution and then determining the iodide content by a standard thiosulphate titration technique. This showed that the available chlorine content had dropped to about 1% presumably due to long term storage.

Further work on improving the polishing technique showed that it was not necessary to give the substrates an initial mechanical lapping or polishing stage. The specimens arrived as sawn from the boat-grown crystal and it was sufficient to mount these at once on the chemical polisher. Polishing was continued until all exposed scratch marks /

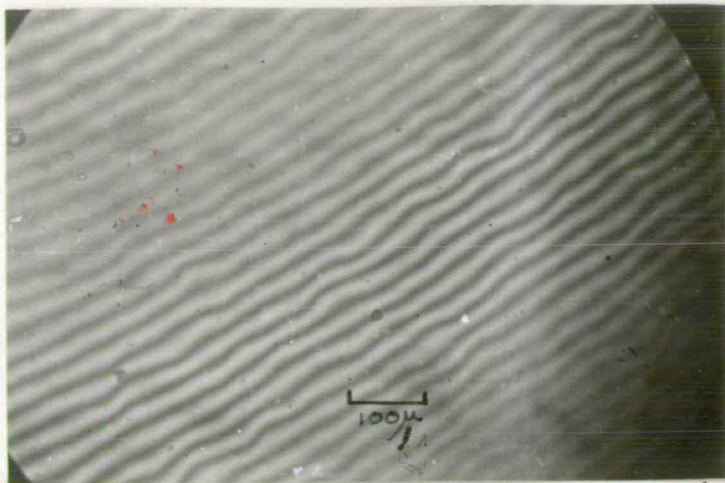
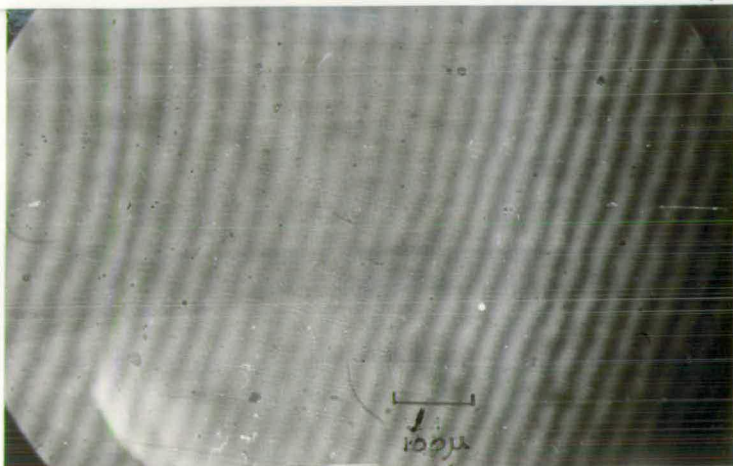
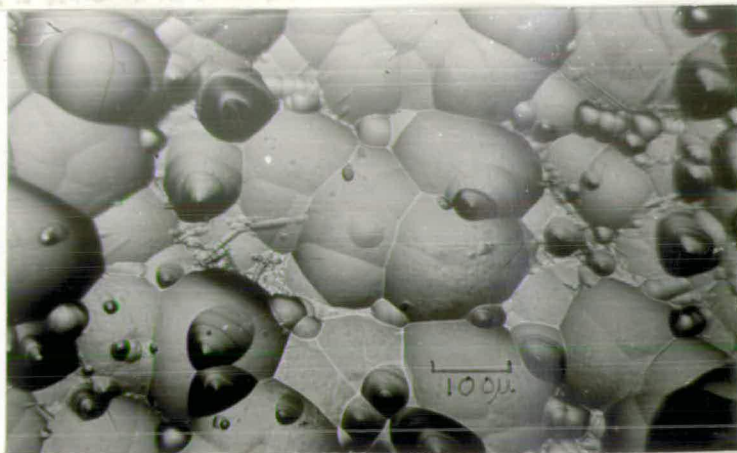


Fig. 6A

Bromine methanol mechanical/chemical polish.
 1 Interference fringe = 2730 Å vertical height.
 GaAs 111B face



Sodium hypochlorite mechanical/chemical polish.
 1 Interference fringe = 2730 Å vertical height.
 GaAs 111B Face



Sodium hypochlorite mechanical/chemical polish
 of GaAs 111A face showing extensive pitting.

marks had disappeared. It was found helpful to filter the polishing solution immediately before use to prevent small crystals from causing occasional fine scratching of the polished surface.

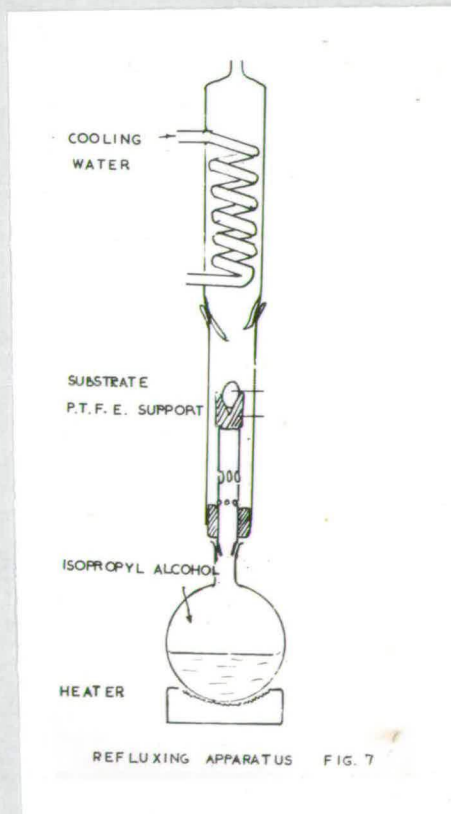
In attempts to polish the 111 A face without further pitting the different concentrations above were tried. Pressure increases were also tried, up to 100 gm cm^{-2} . These did not greatly reduce the pitting formation. Packard⁵⁶ suggests that the increase in polishing solution viscosity limits the etch rate in the surface 'valleys' by slowing the in-diffusion of reactant molecules and the out-diffusion of etch products whilst the high points react quickly with the etch. For this reason a variety of concentrations of glycerol with the sodium hypochlorite solution were tried but none of these improved the quality of the 111 A surface. Gallium arsenide surface orientation of 100 later became available and gave results similar to those for the 111 B face.

3.3 Substrate cleaning

The complete gallium arsenide substrate preparation prior to insertion in the reactor was as follows. The sawn substrate was fixed to a ceramic disc by bonding with 'dental' wax. Excess wax was removed by washing in chloroform. The substrate was chemically polished as described above until a smooth, highly reflecting surface was achieved. It was then washed in de-ionised water. The ceramic disc was warmed to remove the specimen which was again washed in chloroform. It was then rinsed in acetone and washed thoroughly in a stream of de-ionised water. Excess water adhering to the surfaces was blown off with a jet of argon.

Chloroform /

Chloroform was used in preference to trichloroethylene because it appeared to have less non-volatile residue. In later experiments the acetone and water stages were replaced by a simple refluxing apparatus. In this apparatus substrates were washed in a stream of freshly condensed isopropyl alcohol (Fig. 7). Ultrasonic cleaning was not usually employed since it was found that thin specimens of gallium arsenide would occasionally fracture, even when contained in a soft polythene beaker.



Chapter 4

Attempted Growth Experiments4.1 Initial Experiments

Initial experiments were carried out as follows. Ten grammes of gallium metal were placed on the alumina plate with the graphite ring in position. This was loaded into the reactor, so that it could be viewed through the optical window whilst also allowing a line of sight to the graphite heater. In this way the nature of the gallium surface, the temperature of the heater and of the crucible could all be observed. The vial of arsenic trichloride was placed in the glove box. It was opened and the contents transferred to the dismantled gas saturating bottle with a micro-pipette. A p.t.f.e. sleeve was fitted over the cone joint of the bottle which was then assembled and held closed with spring clips. The empty vial and micro-pipette were then sealed in a polythene jar which was transferred to a fume cupboard for future disposal.

The reactor was closed and flushed with high purity argon gas (99.95% pure) at $10 \text{ cm}^3 \text{ S}^{-1}$ for several minutes. The argon was shut off and flow of hydrogen started and run for some minutes with the heaters cold to allow complete flushing of the argon. The gallium heater was then slowly raised in temperature with the cooling water running. Surface tension was seen to form the gallium to an almost spherical mass. When the heater surface reached an optically measured temperature of 900°C the main hydrogen flow rate was adjusted to $10 \text{ cm}^3 \text{ S}^{-1}$. The heating tape on the gas saturator was taken to a temperature of about 70°C , the glycerol bath with stirring motor to 56°C and a hydrogen flow through the arsenic trichloride was set at $1 \text{ cm}^3 \text{ S}^{-1}$. /

$1 \text{ cm}^3 \text{ S}^{-1}$. After a few minutes a black deposit appeared on the reactor walls around the gallium heater. This tended to obscure vision of the gallium metal except through the optical window which remained clear. The system was left running like this for 50 minutes until an arsenic contamination test indicated a slight leak at the gallium heater end of the reactor. It was immediately closed down by bypassing the gas saturator and shutting down the heater supply. The hydrogen gas was left flowing through the reactor to aid the cooling process. The leak was traced to the slackening of the reactor end bolts. It appeared that, as the end of the reactor became warm, the graphitised clamp liner had 'bedded down'. The nuts were further tightened and the reactor end carefully swabbed with a dilute sodium hydroxide solution until the Gutzeit test indicated that all the arsenic had been removed.

The reactor was then run up again as before and left for $2\frac{1}{2}$ hours. At this point the cone joint of the empty Dreschel bottle was forced apart by a build up of gas pressure. Again the reactor was shut down and the trouble traced to the clogging of the sintered glass frit on the inlet tube to the filled Dreschel bottle by a gelatinous precipitate, presumably gallium hydroxide. The glass frit end was therefore removed and further experiments were carried out with the end of the down tube acting as the orifice which introduced the exhaust gas to the sodium hydroxide solution.

By this time the black deposit on the reactor walls had built up into an opaque layer. A view of the gallium metal could only be obtained through the still clear optical window. When at 900°C the surface of the metal appeared to have different temperature regions./

regions. This was thought to be due to the lowering of reflectivity caused by the formation of the sought after 'skin' of gallium arsenic alloy on the surface. Examination showed that a skin had in fact partially covered the surface of the metal.

The system was once again run for one hour as before after which the skin appeared to cover the whole surface. Slight vibrations of the apparatus no longer caused movement of the gallium surface indicating the formation of a solid skin. The reactor was shut down, allowed to cool and then flushed out with argon. The system was then considered ready for the first epitaxial run.

Two small pieces of 111 orientated 1 ohm-cm material (semi-insulating material was not at that time available) were polished on their B faces and cleaned as described in the section on substrate preparation. They were inserted in the reactor, B faces uppermost, one piece lying nearer the gallium/arsenic alloy source than the other. The reactor system was then flushed with argon, the heating tape stirrer and bath immersion heater energised. The hydrogen flow was started, the main flow at $10 \text{ cm}^3 \text{ S}^{-1}$ and the saturator at $1 \text{ cm}^3 \text{ S}^{-1}$. With the intention of producing a surface etch (to remove oxygen atoms and other contaminants) the substrate heater was taken to 850°C and the arsenic trichloride run at 1 per cent (glycerol bath at 65°C) for 5 minutes. The arsenic trichloride was stopped and the heater temperature reduced to 790°C . The gallium heater was then taken up to 890°C and the arsenic trichloride started as before. The reactor was allowed to run like this for 60 minutes before shutting it down. The black deposit had by this time spread around the substrate heater as /

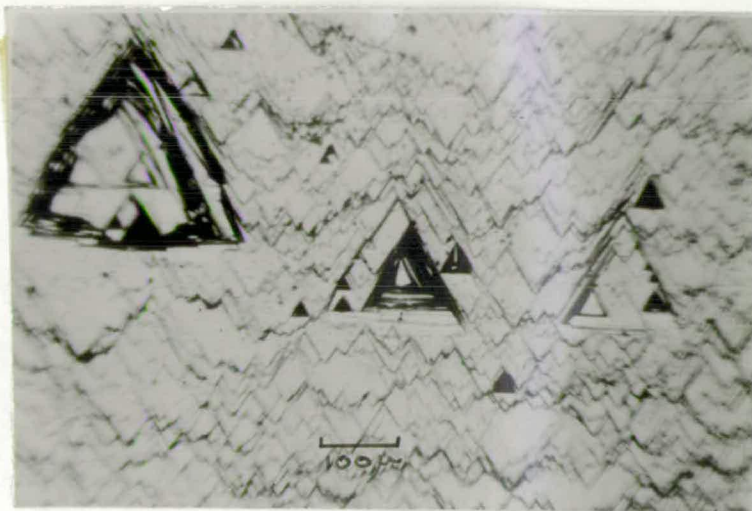
as well but still left the optical windows uncontaminated. After argon flushing the substrates were withdrawn from the reactor and examined under the microscope. The piece which had been nearer the gallium source showed a considerable number of triangular etch pits, and obvious thinning in the neighbourhood of its edges. The other piece showed much less etching, but had a large number of flat bottomed triangular pits together with a series of etched steps across the surface. (Fig. 8). On both pieces there were a number of rounded pits on the A face, especially near the edges, probably indicating the diffusion of vapour phase reactants between substrate and heater.

To find out if the initial intentional etch had caused the heavy etching in this run a small piece of 1 ohm-cm material was chemically polished, weighed and inserted in the reactor. It was given a 5 minute vapour etch with the conditions of the first run and weighed again. There again appeared slight etching on the back surface (111A) and thinning at the edges and an etch rate of 13 micron per minute was measured.

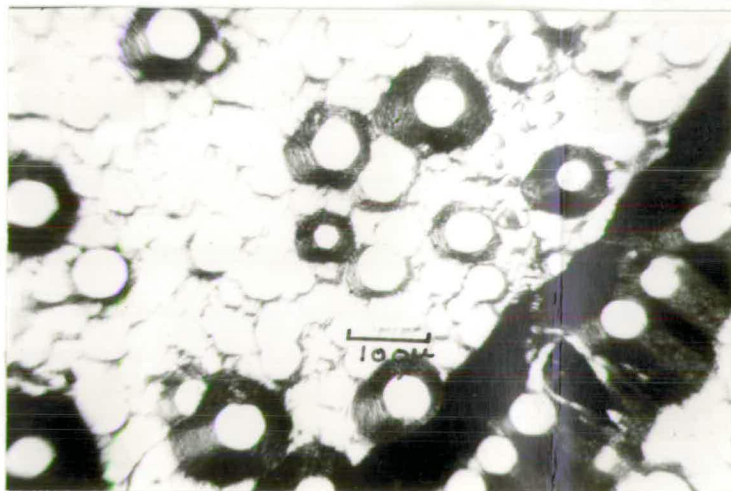
Another epitaxial run was then attempted with conditions as before but with no initial etching and only a 30 minute 'growth' period. Subsequent examination of the substrate by weighing and microscopy showed heavy etching at a rate of 7.8 microns per minute under 'growth' conditions.

4.2 Examination of etching rate to detect the approach of growth conditions

Clearly the heavy etching which had taken place was a result of the reversible deposition reaction proceeding in the 'wrong' direction /



111B Surface after first run, x 100



111A Surface after first run x 100

Fig.8

direction due to incorrect conditions. In order that the correct conditions be achieved it was thought useful to measure the etch rate so that conditions could be brought about which would decrease the etch rate to a 'negative' value thereby achieving growth conditions.

4.3 Systematic Growth runs

It was decided to carry out a series of runs in a systematic manner, in an attempt at correlating beneficial control parameters with growth conditions (or the reduction in etching rate).

In all the following attempted growth experiments the above techniques for flushing the system were used. Etch rates, where indicated, were measured from weight loss assumed to come evenly from the exposed surface only. The reactor walls and windows were cleaned when any deposit appeared on the windows. Since growth was ~~not~~ obviously ^{not} being achieved a quartz boat coated with a thin layer of graphite was used to hold the gallium. (The graphite coating was formed by burnishing a dried layer of 'Aquadag' which had been painted on the surface. The intention was to prevent the gallium from wetting the quartz). It was intended to replace this if growth conditions were achieved and purity was being sought. The following were the principal variables during experiments :

Table 3	<u>Varied from</u>
Substrate temperature	650°C to 850°C
Source temperature	800 to 1,050°C
Substrate position	All positions of the heater
Substrate orientation	111 A and 111 B sapphire
Flow rate	$12\text{cm}^3\text{S}^{-1}$ to $2\text{cm}^3\text{S}^{-1}$
AsCl_3 partial pressure	15 Torr to 0 Torr
Time of run	5 minutes to 1 hour

In /

In no case, however, was obvious growth achieved and in every case some form of etch pit was found on the gallium arsenide substrate. Sapphire substrates were also used and although no highly crystalline deposit was expected, they would have readily shown any form of gallium arsenide which remained on their surfaces. They also had the considerable advantage of not being etched under any of the reactor conditions, thereby saving expensive and valuable semiconductor material. (Crystalline growth of gallium arsenide on sapphire has been achieved by Manasevit¹³ and several others). In all but the earliest experiments the initial etching stage (where the gallium source is not initially heated) was omitted.

After the reactor had been in use for some time two runs were carried out in which a 111B polished gallium arsenide face was heated in a stream of hydrogen only, positioned on the substrate heater. The intention was to see if thermal etching was responsible for any of the weight loss during runs. The temperature was 750°C and both experiments were carried out for 15 minutes. In both cases there appeared a few shallow flat bottomed triangular etch pits though no weight loss could be detected.

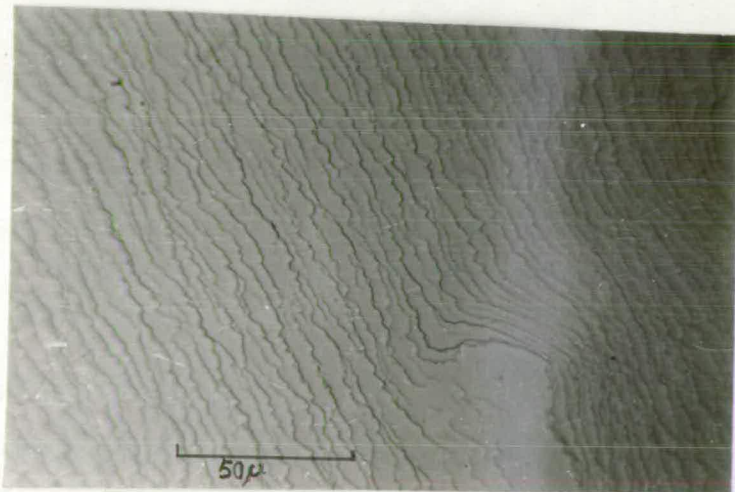
Table 3 indicates the principle growth experiments with the original system. During these the graphite heater for the gallium source broke once and was replaced by a similar bromine purified high density graphite heater. An additional 5 gm gallium metal was added and 're-charged' with arsenic for 2 hours. The arsenic trichloride was replenished once to maintain a sufficient depth within the saturator to allow full saturation.

In /



Fig. 8A

Hydrogen thermal etching x100



Hydrogen thermal etching x450



Typical 'growth' run etching of GaAs III A face showing characteristic triangular pits and steps

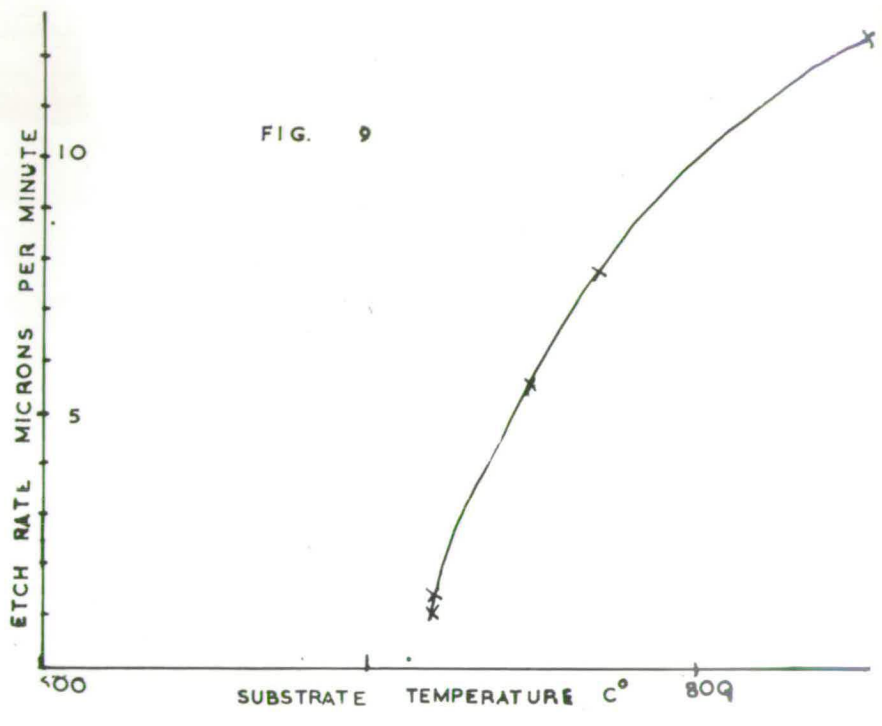
In the indicated cases 'before and after' weight measurements were carried out indicating the approximate etch rate. These, together with the already noted second run and the vapour etch rate experiment were plotted as a function of substrate temperature (Fig. 9). This remarkably smooth curve indicates the close relationship between etch conditions and substrate temperature. Attempts at reducing the temperature below 700°C to see if the curve would 'cross the axis' into growth conditions, proved unsuccessful.

Light etching still occurred, though in an unpredictable manner.

4.4 Modified Runs

To determine if there was any reduction in etch rate caused by better positioning of the substrates in the neighbourhood of the gallium source a piece of alumina plate was laid at one end of the quartz boat in an area which had been previously shown to remain out of contact with the gallium/arsenic source. Two pieces of polished 111 B gallium arsenic were laid on this plate, one some 5 mm nearer the source. The heater was taken to 900°C to allow the substrates to reach about 780°C. A flow rate of $11 \text{ cm}^3 \text{ s}^{-1}$ with arsenic trichloride p.p. 7.6 mm Hg was maintained for 16 minutes. Etch rates were 4.2 microns/minute and 8.0 microns/minute, the piece nearer the gallium ^{having} the slower etch rate.

It was considered at this stage that the arsenic and gallium chloride components of the vapour phase were being 'stripped out' leaving a high percentage of hydrogen chloride. The rapid convection currents /



currents inherent in the system were believed to be causing cooling of vapour by prolonged contact with the cold reactor walls. For this reason a thin sheet of mica was formed into a tunnel (largely out of contact with the reactor walls) covering the gallium source and a polished substrate in a similar arrangement of the system in the previous experiment. This was run for 18 minutes under the above conditions and the resultant substrate displayed an etch rate of 4.6 micron/minute. It was not possible to measure temperatures accurately because the mica sheet rapidly became opaque with the dark deposit. On subsequent examination of the gallium arsenide "skin" there were found a large number of crystalline needles similar to those reported by Barns and Ellis⁴² suggesting a V.L.S. type growth.

In an attempt to locally simulate the usual furnace type of epitaxial reactor a quartz tunnel, made from a 1 cm deep upturned quartz boat with the ends removed, was placed over the source and substrate. The substrate was supported on a piece of graphite 3 mm thick which tended to ~~short circuit~~ parallel with the heater and thus locally reduce the temperature. Again it was not possible to measure temperatures accurately but optical pyrometry showed the strip heater to be about 900°C and the substrate support about 150°C lower. The results of this run again showed that some etching was occurring. The surface of the quartz tunnel bore a dark deposit on whose surface there were a large number of shiny metallic droplets.

4.5 Analysis of reactor deposits

In order that a determination of deposited material could be made, it was decided to carry out some microanalytical chemistry on samples taken from the reactor walls and from the quartz tunnel described /



GaAs 'whiskers' x100

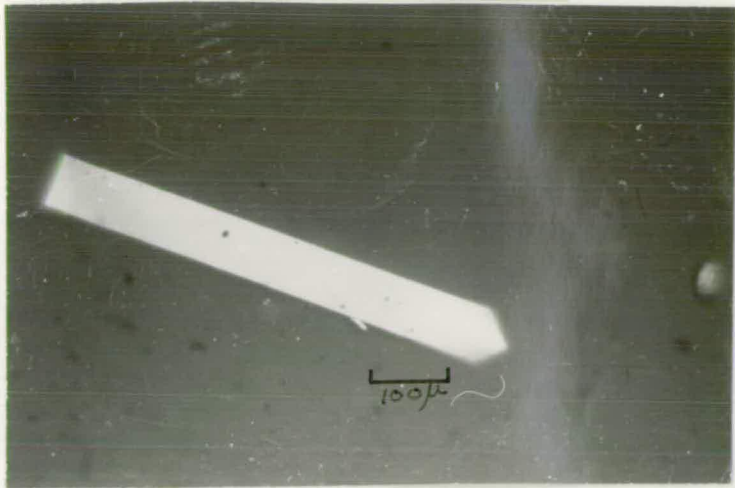
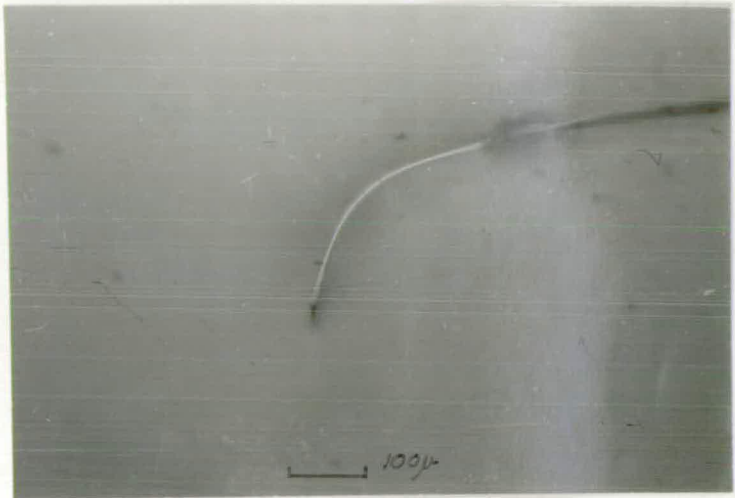
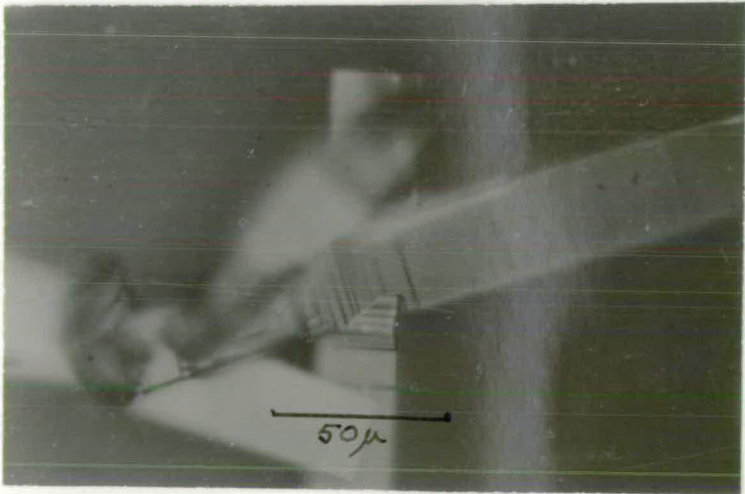


Fig. 9A

Flat whisker



Edge of bent whisker



Interaction of whiskers

described above. The samples were analysed for their arsenic and gallium content by colorimetric determinations of traces of metals described by Sandell⁵⁸.

To carry out these determinations it was necessary to completely dissolve the specimens. They were boiled in concentrated nitric acid and the solution evaporated to dryness. To this was added some 1M ammonia solution causing all gallium to be precipitated as the hydroxide which was extracted by means of a centrifuge, the arsenic remaining in solution. The gallium hydroxide precipitate was dissolved in dilute nitric acid and made up to a noted final volume. Some of this solution was then processed by a modification to Sandell's method in which the gallium hydroxyquinolate, formed by reacting the sample with oxine solution, was extracted with amylacetate instead of chloroform. This produced a yellow colour whose intensity was measured by means of a Perkin Elmer spectrophotometer at 395 millimicrons by comparison with a series of known concentration gallium solutions including a 'blank'.

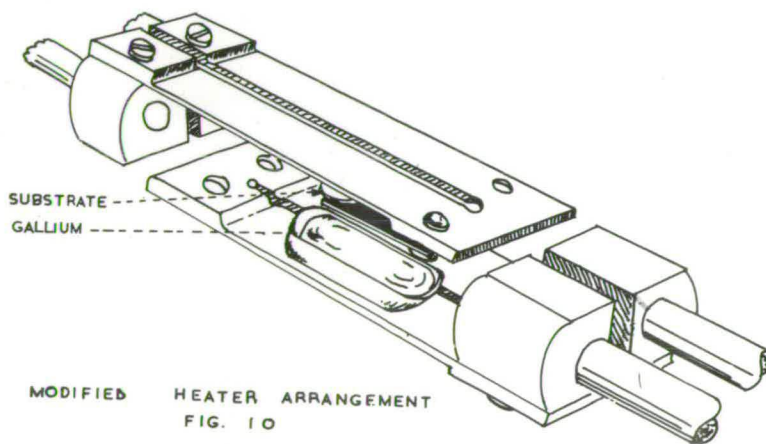
The arsenic solution was evaporated to dryness and the residue dissolved in a known volume of dilute hydrochloric acid. To determine the amount of arsenic a colorimetric technique was again used. An arsenomolybdate complex, formed by reacting the arsenic solution with ammonium molybdate, was reduced with hydrazine sulphate to form a characteristic blue molybdenum colour. This was compared with a number of known arsenic samples in the Perkin Elmer spectrophotometer. Sandell gives the absorbency measurement wavelength for this test as as 830 millimicrons. Unfortunately, the available spectrophotometer measures only to a maximum wavelength of 750 millimicrons resulting in

a loss of sensitivity. The blue colour which is characteristic of this test is not very stable, and when fresh specimens were made their absorbency was plotted immediately. One volume of the wall sample collected contained almost equal quantities of arsenic and gallium, whereas one volume of the sample taken from the quartz tunnel contained more than ten times as much gallium as arsenic.

4.6 Growth runs with re-positioned heaters

With the intention of achieving at least some epitaxial gallium arsenide the reactor tube was extensively modified as shown in Fig. 10. As can be seen the substrate heater is held inverted over the gallium source heater. Both graphite heaters were sawn along most of their length and the current supplied from the split end. The gallium metal was held in a small vitreous carbon crucible whose fairly high electrical resistance (due to its thin base and the nature of the material) did not appear to cause an important drop in temperature between heater and gallium. This arrangement allowed the crucible to sit on just one side of the heater (the hottest side). The substrate was held in contact with the inverted heater by means of a graphite screw and small pyrolitic graphite clip. In this way a very small area of the substrate was masked thus allowing rapid, though not conclusive, diagnosis of the presence of deposited material.

Though both heaters could be seen through one of the optical windows (the lower heater through the slot in the upper) it was found in practice that the window rapidly became obscured with deposited material. For this reason a graph of thermocouple e.m.f. was plotted against measured substrate heater current and this was found quite reproducible. The sheathed thermocouple was clamped by means of the pyrolitic /



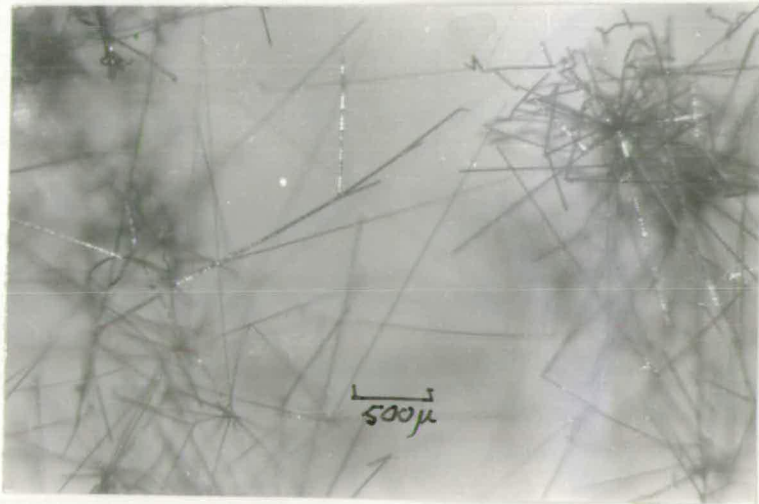
pyrolytic graphite clip, the junction in contact with the surface of the heater. The leads emerged from the reactor through two small holes in a 'Sindanio' spacer clamped between the brass end-piece and the reactor buttress joint. Hydrogen gas flowed through the reactor and curves were plotted for different positions of the gallium source Variac (80%, 90% and 100% of full voltage). This was found to have very significant effect on the substrate temperature, especially at low temperatures. Current was measured by means of a 20:1 current transformer connected to an AVO meter and looped over one of the conductors. The laboratory ambient temperature was measured with another thermocouple in series with the first (both were of platinum/13% platinum rhodium). Thermocouples e.m.f.'s (opposed) were measured with a Solatron digital voltmeter.

Because of the high cost, gallium arsenide was not used as a substrate whilst growth conditions were being sought. Small sapphire substrates, chemically polished in boiling orthophosphoric acid, were chosen at first because any non-transparent deposit could readily be seen. The procedure during each run was as follows: the system was flushed with hydrogen for 10 minutes and then the substrate heater run up to the required temperature; the gallium heater was then taken up to its maximum temperature and the arsenic trichloride flow started. A series of ten runs was done in this manner in which the temperature of the substrate was decreased from 740°C to 450°C. In most cases there was very little or no deposit. The concentration was kept as 1 part arsenic trichloride in 100 parts of hydrogen with a total flow of $11 \text{ cm}^3 \text{ s}^{-1}$. At temperatures around 600°C there appeared a few metallic /



Fig. 10A

Light deposit of GaAs (dark area)
on sapphire substrate $\times 450$



Whiskers grown with modified heater
arrangement $\times 20$

metallic droplets on the sapphire substrate. These were partially covered with a faceted 'skin' suggesting a type of v.l.s. growth. At slightly lower temperatures than this, and also in areas of the heater known to be cooler than the substrate area, there appeared extensive needle growth. Many of these needles were more than 10 mm long after a 30 minute run and most appeared to nucleate from a gallium droplet (either on the heater or trapped within the dense needle lattice). The temperatures at which very thin deposits over the substrate were occasionally seen were noted and germanium was then employed as the substrate.

Germanium was chosen here because epitaxial growth of gallium arsenide has been reported on this substrate. Amick⁵⁹ has described the single crystal growth of gallium arsenide on germanium and Meiran⁶⁰ has analysed the degree of crystallinity obtained by means of reflection x-ray topography. It seems more probable that initial nucleation will take place on the diamond lattice structure of germanium than on the hexagonal lattice of sapphire. Germanium has been seen to etch much less quickly in hydrogen chloride gas than gallium arsenide and so was useful for these exploratory runs.

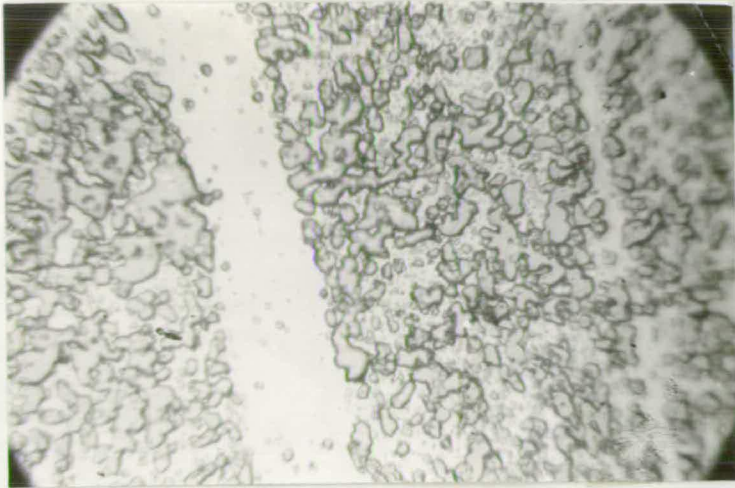
A slice of 111 orientated germanium was divided into a number of small pieces and chemically polished in CP-4 etch solution - nitric acid, hydrofluoric acid, glacial acetic acid and bromine. Again runs were made starting at a substrate temperature of 670°C and decreasing in small steps to 460°C and then back to the 'heaviest' growth conditions at around 560°C. Several runs were carried out with small temperature differences, time variations and flow changes. Some runs were carried out at higher substrate temperature of 760°C.

Film thicknesses were measured by 5° angle lapping (using successive diamond polishing grit down to 1/4 micron) in conjunction with microscope interferometry or by geometrical bevel length measurement. The gallium temperature was the maximum achievable of 900°C. Several layers of gallium arsenide were deposited, the thickest being 40 microns. Other were seen as small faceted plateaus around deposited gallium droplets.

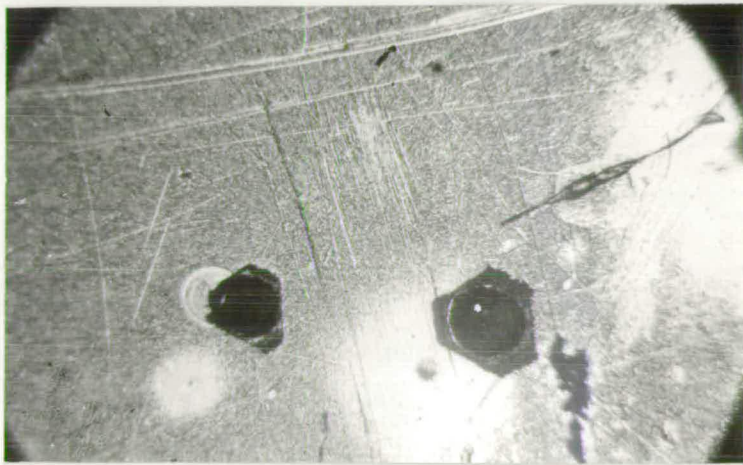
No electron diffraction work was done on the deposited layers. It was expected that epitaxy, had it occurred, would have been detected by noting any aligned defects, such as stacking faults. For this purpose a selective etch, 1:HF, 3:HNO₃, 4:H₂O, 1%AgNO₃ (Williams³⁴) was used.

A few unreproducible layers were deposited in which there were areas of orientated defects indicating aligned single crystal layers, though of poor quality. These occurred at temperatures just below those at which growth decreased to zero. The germanium substrates were then replaced by gallium arsenide and again, on a few occasions, small regions of epitaxy were observed.

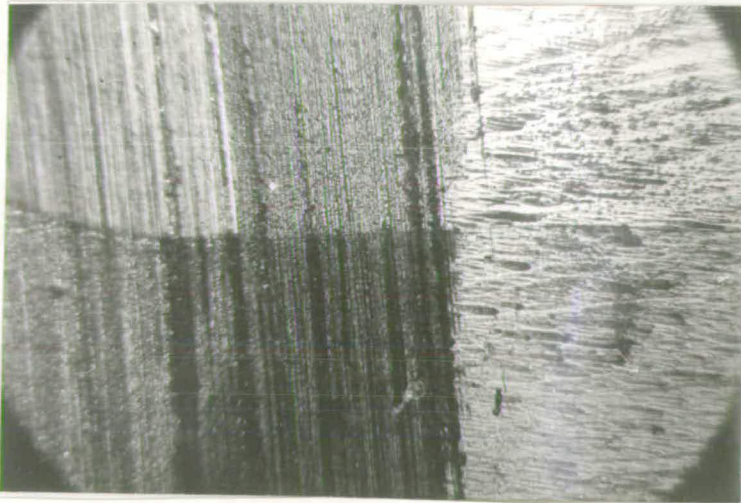
Despite this limited success it was decided to terminate the experiments since the reactor design was considered to be too restricting for good growth control. That growth had been achieved in a cold-walled system promised that a future reactor working on the same principal but with a more flexible design, may yet obtain ultra high purity epitaxial gallium arsenide films.



Isolated deposits of GaAs on Ge
x450



Faceted growths of GaAs originating
from Ga droplets on Ge, x 100



Ge substrate GaAs bevel GaAs surface

| Light chemical
| stain.

Thick layer of GaAs on Ge
5° bevel lapped surface x100

Chapter 5

Chemical Reactions5.1 Reported Reactions

The chemical reactions which occur in the formation of gallium arsenide are of great significance to the crystalline and electrical properties of the material produced. In particular, as Shaw^{31,32} has shown, the gallium to arsenic ratio of the reactants arriving at the substrate have considerable effect on the electrical properties of the film.

The initial reaction is the reduction of the arsenic trichloride which all authors agree is:

$$4\text{AsCl}_3 + 6\text{H}_2 \rightarrow 12\text{HCl} + \text{As}_4$$

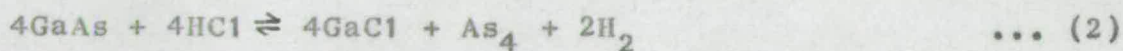
$\Delta H_{1000^\circ\text{K}} = 46.8 \text{ k cal/mole}$
... (1)
 $\Delta F_{1000^\circ\text{K}} = -46.2 \text{ k cal/mole}$

Eddols³⁰ and others allow saturation of the gallium metal with arsenic to occur before growth runs are started. This saturation occurs at 2.25% atomic weight of arsenic after which the skin of gallium arsenide appears on the surface (Hall²⁹). This reaction may be represented by

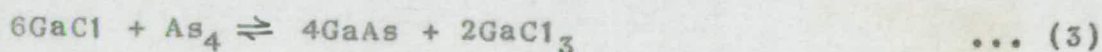


Before this occurs no arsenic appears at the exhaust end of the reactor but gallium is transported as a lower chloride. The actual transport of gallium during growth therefore begins with a reaction between gallium arsenide and the incoming gases.

Williams³⁴ gives the reaction with the gallium arsenide skin as :



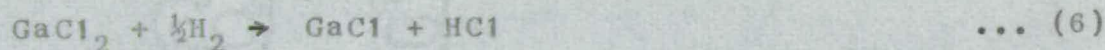
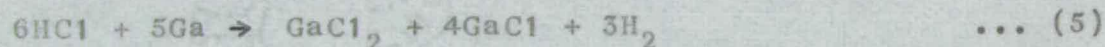
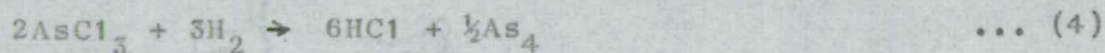
The deposition of the gallium arsenide at the substrate is given by Williams,³⁴ Eddols³⁰ and others, as :



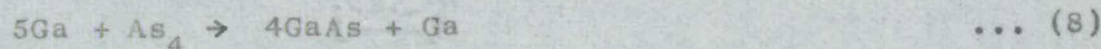
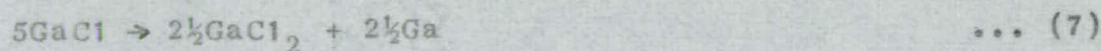
with /

with the gallium trichloride condensing (below 201°C) or crystallising (below 78°C) in the exhaust system beyond the furnace. Zuegel²¹ in his analysis of the gallium arsenide/chlorine system shows this reaction takes place reversibly between 640°C and 980°C.

Taylor⁴¹, however, sees the reactions differently. He does not attempt to form a gallium skin before growth but claims that rate of formation and transport of chloride is constant throughout the runs, both during and after saturation of the gallium with arsenic. Vapour transport is by gallium monochloride as before :



At the substrate, however, a disproportionation reaction takes place :



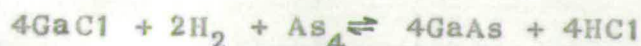
An analysis of the exhaust products from this reactor showed that the condensed liquid formed was gallium dichloride and that metallic gallium also formed (in amounts dependent on the growth rate of gallium arsenide on the substrate). Joyce and Mullin⁶¹ show that droplets of gallium on the gallium arsenide surface (causing small growth pyramids) may result if a gallium source is used which is only partially covered with the gallium arsenide skin.

Since the vapour pressure of gallium metal at 800°C is very low (less than 0.001 Torr) it may be assumed that there will be no significant transfer of gallium in its elemental form. Any gallium which appears in elemental form at the exhaust end of the reactor must therefore result from a reaction at the surface where it appears, presumably reaction (7).

Taylor also shows that hydrogen is not necessary as a carrier gas; he has also used argon for this purpose. It produced epitaxial layers at similar growth rates but at substrate temperatures some 50°C lower than in the hydrogen transport system and only gallium dichloride condensed at the exhaust region. Zuegel's conclusions that gallium trichloride is the only gallium compound formed when gallium arsenide is deposited is proved only for his system of chlorine, gallium and gallium arsenide. It does seem probable, however, that Taylor's argon transport system has similar conditions to those which Zuegel suggests and does not involve disproportionation of gallium monochloride into gallium dichloride and gallium. The gallium dichloride found at the exhaust end of Taylor's argon system may, therefore, be due to other reactions taking place at low temperatures. It is therefore also possible that these reactions (producing the dichloride and gallium) take place in his hydrogen transport system in the cooler regions and not at the substrate. Any excess gallium appearing on the substrate may be due to a relative deficiency of arsenic

5.2 Probable deposition reactions

From the above conflicting results and conclusions there appear two possibilities as to the nature of the deposition reaction. The first is that, if it is believed that gallium monochloride is the only vapour phase gallium compound existing at deposition temperature, then the deposition reaction will most likely be the etching reaction (2) in reverse:



The direction in which this reaction proceeds is therefore dependent on temperature and relative proportions of reactants. The second possibility would occur if, due to the presence of hydrogen chloride, other /

other gallium chlorides did exist in the vapour phase at the deposition temperatures. Until a thorough study of the hydrogen chloride, gallium, hydrogen and gallium arsenide system is made, no conclusive proof of this yet exists. The presence of droplets of gallium on the substrate could, however, suggest some sort of disproportionation reaction. The most likely possibility is that all the reactions suggested by the various authors do occur at some combinations of conditions and perhaps as intermediate steps in an overall reaction.

5.3 The effect of the substrate on growth

Most reported reactors seem to suffer from an accumulation of material on the hot reactor walls (Joyce and Mullin⁶¹, Eddols³⁰ et al) thus causing a depletion of materials in the vapour phase and hence uncertainty regarding concentrations within the reactor. Shaw⁶², who does not allow arsenic to come in contact with the gallium source, uses precise adjustment of his reactor system to grow gallium arsenide selectively in holes in a silica mask. At optimum conditions he reports no deposit on the mask or on the reactor walls. This indicates that the gallium arsenide substrate itself has some catalytic effect on the chemistry of the deposition reaction.

The different growth rates which result from the use of different substrate orientations indicates that not only the surface but the surface polarity must significantly affect the deposition reaction rate. Barber and Heasell⁶³ have described a model of a general III-V compound single crystal and shown how this model /

model applies to the different growth (and etch) rates observed between the 111A and B faces. The A faces (group III atoms) are shown to be more 'noble' or less chemically reactive than the B faces (group V atoms). In addition the A faces are more disordered than the B faces due to a higher degree of bonding strain. Shaw³¹ relates the relative polarity of different planes to his experimentally observed growth rates and shows a good degree of agreement between them.

5.4 Vapour etching

Vapour etching in the system is also an important reaction. As has been seen it probably occurs at the gallium arsenide skin according to reaction (2) in most systems. It may also occur however, with arsenic trichloride only, as has been shown by Taylor⁴¹ in his argon transport system. The arsenic trichloride is dissociated at the etching temperatures and it is assumed that the chlorine constituent is responsible for the etching reaction. Taylor reports that the arsenic trichloride vapour tends to pit the 111 A surface but produces smooth 111 B surfaces. The experimental work in this report shows that in vapour phase etching, where hydrogen chloride is the principal or only etchant, both surfaces may well be attacked rapidly in a manner which produces pitting. Careful control of the initial substrate etching stage is thus very necessary since the quality of the final film will depend on the quality of the substrate surface.

The vapour phase etching reported in the experimental section which occurred when the substrate was heated in the reactor in /

in a hydrogen atmosphere was at first considered to be due to the evaporation of residual chloride from the surface of the heaters. There is, however, a possibility of thermal etching of gallium arsenide at high temperatures in which arsenic dissociates from the surface and volatilises. Thurmond⁶⁴ gives the equilibrium vapour pressure of arsenic over gallium arsenide at 750°C to be about 10^{-8} atmosphere. Using the Langmuir equations :

$$W = 0.0585 P \frac{M}{T} \quad \text{gm cm}^{-1} \text{S}^{-1}$$

P = vapour pressure. Torr
 M = molecular weight
 T = absolute temperature °K
 W = rate of evaporation
 gms cm⁻² S⁻¹

$$\text{Etch rate} = \frac{W}{\text{density of GaAs}}$$

— 0.8 micron per hour.

This is the thermal etch rate of gallium arsenide at 750°C assuming that atomic arsenic leaves the surface. It also assumes that no arsenic returns to the surface, a fact that is only valid in high vacuum conditions. The actual etch rate will be therefore somewhat less than this over the whole surface. In small areas, however, especially if etch pits form, arsenic atoms may not readily return to the area from which they came, and this rate may be approached. Although it is extremely difficult to measure such slow etch rates it is considered that the small flat etch pits observed in this experiments were due to this thermal etching.

Chapter 6

Growth and etching in the reactor6.1 Convection problems

The experimental section has shown that there was only poor growth of gallium arsenide in the reactor. The specialised exception, the needle crystals formed at low temperatures, will be considered later.

Bearing in mind the ~~the~~ chemical considerations ^{of chapter 5} it is necessary to examine growth difficulty by investigating the cause of etching conditions. The extremely rapid etching which usually occurred was found to vary mainly with substrate temperature. As was mentioned in the experimental section it was considered that arsenic and gallium compounds were being 'stripped out' of the vapour phase due to condensation caused by prolonged contact with the cooled reactor walls. This was clearly visible as a run was started with a clean reactor tube. After some ten minutes the whole tube became opaque with deposited material. The only vapour phase reactants in the system at low temperatures were hydrogen and hydrogen chloride. Thus a very high proportion of hydrogen chloride was present at the heated substrate where it could cause the etching reaction (equation 2).

An accurate picture of the flow conditions within the reactor was considered to be unobtainable since convection was obviously responsible for the predominant flow patterns. See Fig. 10A. In order that some idea of relative gas velocities within the reactor could be obtained a simple arithmetical model was conceived as follows : /

follows :

To find the maximum velocity of a convection produced gas flow in the reactor assume :

- that purely buoyancy forces act on small volume V cc of the gas,
- that the maximum velocity of the gas V cm S^{-1} is achieved after it has uniformly accelerated through a distance of 2 cm from the heater surface to the cold reactor walls,
- that the initial gas velocity, i.e. the gas velocity at the heater surface is 0 cm S^{-1} ,
- that the temperature of the gas at the heater surface is 1073°K
- that the temperature of the cooled gas is 373°K
- that the vapour density is inversely proportional to its temperature

v = velocity of gas, cm S^{-1} V = volume of gas under consideration, cm^3

T_c = temperature of cooled gas, $^\circ\text{K}$ T_H = temperature of hot gas, $^\circ\text{K}$

g = gravitational constant 981 cm S^{-2}

ρ_c = density of cooled gas, gm cm^{-3} ρ_H = density of hot gas, gm cm^{-3}

$$v^2 = 2 \times \text{accel.} \times \text{distance}$$

$$= 2 \times \frac{\text{upthrust on gas}}{\text{mass of volume } V} \times \text{distance}$$

$$= 2 \times \text{distance} \times \frac{(\text{weight of gas displaced at } T_c - \text{wt. of gas})}{\text{weight of hot gas}} g$$

$$= \frac{2 \times 2V(\rho_c - \rho_H)g}{\rho_H V}$$

$$= 4 \frac{\rho_c}{\rho_H} - 1 \quad g$$

$$= 4g \frac{T_H}{T_C} - 1$$

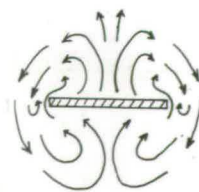


FIG. 10A
SUGGESTED
CONVECTION
PATTERNS.
CROSS SECT
VIEW

$$\therefore v = 2.86 \text{ cm s}^{-1}$$

The velocity along the axis of the tube is, at a flow rate of $11 \text{ cm}^3 \text{ s}^{-1}$

$$\frac{11}{\text{cross sectional area of the tube}} = 0.55 \text{ cm s}^{-1}$$

Though this calculation is based on a very loose model it does tend to indicate that convection velocities produced by the very steep thermal gradients present in the reactor were considerably greater than the axial reactor flow velocities. The vapour phase reactants were, therefore, in prolonged contact with the cooled walls before they reached the substrate. All the possible gallium compounds and the arsenic were no longer in the vapour phase at the temperature of the reactor walls. It is, therefore, clear that the predominant vapour phase reactant at the substrate surface was hydrogen chloride.

The chemical microanalysis on the cold wall samples indicated that approximately even amounts of arsenic and gallium were being condensed there. In the quartz tunnel experiment the much higher proportion of gallium to arsenic found on the tunnel was not necessarily an indication of the constituents in the vapour phase at that region. It is believed that the surface temperature at this point would have been above the temperature at which arsenic sublimates and hence, unless combination to gallium arsenide had taken place, most of the arsenic would not have remained on this surface.

In /

In an attempt to prevent etching conditions occurring the re-arrangement of electrodes in the second series of runs was made. Though this system was less flexible (making temperature measurement and substrate positioning more difficult) it appeared that it might reduce some of the reactant loss from the vapour phase. The etching rate in this system was clearly less than in the previous one, to the extent that at low temperatures deposition took place. Unfortunately at these temperatures there is too low a surface mobility of the nucleation centres to allow good epitaxy. Walton⁶⁷ shows that the threshold temperature for epitaxy is, for a particular substrate surface and deposition material, proportional to the reciprocal of the logarithm of the rate at which material arrives at the surface. Hence low rates of material arrival at the surface give rise to high epitaxial threshold temperatures. It is believed that the even greater temperature gradients caused by re-positioning of the heaters caused considerable convection currents which affected the narrow region between substrate and heater. A high proportion of the reactants must again have been rapidly condensed on the reactor walls. In fact, the build up of compounds on the walls was seen to be very rapid, although of course more localised than with the original heater arrangement.

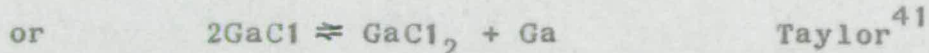
6.2 Vapour/Liquid Solid Growth

The small growth pyramids observed on the germanium substrates are believed to be formed when a droplet of gallium is present on the surface. When the gallium solution becomes supersaturated with arsenic from the vapour phase, crystal growth occurs. /

occurs. The resulting growths usually had a triangular cross section such as observed by Barns and Ellis⁴² who suggest that this represents growth in the 111 direction. An important feature of this type of growth is that it occurs very rapidly since the vapour etching at the growth interface is prohibited, thus allowing growth in conditions where there is clearly a great excess of hydrogen chloride. The exposed gallium arsenide plateau produced is presumably etched by the hydrogen chloride vapour and so does not extend appreciably. The actual formation of such pyramids is therefore complex in analysis since it depends on growth orientation, relative surface areas of facets and growth faces and relative proportions of reactants.

From the point of view of this report, however, an equally significant consideration is to determine how the gallium droplet arrived at the surface. Clearly the germanium substrate cannot supply the gallium in the manner Joyce and Mullins⁶¹ suggest is possible for gallium rich gallium arsenide. There are two distinct possibilities. The first is that the gallium arsenide skin on the gallium source may rupture at high temperatures and cause small droplets of the liquid gallium to be thrown upwards from the surface. At room temperatures the gallium arsenide skin is clearly under some stress some minutes after removal from the reactor. That this happens at high temperatures, and with sufficient violence to cause droplets to be ejected from the surface seems very unlikely. A possible explanation is that at these relatively low temperatures some form of disproportionation reaction is /

is occurring, either



Most probably, the reduction of the monochloride with hydrogen occurs

$$2\text{GaCl} + \text{H}_2 \rightleftharpoons 2\text{Ga} + 2\text{HCl}$$

With this arrangement of heaters a relative arsenic deficiency in the vapour phase was quite probable since arsenic trichloride may have reacted with the hydrogen at all the heater surfaces and by convection and cooling the arsenic vapour condensed on the walls. The gallium monochloride is, on the other hand, confined at first to the space between source and substrate before meeting the cooled walls. Thus a deficiency of arsenic would occur allowing the gallium disproportionation and v.l.s. growth to take place at the substrate.

6.3 Needle Growth

The extensive needle growth which occurred on large regions of the substrate and on the substrate heater were not thought to have resulted from a similar mechanism. The conditions which give rise to the lengths of these needles and the low temperatures at which they must have formed are not so readily explained. In such a cooled wall reactor it seems probable that there were very steep thermal gradients in the vapour around the heaters. The needles always grew from the substrate heater and always downwards towards the gallium source and seemed to grow over a very limited heater temperature range. From this it is deduced that either the growth of these needles is not very temperature sensitive - in which case /

case the effect of substrate heater temperature on growth must have been on the production of growth controlling vapour flow patterns; or iso-thermals, due to the thermal conduction of the needles or an isothermal region between the heaters, were maintaining the necessary growth temperatures.

High power optical microscopy showed these needles to have an almost round cross section with no metallic droplet at their tips and chemical microanalysis showed them to be gallium arsenide. The growth of such whisker crystals is not yet fully understood but Cabrera and Coleman⁶⁵ suggest a migration of arriving atoms from the sides of the whisker to the tip. The whiskers observed in the quartz tunnel experiment, growing from the gallium surface, were quite different. In this case they appeared exactly like those photographed by Barns and Ellis⁴², that is, flat blades with triangular ends tipped by small metallic droplets. The difference here, however, is that Barns and Ellis⁴² produced short crystals of varying cross section and random shape with gallium and only achieved the flat ribbon whiskers when gold or some other metals were used as solvents.

Conclusion

Chapter 7

The most important unanswered question in the technology of epitaxial gallium arsenide is whether electrically active impurities or crystalline structural defects are imposing the upper limit on the electrical quality. Unless the actual impurity atoms or defects can be identified and related to the electrical properties of the material this question will remain unanswered.

Analysis and correlation of the published literature indicates that there exists at the present time an insufficient amount of knowledge concerning the chemistry of the vapour phase deposition of epitaxial gallium arsenide. The fact that the proportions of the constituents arriving at the substrate have an effect on the electrical properties of the layers produced in that a more intensive study of the deposition reactions is necessary.

There is evidence to show that the presence of quartz in the epitaxial reactor may be a source of impurities and it is singled out by many authors as the most probable cause of contamination. The reactor described in this report was designed with the intention of eliminating all heated quartz surfaces, with the hope of achieving an epitaxial layer of gallium arsenide whose electrical properties would surpass those obtained in the more conventional epitaxial reactors.

No high quality layer was obtained; condensation of the reactants on the cold reactor walls causing reactant depletion in the /

The vapour phase and consequent etching by the remaining hydrogen chloride is blamed for this lack of success. The case against the use of quartz therefore remains unproved. A reactor which makes use of high temperature materials other than quartz, such as high purity graphite and perhaps alumina, and has independent control of the reactants arriving at the substrate, may still achieve better performance than those obtained by the epitaxial reactors used at present. Certain features of such a reactor are worth consideration. The replacement of the gallium/gallium arsenide source by the use of gallium trichloride may be of some advantage in maintaining constant gallium partial pressures during a growth run. The problems of diminishing surface areas and possible gallium arsenide skin rupture would be reduced. The use of a gallium source which is not permitted to come into contact with arsenic vapour, or the use of bulk crystalline gallium arsenide source is also worth consideration. Since elemental arsenic is available with high purity it may be an improvement if sublimed arsenic in a hydrogen carrier gas were employed thereby reducing the amount of hydrogen chloride present in the reactor.

If a cold wall system were to be employed again some study of the flow patterns and their modification would require study by techniques such as those of Schlieren. Convection induced vapour transport might be put to advantage in permitting an efficient and fast growth. The considerable lack of control of vacuum system and 're-growth from the melt' techniques suggest that these will not be useful for microwave gallium arsenide devices.

A P P E N D I X

A number of experiments was set up in order to analyse the electrical properties of the anticipated epitaxial layers.

A.1 Ohmic contacts

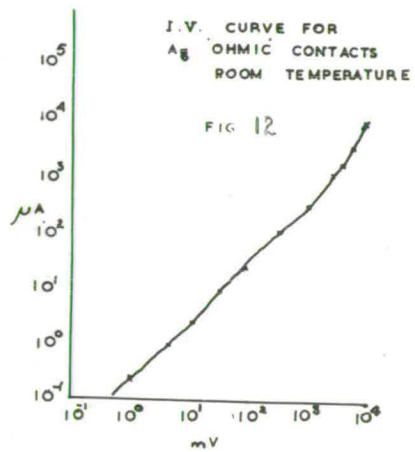
Ohmic contacts, whilst not difficult to produce with low resistivity material, present considerable problems when the material has a resistivity of about 0.5 ohm cms and upwards. Since it was intended to produce high resistivity layers some different types of ohmic contacts were tried. A number of contacts were bonded to the periphery of a 3 ohms cm substrate. The nature of the contacts was ascertained by measuring the voltage/resistance characteristics between a pair of the contacts and by measuring the photovoltage produced when one contact was illuminated strongly by a microscope lamp with the other shielded from the light. A simple apparatus was constructed for the Van der Pauw⁴⁶ type measurement and was also used for this purpose (Fig. 13). Ohmic contacts to semiconducting materials are usually formed by heating deposited metallic contacts on the surface of the semiconductor such that they alloy with the semiconductor. After deposition the contacts were heated until the photovoltage was reduced to zero. The samples were nominally 3 ohm cm 111 orientated substrates with contacts applied to the chemically polished B face. Substrates were washed in isopropyl alcohol in the re-fluxing apparatus prior to deposition. Evaporated contacts were applied by evaporation at 10^{-6} Torr in an oil diffusion pumped vacuum system with the substrate held at a temperature of 100°C.

The /

The evaporated layer was then masked with photo-resist and exposed to give a pattern of contacts round the periphery of the substrate. The resist was developed and the exposed layer was etched with dilute nitric acid leaving the contacts. After deposition the contacts were heated in high purity argon gas for ten minutes at a series of temperatures starting from 200°C and increasing by 20°C increments until the photovoltage had dropped to zero (<0.05mV). Tin and indium spheres, approximately ½ mm in diameter were laid on the cleaned surface prior to heating.

<u>Material</u>	<u>Deposition Technique</u>	<u>Temperature for zero photo voltage</u>	<u>Resistance between contacts</u>
Tin spheres	Laid on surface	320°C	Very high resistance
Tin spheres	Laid on the surface with stannous chloride in acetone flux	340°C	Very high resistance
Indium spheres	-do-	300°C	Approx. 2000 ohms between contacts
Silver	Evaporated	450°C	30K (see curve, Fig. 12).
Tin	Evaporated	Did not wet surface properly.	

Though all but the evaporated tin contacts bonded well mechanically they gave very high resistance values. This is thought to be due to surface contamination prior to deposition. The argon gas was not dried when used and the tin and indium may have had thin oxide coatings. The substrate preparation may also have been at fault. None of these contacts would have been suitable for devices /



devices. For the Van der Pauw resistivity and Hall mobility measurements, however, the high resistance and even any rectifying effects of the contacts are of no importance. The indium contacts therefore, because of their low resistance, and especially their low bonding temperature appear the most useful for electrical evaluation of the layers produced.

A2. Resistivity and Hall Mobility

To make a determination of impurity levels a series of resistivity measurements is usually made at a wide range of temperatures. Though very low temperatures were not available in the laboratory a variety of melting organic solvents provided low temperature baths. These frozen solvents were prepared by freezing in liquid air. The measurement temperatures were as follows :

293°K	Room temperature
250.1°K	Melting carbon tetrachloride
209.5°K	Melting chloroform
186.6°K	Melting trichlorethylene
178.0°K	Melting acetone
156.0°K	Melting diethyl ether

Liquid air itself was not used as a temperature bath since its boiling point drops in temperature as the nitrogen component boils off more rapidly than the oxygen component.

Resistivity measurements by the Van der Pauw technique were carried out successfully at all these temperatures, the substrate specimen being attached to an 'S.R.B.F.' rod which was immersed /

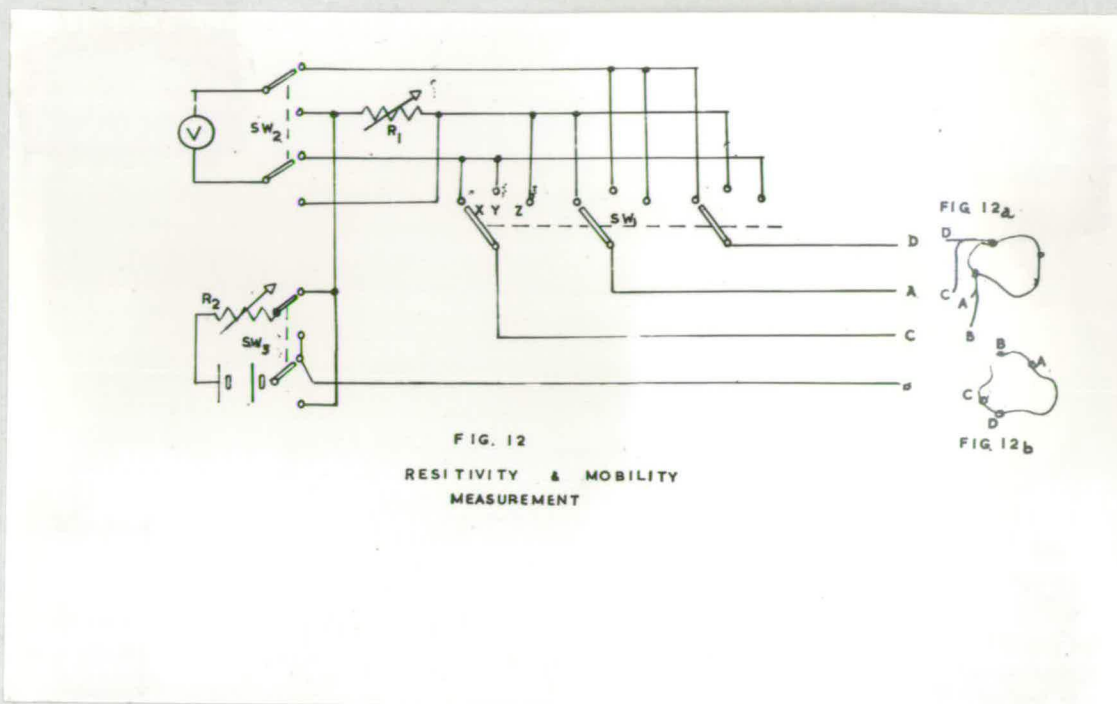


FIG. 12
RESISTIVITY & MOBILITY
MEASUREMENT

For ohmic contact resistance measurement one contact is connected to terminals B and C and the other to terminals A and D with SW₁ at position X (Fig. 12a). For different settings of R₂ (which varies the current flow) the resistance substitution box R₁ is adjusted such that V measured by a digital voltmeter is the same for both positions of SW₂. The resistance between the ohmic contacts is the value of R₁ and the voltage across the contacts is given by V. SW₃ is changed over and the readings repeated. For Van der Pauw measurement terminals A, B, C, D are connected to four peripheral contacts on the specimen. (Fig. 12b). With SW₁ in position X, the value for R_{AB,CD} (i.e. the value $\frac{V_{CD}}{I_{AB}}$ is measured, /

measured, as above, for both directions of SW_3 and similarly the value of $R_{BC,AD}$ with SW_1 in position Z.)

Hall measurements are made by switching SW_1 to position Y. $R_{BD,AC}$ is measured with and without a magnetic field applied across the specimen.

immersed in the melting solvent. The temperature range was not, however, sufficiently extended into the low temperature regions to make any useful assessment of impurity levels but mechanical strength of the contacts appeared to be stable throughout the temperature range.

Hall mobility measurements were carried out at room temperature with a 10^3 Gauss magnetic field using the Van der Pauw technique. The magnitude of the mobility and the conductivity type were both found to be as stated by the crystal suppliers.

The three point probe method for measuring resistivity was found to be satisfactory. The circuit employed was as follows :

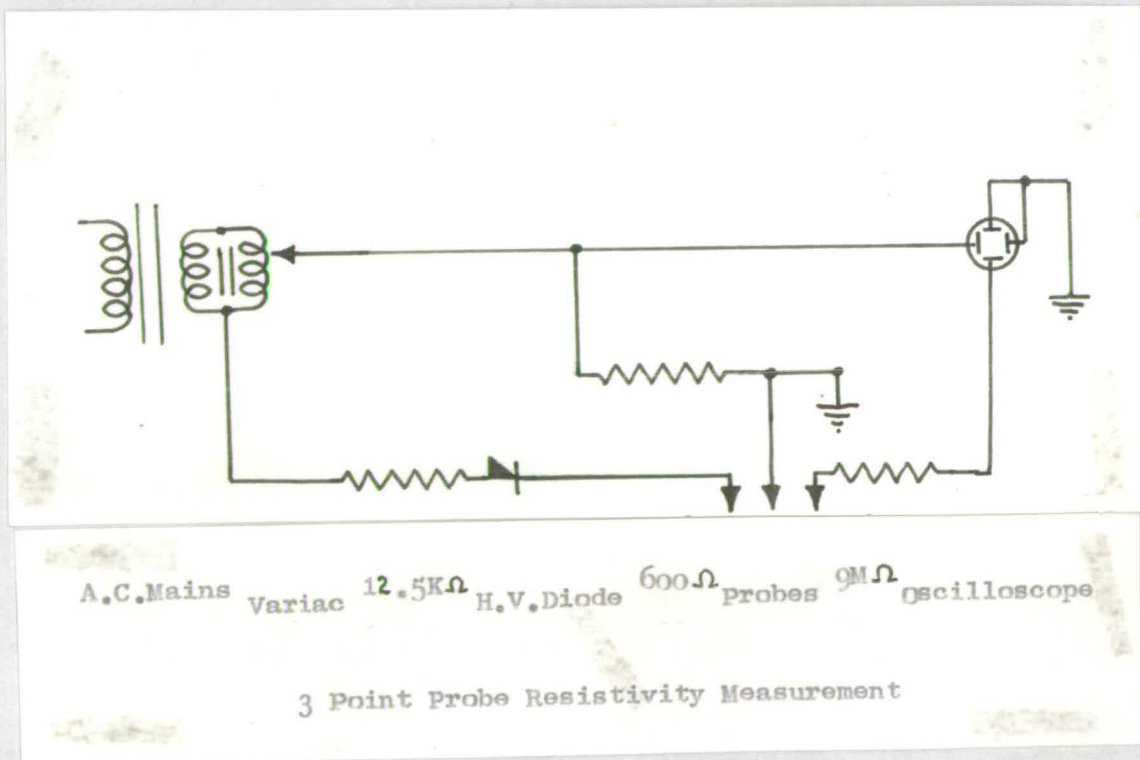


Fig. 13A

The outside probes were made of springy brass strips and the central probe was made from a sharpened tungsten wire. The system was calibrated for known samples of gallium arsenide by increasing the voltage from the variac until the oscilloscope trace just started to 'turn over'. The variac setting ~~setting~~ was then noted and related to the semiconductor's resistivity.

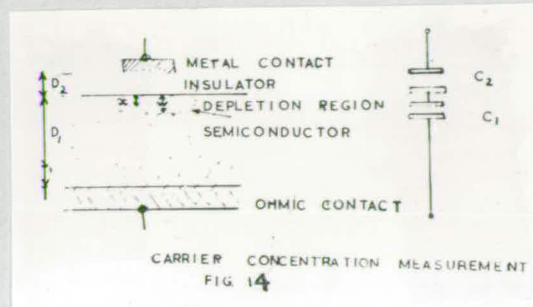
Though this method is basically non-destructive it was found that, if breakdown occurred, a sufficient current passed to damage a small area around the probe. It would be quite practical to make a pulsed circuit in which voltage is applied for only a very short duty cycle thereby allowing sufficient time for destructive heat to dissipate.

A3. Carrier concentration

In order to measure carrier concentration an evaporated layer of tin was deposited in a vacuum system onto a substrate already bearing ohmic contacts. The new tin layer was etched into a number of small areas as for the ohmic contacts. A graph of voltage versus capacitance for this reverse biased Schottky junction was made by measuring the capacitance change for voltages up to 5 V. For this purpose a 10 KHz signal at a few mV was passed through the diode, amplified by means of a tuned amplifier, detected by means of a diode bridge and capacitor and measured with a digital voltmeter. The biasing voltage was applied with a 10-turn potentiometer. This system was calibrated with a number of capacitors of known value.

From the results of this experiment it was clear that surface contamination in some form must have been present presumably due to inadequate cleaning or vacuum deposition techniques. In order to obtain a different system for carrier concentration measurement which does not rely so much on extremely careful substrate preparation a 'space charge varactor' diode was investigated. This is a metal-insulator-semiconductor device in which a change of capacitance can be caused, as in the Schottky diode, by increasing the size of the junction depletion region by means of an applied electric field. (Fig. 14)

A simplified mathematical analysis of this device for carrier concentration measurement is as follows.



All units in m.k.s.a. units.

- D_1 = Thickness of semiconductor
- D_2 = Thickness of dielectric
- W = Depletion width
- A = Area of diode = area of 'plates'
- ϵ_1 = Relative permittivity of semiconductor
- ϵ_2 = Relative permittivity of dielectric
- ϵ_0 = Permittivity of free space
- n = carrier concentration (assuming carriers are all ionised at measurement temperature and one type predominates)
- V_{app} = Applied voltage
- V_1 = Voltage across depletion region
- V_2 = Voltage across dielectric
- Q = Charge on plates
- C_1 = Capacitance of capacitor 1
- C_2 /

C_2 = Capacitance of capacitor 2

e = Electron charge

x = Distance from semiconductor surface to a point in the depletion region.

V_x = Voltage at x .

$$C = \frac{C_1 C_2}{C_1 + C_2} = \frac{\frac{\epsilon_0 \epsilon_1 A \epsilon_0 \epsilon_2 A}{WD_2}}{\frac{\epsilon_0 \epsilon_1 A}{W} + \frac{\epsilon_0 \epsilon_2 A}{D_2}}$$

$$\therefore C = \frac{\epsilon_0 \epsilon_1 \epsilon_2 A}{\epsilon_1 D_2 + \epsilon_2 W} \quad \dots (1)$$

providing $0 \leq W \leq D_1$, and assuming no fringing fields

$$\text{Now } V = \frac{Q}{C}$$

$$V_1 = Q \frac{W}{A \epsilon_1 \epsilon_0} = V_{app} C \frac{W}{A \epsilon_1 \epsilon_0} = V_{app} \frac{\epsilon_0 \epsilon_1 \epsilon_2 AW}{(\epsilon_1 D_2 + \epsilon_2 W) A \epsilon_1 \epsilon_0}$$

(substituting (1) for C where V_x = voltage at x)

$$V_{app} = V_1 \left(1 + \frac{\epsilon_1 D_2}{\epsilon_2 W}\right) \quad \dots (2)$$

Now assuming a potential gradient in the depletion region only in the direction x we have, by Poisson's equation :

$$\frac{d^2 V}{dx^2} = \frac{-\text{charge carrier concentration}}{\text{permittivity}}$$

$$\therefore \frac{d^2 V}{dx^2} = \frac{en}{\epsilon_0 \epsilon_1} \quad (\text{negative signs of electron charge and Poisson's equation cancelling})$$

$$\therefore \frac{dV}{dx} = \frac{enx}{\epsilon_0 \epsilon_1} + \text{constant}$$

$$\text{when } x = W, \frac{dV}{dx} = 0$$

$\therefore /$

$$\therefore \frac{dV}{dx} = \frac{en}{\epsilon_0 \epsilon_1} (x-W)$$

$$V_1 = \frac{en}{\epsilon_0 \epsilon_1} \left[\frac{1}{2}x^2 - Wx \right]_W^0 = \frac{enW^2}{2\epsilon_0 \epsilon_1}$$

$$\therefore \text{in (2) } V_{app} = \frac{enW^2}{2\epsilon_0 \epsilon_1} + \frac{\epsilon_1 D_2}{\epsilon_2 W} \frac{enW^2}{2\epsilon_0 \epsilon_1}$$

$$\text{from (1) } C = \frac{\epsilon_0 \epsilon_1 \epsilon_2 A}{\epsilon_1 D_2 + \epsilon_2 W}$$

$$\therefore W = \frac{\epsilon_0 \epsilon_1 \epsilon_2 A - C \epsilon_1 D_2}{\epsilon_2 C}$$

$$\text{when depletion layer } W = 0 \text{ let } C = C_0 \therefore A = \frac{C_0 D_2}{\epsilon_0 \epsilon_2}$$

$$\therefore W = \frac{\epsilon_0 \epsilon_1 \epsilon_2 \frac{C_0 D_2}{\epsilon_0 \epsilon_2} - C \epsilon_1 D_2}{\epsilon_2 C} = \frac{\epsilon_1 D_2 (C_0 - C)}{\epsilon_2 C} \quad \dots (3)$$

$$\therefore V_{app} = \frac{en \epsilon_1^2 D_2^2 (C_0 - C)^2}{2 \epsilon_1 \epsilon_0 \epsilon_2^2 C^2} \left[1 + \frac{\epsilon_1 D_2}{\epsilon_2} \frac{\epsilon_2 C}{\epsilon_1 D_2 (C_0 - C)} \right]$$

$$\therefore V_{app} = \frac{e D_2^2}{2 \epsilon_0} \frac{\epsilon_1}{\epsilon_2} \left\{ \frac{C_0}{C} \left(\frac{C_0}{C} - 1 \right) n \right\}$$

Thus charge carrier concentration n is a function of V_{app} , C , C_0 , the thickness of the dielectric layer, relative permittivity of the semiconductor and of the dielectric.

If VC is plotted on a Y-axis and C^{-1} on an x-axis the carrier concentration is given by :

$$- \frac{2 \epsilon_0 \epsilon_2^2}{e D_2^2 \epsilon_1 C_0} \text{ (Y-axis intercept)}$$

To /

To find the sensitivity of such a measurement in a particular sample of 1 ohm cm uncompensated n-type gallium arsenide ($n = 10^{15}$ carriers per cm^{-3}) using K.T.F.R. photoresist as the dielectric (see following section) the calculation is as follows : Assume a resist layer thickness of 0.2 microns and a metal contact area of 0.5 mm^2 . The breakdown voltage of the resist is given as 72 volts per micron. The 0.2 micron layer will therefore breakdown at about 14 volts so a maximum applied voltage of $V_{\text{app}} = 10\text{V}$ will be considered.

$$\text{For } V_{\text{app}} = 0\text{V} \quad C = C_0 = \frac{A \epsilon_2 \epsilon_0}{D_2}$$

$$= 55.4 \text{ pF}$$

Now for $V_{\text{app}} = 10 \text{ V}$

$$C = C_0 \frac{1 + 4 \frac{V_{\text{app}}}{K}}{2 \frac{V_{\text{app}}}{K}} \quad \text{Where } K = \frac{e D_2^2 \epsilon_1 n}{2 \epsilon_0 \epsilon_2}$$

$$\therefore \frac{V}{K} = 13.3$$

$$C = 13.3 \text{ pF}$$

There is therefore a quite useable capacitance change (approx. 400%) for an increase in applied voltage ^{range} of 10 volts.

In order that this theory might be of some practical use it was decided to form a metal/dielectric/semiconductor diode.

It is possible to deposit a layer of silica on gallium arsenide by the decomposition of various volatile silicon compounds (Shaw⁵²). These methods, however, usually involve high temperatures and this was considered as unsuitable for measurements on high purity materials because of the possibility of /

of contamination. The technology of photo-resist has now reached an advanced state of development and very thin layers may be evenly deposited having (for Kodak Thin Film Resist) a dielectric constant of approximately 2.5 and a breakdown voltage of some $5 \times 10^4 \text{ cm}^{-1}$.

Thus such a film was deposited on a piece of gallium arsenide bearing an ohmic contact on the back. Photo-resist deposition was as follows. The substrate was heated at 100°C for a half hour to dry it. K.T.F.R. was chosen as it is a negative resist, that is, it becomes polymerised and passive on exposure to U.V. light. A mixture of 1 part resist plus 1.5 part thinners was applied to the substrate which was spun at 1,800 r.p.m. for 60 seconds. It was then dried for 5 minutes and baked at 80°C for 20 minutes. After exposure to a U.V. lamp for 60 seconds it was post-baked for 30 minutes at 350°C . This produced ^avery stable and even resist layer of 0.2 microns thickness.

A metal contact was made by inserting a fine piece of gold wire into a hypodermic needle, the tapered point of which had been removed. The needle end was then ground flat and dipped in clean mercury. A small droplet of mercury adhered to the gold and, with the whole needle clamped in a micropositioning device, formed a non-rigid contact which could be lowered onto the photo-resist surface. The oscillator, amplifier and detector used for the Schottky voltage/capacitance measurements were again employed but only unstable signals could be detected. A gold coated glass substrate was then tried in place of the gallium arsenide, the photo-resist /

photo-resist applied as before and the mercury probe brought into contact with the resist. By viewing this operation through a low power binocular microscope it was seen that each contact made resulted in immediate and extensive reaction with the gold underneath the resist. It was, therefore, clear that the photo-resist was allowing the penetration of mercury to the gold. Thus the photo-resist is blamed for the lack of results achieved by this method. A number of different post-baking treatments on the photo-resist was tried, such as baking to 400°C for one hour but no success was achieved.

Low temperature vacuum deposition of dielectrics, such as silicon monoxide, may prove suitable instead of photo-resist. Vacuum deposition of a metallic contact on top of the insulator may also have advantages since if the area of the contact is accurately defined the thickness of the insulator need not be known.

For ohmic contacts to the epitaxial layer it would be necessary to use a semiconducting, rather than semi-insulating, substrate of the same conductivity type as the epitaxial layer. This could be achieved by using a pilot substrate during growth. A better method however would be to deposit the contacts on the epitaxial surface, with the semi-insulating substrate remaining electrically inactive. Provided that the depletion region spreads (for maximum applied voltage) only a small fraction of the epitaxial layer thickness the approximation to a parallel plate capacitor will still hold.

References

1. JENNY, C.A. The status of transistor research in compound semiconductors.
Proc. Inst. Radio Engrs 46 (6) June, 1958 pp. 595-968
2. SZE, S.M. and IRVIN, J.C. Resistivity, mobility and impurity levels in GaAs, Ge and Si at 300°K.
Solid-St. Electron. 11, 1968. pp. 599-602
3. KANG, C.S. and GREENE, P.E. Epitaxial GaAs grown from Ga solution.
Appl. Phys. Letters, 11 (5), 1st Sept. 1967.
4. RIDLEY, B.K. and WATKINS, T.B. The possibility of negative resistance in semiconductors.
Proc. Phys. Soc. 1961, pp. 293
5. GUNN, J.B. Instabilities of current in III-V semiconductors.
IBM J. Res. Dev. April, 1964. pp. 141-159
6. KING, G. et al. An Assessment of epitaxial GaAs for use in Gunn effect devices.
Inst. Symp. on GaAs, Reading 1966, London, Inst. of Phys. and the Physical Soc., 1967. pp. 184-188.
7. WOLFE C.M. et al. Epitaxial GaAs for high-efficient Gunn Oscillators.
Electrochem. Technol. 6, (5-6), May June, 1968. pp. 208-214
8. TIETJEN, J.J. et al. Vapour phase growth of gallium arsenide microwave diodes.
Solid-St. Electron. 9 (11-12) Nov. - Dec. 1966, pp.1049-1053.
9. JOYCE, B.A. Growth and perfection of chemically deposited epitaxial layers of Si and GaAs.
J. Crystal Growth, 3 (4) 1968, pp. 43-59.
10. /

10. ALLEN, J.W. Nature 1960, pp. 403
11. BAILEY, L.G. Preparation and properties of III-V compounds for radiative processes.
Trans. metall. Soc. A.I.M.E. 239 (3), Mar. 1967, pp. 310-320
12. MEHAL, E.W. et al. GaAs epitaxial technology for integrated circuits.
Trans. metall. Soc. A.I.M.E. 236 (3), Mar. 1966, pp. 263-267
13. MANASEVIT, H.M. Single-crystal gallium arsenide on insulating substrates.
Appl. Phys. Letters, 12 (4) Feb. 1968, pp. 156.
14. CRONIN, G.R. and HAISTY, R.W. J. Electrochem. Soc. 111, 1964 pp. 874.
15. HOYT, P.L. and HAISTY, R.W. The preparation of epitaxial semi-insulating GaAs by iron doping.
J. Electrochem. Soc. 113 (3), March 1966, pp. 296-297.
15. NELSON, H. Epitaxial growth from the liquid state and its application to the fabrication of tunnel and laser diodes.
RCA Rev. Dec. 1963, pp. 603-615.
17. BOLGER, D.E. et al. Preparation and characteristics of gallium arsenide.
Int. Symp. on GaAs, Reading, 1966, London, Inst. of Phys. and the Physical Soc. 1967, pp. 16-22
18. LAWLEY, K.N. Vapor Growth parameters and impurity profiles on n-type GaAs films grown on n* GaAs by the hydrogen water vapour process.
J. Electrochem. Soc. 113 (3) March, 1966, pp. 240-245.
19. /

19. GOTTLIEB, G.E. and CORBOY, J.F. Epitaxial growth of GaAs using water vapour
RCA Rev. Dec. 1963, pp. 585-595
20. COCHRAN, C.N. and FOSTER, L.M. Vapour pressure of gallium, stability of gallium suboxide vapor and equilibria of some reactions producing gallium suboxide vapor.
J. Electrochem. Soc. 109 (2) Feb. 1962, pp. 144
21. ZUEGEL, M.A. Vapor phase equilibria in the gallium-chlorine and gallium arsenide-chlorine system.
J. Electrochem. Soc. 112 (11) Nov. 1965, pp. 1153
22. GOLDSMITH, J. and OSHINSKY, W. Vapor-phase synthesis and epitaxial growth of GaAs.
RCA Rev. Dec. 1963, pp. 546-555.
23. RUBENSTEIN, M. and MYERS, E. Epitaxial synthesis of GaAs using a flow system.
J. Electrochem. Soc. 113 (4) April, 1966, pp. 365-367
24. KERN, W. Zone refining of gallium trichloride; radiochemical method for determining the distribution of components in a column and its application in analysing the zone refining effectiveness in purifying gallium trichloride.
J. Electrochem. Soc. 110 (1), Jan. 1963, pp. 60
25. GOLDSMITH, N. et al. Preparation of high purity gallium.
J. less common metals, 4 1962, pp. 564
26. TIETJEN, J.J. and AMICK, J.A. The preparation and properties of vapor-deposited epitaxial $\text{GaAs}_{1-2}^{\text{P}}\text{x}$ using arsine and phosphine.
J. Electrochem. Soc. 113 (7) July, 1966, pp. 724-728
27. /

27. HANDBOOK OF CHEMISTRY AND PHYSICS. 45th ed. Cleveland, Ohio, Chemical Rubber Company.
28. EFFER, D. Epitaxial growth of doped and pure GaAs in an open flow system. J. Electrochem. Soc. 112, (1) Oct, 1965, pp. 1020-1025
29. HALL, R.N. J. Electrochem. Soc. 110 1963, pp. 385
30. EDDOLS, D.V. et al. The preparation and properties of epitaxial gallium arsenide.
Int. Symp. on GaAs, Reading, 1966, London Inst. of Phys. and the Physical Soc., 1967, pp. 3-9.
31. SHAW, D.W. Influence of substrate temperature on GaAs epitaxial deposition rates.
J. Electrochem. Soc. 115 (4), April, 1968
32. SHAW, D.W. et al. Gallium arsenide epitaxial technology.
Int. Symp. on GaAs, Reading, 1966, London, Inst. of Phys. and the Physical Soc., 1967. pp. 10-15.
33. MOEST, R.R. The substrate orientation effect on impurity profiles of epitaxial GaAs films.
J. Electrochem. Soc. 113 (2) Feb. 1966, pp. 141-146.
34. WILLIAMS, F.V. Structural defects in epitaxial gallium arsenide.
Inst. Symp. on GaAs, Reading 1966, London, Inst. of Phys. and the Physical Soc., 1967, pp. 27.
35. CONRAD, R.W. et al. Preparation of high purity epitaxial GaAs from the elements. Solid-St. Electron. 10, 5th May 1967, pp. 507-509.
36. EDMOND, J.T., J. Appl. Phys. 31 1960, pp. 1428
37. EKSTROM and WEISBERG GaAs contamination during crystal growth.
J. Electrochem. Soc. 109 (4) April, 1962, pp. 321-327.

38. GANSAUGE, P. and HOFFMEISTER, W. Radiotracer measurements of a contamination in GaAs from quartz.
Solid-St. Electronics (GB) 9 (1) Jan. 1966, pp. 89
39. STEARNS, R. and McNEELY, J. Silicon contamination of GaAs.
J. Appl. Phys. 37 (2) Feb. 1966, pp. 933
40. SPITZER, W.G. and ALLERD, W. Site transfer of Si in GaAs.
Appl. Phys. Letters, 12 (1) 1st Jan. 1968, pp. 5
41. TAYLOR, R.C. Epitaxial deposition of GaAs in an argon atmosphere.
J. Electrochem. Soc. 114 April 1967. pp 410
42. BARNS, R.L. and ELLIS, W.C. Whisker crystals of gallium arsenide and gallium phosphide grown by the vapor-liquid-solid mechanism.
J. Appl. Phys. 36 (7) July, 1965, pp. 2296
43. LIGHT, T.B. et al. Formation of thick semi-insulating GaAs films by flash evaporation.
J. Electrochem. Soc. 115 (8) Aug. 1968, pp. 875
44. BIEDERMANN, E. and BRACK, K. Preparation of GaAs specimens for transmission electron microscopy.
J. Electrochem. Soc. 113 (10) Oct. 1966 pp. 1088
45. HILTON, R.A. and JONES, C.E. Measurement of epitaxial film thickness using an infra red spectrometer.
J. Electrochem. Soc. 113 (5) May, 1966, pp. 472-478
46. VAN DER PAUW, L.J. A method of measuring specific resistivity and Hall effect of discs of arbitrary shape.
Phillips Res. Rep. 13 (1) Feb. 1958, pp. 1-9
47. /

47. NORWOOD, M.H. Three point probe calibration for GaAs.
J. Electrochem. Soc. 112 (8) Aug. 1965, pp. 875
48. SCHLICKMAN, J.J. Sensitive oscillographic capacitance vs voltage plotter.
Rev. Scient. Instrum. 37 (6) June 1966, pp. 803-804
49. SMITH, B.L. The effect of surface treatment on GaAs Schottky barrier diodes.
Solid-St. Electron. 11 1968, pp. 502-504
50. SCHMIDT, W.A. Evaporated ohmic contacts on GaAs.
J. Electrochem. Soc. 113 (8) 1966, pp. 860
51. SALOW, H. and GROBE, E. Ohmic contacts for Gunn elements.
Z. angew. Phys. 25 (3) Aug. 1968, pp. 137-140 (in German)
52. JONES, C.E. and HILTON, A.R. The depth of mechanical damage in gallium arsenide.
J. Electrochem. Soc. 112 (9) Sept, 1965, pp. 908-911
53. REISMAN, A. and ROHR, R. Room temperature chemical polishing of Ge and GaAs.
J. Electrochem. Soc. 111 (12) Dec. 1964 pp. 1425-1428
54. SULLIVAN, M.V. and KOLB, G.A. Chemical polishing of GaAs in bromine methanol.
J. Electrochem. Soc. 110 June, 1963, pp. 585-587
55. LOWEN, J. Gallium arsenide surface preparation.
J. Electrochem. Soc. 112 (10) Oct. 1965, pp. 1657
56. PACKARD, R.W. Notes on the chemical polishing of gallium arsenide surfaces. J. Electrochem. Soc. 112 (8) Sept. 1965, pp. 871-872
57. /

57. JONA, F. and WENDT, H.R. Pyrometric measurements of Si, Ge and GaAs wafers between 100° and 700°C.
J. Appl. Phys. 37 (9) Aug. 1966, pp. 3637
58. SANDELL, E.B. Colorimetric determination of traces of metals. 2nd ed. New York, Interscience, 1950, pp. 183-185.
59. AMICK, J.A. The growth of single crystal gallium arsenide layers on germanium and metallic substrates. RCA Rev. 24 Dec. 1963, pp. 555
60. MEIRAN, E.S. Reflection x-ray topography of GaAs deposited on germanium.
J. Electrochem. Soc. 114 (3) March 1967, pp. 292-295
61. JOYCE, B.D. and MULLIN, J.B. Pyramid formation in epitaxial gallium arsenide layers.
Int. Symp. on GaAs, Reading, 1966, London, Inst. of Phys. and the Physical Soc. 1967
62. SHAW, D.W. Selective epitaxial deposition of gallium arsenide in holes.
J. Electrochem. Soc. 113 (9) Sept. 1966 pp. 904-908
63. BARBER, H.D. and HEASELL, E.L. Polarity effects in III-V semiconducting compounds
J. Physics Chem. Solids. 26 (10) Oct. 1965, pp. 1561-1570
64. THURMOND, C.D. J. Physics Chem. Solids. 26 1965, pp. 785-802
65. CABRERA, N. and COLEMAN, R.V. Theory of crystal growth from the vapor. Gilman, J.V. etc. The art and science of growing crystals. New York, Wiley,
66. WALTON, D. J. Appl. Phys. July, 1963, pp. 1827.