

INVESTIGATION OF A NOVEL TECHNIQUE FOR LPE

A thesis submitted for the degree of Doctor of
Philosophy of the University of London and for
the Diploma of membership of the Imperial College.

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July 1989

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ABSTRACT

A novel technique for liquid phase epitaxy has been developed. This technique has been named Rotating Disk Liquid Phase Epitaxy, RDLPE. A series of experiments, growing InP epitaxial layers on (100) InP substrates have been conducted in order to investigate the efficacy of this novel technique. RDLPE involves the dropping of a supersaturated solution onto a rotating substrate.

From a theoretical appraisal of the hydrodynamics of this technique, important advantages over conventional LPE techniques have been predicted.

In order to allow epitaxial growth by RDLPE, equipment was designed and built, evolving gradually as a result of information obtained during the course of the experiments. A novel method of suppressing substrate decomposition, was also incorporated into the design.

During early experiments, it became apparent that the area covered by melt during a run was limited by the substrate rotation rate. A theory was suggested to explain this, and was found to agree with the observed result that the radius of the area covered, was proportional to (rotation rate)^{-1/4}.

Despite the limited coverage, layers were successfully grown using this technique. It was found that a step-cool of 13 °C, a substrate rotation rate of 200 rpm and the substrate 2 °C cooler than the melt gave the best layer. The furnace temperature for all these experiments was initially 656 °C and the melt was dropped onto the substrate at 4 g/sec. Conditions other than these, resulted in either, incomplete merger of islands (i.e. pits left in the layer), or growth features associated with conditions of constitutional supercooling. Detailed

explanations of these results have been given.

During the experimentation, a range of growth features were observed, at least one, being unique to RDLPE. Analysis revealed important information as to their formation and explanations for these features have been postulated.

ACKNOWLEDGEMENTS

I am indebted to my supervisor at Imperial College, Dr B.A. Unvala for his time, help and advice throughout the course of this work. Also to the late Dr E.A.D. White whose help was invaluable.

I should like to thank all my friends and colleagues at Imperial College, and in particular A. Wojcik, for their help and support throughout.

I should also like to record my appreciation to British Telecommunications Research laboratories, for the material they provided and for the use of their electrochemical profile plotter.

Financial support was provided by the Science and Engineering Research Council, to whom I am indebted.

Finally, I should like to thank my mother and father for their help and support throughout this work.

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INTRODUCTION

The invention of the transistor in 1947 and its later embodiment in junction form, was the start of a new era in electronics.

This revolution in electronics, resulted from the practical realisation of the useful properties of semiconductors. These materials form a group, whose conductivities lie between metals and insulators, varying strongly, and in a calculable manner, with temperature and small impurity concentrations.

The initial work in this field was carried out on germanium, because it was a very tractable material, it was however realised that silicon offered a large potential, but could not practically be used at the time.

In 1954 silicon emerged at last as a transistor material and since then many new devices have been developed from this technology, with ultimately, large size reductions to these devices being possible. No other material has been as extensively developed, nor offers the natural oxide surface that affords many processing and device advantages.

Si and Ge have certain limitations. Some of the most notable are as follows:

- i) Their bandgaps are indirect and fixed, they are thus useless as light emitters, and even in the infrared they emit poorly.
- ii) Their indirect energy band structure is not suitable for transferred electron devices.
- iii) As a solar energy converter the bandgap of Si is too small for high efficiency, and for some applications its absorption coefficient is too low.

These limitations are thus the basis for the interest in compound semiconductors, and their application to advanced electronic devices.

One of the most important of such groups of semiconductors are binary, ternary and quaternary compounds of the group III and V elements. It is possible using these compounds, to overcome all the previously mentioned problems with silicon and germanium.

Many of the devices using these materials require layers to be deposited onto a single crystal substrate. This deposition is done "epitaxially" (i.e. the layer is grown such that there is an orientation relationship between the layer and the substrate), and a number of techniques have been developed to achieve this. One of the more important of these methods is Liquid Phase Epitaxy (LPE).

The requirements of growth techniques have gradually become more stringent. In addition, because of the disadvantages that are associated with LPE in its conventional form, it is becoming increasingly difficult to produce the required devices and to keep up with the advances made in other techniques.

The aim of this work, therefore, was to develop a new technique for LPE, which from a theoretical consideration, promised to overcome the major problems associated with conventional LPE. Thus, it was necessary to design and construct equipment, specific for this purpose, to firstly, grow a layer and ultimately, to conduct further experiments to investigate the effect of different growth conditions on the layers obtained.

As the work proceeded, it was found that the design and construction of the equipment could not be separated from the experimentation, and they proceeded hand-in-hand, with new additions being made to the apparatus throughout the work in order to improve the technique.

This thesis, after giving the relevant background information to the work in this field, contains details of the equipment designed and built, together with the experiments undertaken, and ultimately the results of the research conducted. This has been set out in six chapters, which it is hoped will take the reader progressively through the subject. A brief outline is given below.

Chapter One gives a brief introduction to epitaxy and the four main techniques of achieving it.

Chapter two gives a detailed review of the different LPE techniques, and the problems associated with them. Particular attention is given to the sliding boat method.

Chapter three discusses InP, which was the material used for both the epilayer and the substrates in this work. Included, are device applications for InP, and the practical considerations when using it for LPE.

Chapter four develops the theory behind this novel rotatory technique and gives the expected advantages, resulting from it.

Chapter five describes and discusses the design and the development of the apparatus for this new technique.

Chapter six describes and discusses the results of growth experiments.

Finally, chapter seven summarises the results and discusses the future development of the new technique.

CHAPTER 1. GENERAL REVIEW

1.1 INTRODUCTION TO EPITAXY

The word epitaxy is derived from the Greek, epi meaning upon and taxis meaning arrangement. Hence epitaxy is the growth of one crystal upon another with a definite orientation relationship and is sometimes described as oriented overgrowth.

Epitaxy became of technological importance when it was found that the growth of silicon epitaxial layers ("epilayers"), on silicon could be used to produce material of high quality. This made it possible to grow thin layers of different doping characteristics on a substrate, producing more abrupt p-n junctions and other interfaces than was otherwise possible.

The development of devices fabricated from III-V compounds and devices built up of layers of semiconducting material which are often ternary or quaternary, has made epitaxy technologically invaluable.

Three different types of epitaxial growth may be defined, these are:

i) **Homo-epitaxy.** This is the growth of an epitaxial layer of the same material as the substrate (e.g. InP layer on InP substrate).

ii) **Hetero-epitaxy.** This is the growth of an epilayer of a material of the same crystal structure as the substrate, e.g., (Ga,In)As layer on an InP substrate.

iii) **Heterostructural epitaxy.** This is the growth of an epilayer with a different crystal structure to that of the substrate. In this case epitaxy is possible because the epilayer grows in an orientation that has similar atomic spacing and symmetry of atomic arrangement to that of the substrate, (e.g. GaAs layer on Spinel).

1.2 TECHNIQUES FOR EPITAXIAL CRYSTAL GROWTH

The need to grow epilayers has led to the development of a number of different growth techniques. It is not the intention of this thesis to describe these in detail. However, to give the reader some background knowledge, the main techniques will be described very briefly. References to more detailed works are also given, should the reader wish to obtain further information.

1.2.1 Liquid Phase Epitaxy (LPE)

LPE involves the precipitation of material from a cooling solution on to an underlying substrate. The solution and the substrate are kept apart in the growth apparatus and the solution is saturated with the growth material until the desired temperature is reached. The solution is then brought into contact with the substrate surface and allowed to cool at a rate, and during a time interval, suitable for the growth of a layer of the desired thickness. When the substrate is a single crystal and the lattice constant of the precipitating material is similar or the same, as that of the substrate, then the resulting layer growth is epitaxial. This technique will be discussed in far greater detail in the following chapters. However, for a review on LPE the reader is referred to Hsieh [1].

1.2.2 Vapour Phase Epitaxy (VPE)

This technique utilises chemical vapour transport. For the growth of a III-V semiconductor compound, the group III and V elements are transported in the vapour phase as volatile halides and hydrides respectively. These vapours flow through a furnace where they react and deposit epitaxial layers on the substrate. The dopants required to produce device structures are introduced in a similar manner. For a detailed review of VPE the reader is referred to Pogge [2].

1.2.3 Metallo-Organic Vapour Phase Epitaxy (MOVPE)

This technique is, in essence, very similar to VPE, except that metallo-organic compounds of the group III or II elements are used instead of their halides. The group V or VI elements are generally introduced as hydrides.

The technique of MOVPE is now widely used and unlike with VPE, there are many suitable volatile compounds available for use. The technique is also capable of simultaneous growth over multiple substrates, producing epitaxial layers of excellent quality with good reproducibility.

Moss [3] and Moss and White [4] give a more detailed description of the equipment and chemical considerations of the technique.

1.2.4 Molecular Beam Epitaxy (MBE)

MBE is basically a rather sophisticated evaporation process. Epitaxial deposition occurs from molecular or atomic beams in ultrahigh vacuum.

The beams are usually generated thermally in sources known as Knudsen cells. The beams are controlled by shutters and travel in rectilinear paths to the substrate where they condense and grow under controlled temperature conditions. MBE equipment is often provided with in situ analysis facilities. For a review of the subject the reader is referred to Chang [5].

CHAPTER 2. REVIEW OF WORK ON LIQUID PHASE EPITAXY (LPE)

2.1 BACKGROUND

As already mentioned, the modus operandi of LPE depends on the fact, that as the temperature of a solution drops, the solubility of the dilute constituent in the liquid solvent decreases. Thus by cooling an already saturated solution in contact with a single crystal substrate, one can cause the deposition of an epitaxial layer.

Since a solvent is required for the material to be deposited by LPE, the usefulness of the process is limited to applications where a solvent can be found which does not adversely effect the epitaxially deposited layer. Fortunately, this is generally not a problem, since one of the constituents of the material to be deposited can be used as the solvent.

The advantages of LPE over other techniques such as VPE, has led to its development as one of the main techniques for epitaxial crystal growth. These advantages are:

- i) LPE equipment is simpler and cheaper.
- ii) Higher deposition rates can be achieved, thus allowing the growth of thick epitaxial layers in convenient time periods.
- iii) A wider choice of dopants.
- iv) LPE is generally safer as it involves the less extensive use of hazardous chemicals.
- v) Growth of aluminium containing semiconductors is possible by LPE. The gases for the growth of such compounds by VPE involves the use of corrosive vapours. Thus LPE initially provided the easiest route to the growth of these layers.
- vi) LPE can produce layers of excellent crystallographic perfection. This has led to the widespread use of LPE for the growth of LED and

laser structures.

Great advances have been made in some of the other epitaxial growth techniques, particularly MOVPE, and in order to remain competitive it has become necessary to improve LPE, which basically, has changed little since the development of the sliding boat apparatus in 1971 (discussed in section 2.2.3).

The following sections describe in detail the development of the LPE technique. Particular attention is given to the sliding boat LPE apparatus which remains the primary route to the growth of epitaxial layers by LPE. The limitations of the various apparatus are also discussed and these form the justification for the development of the novel LPE equipment of this work.

2.2 LPE EQUIPMENT

The growth of layers of controlled thickness and composition by LPE requires equipment designed to allow a solution (the "melt"), of the desired composition, to be placed in contact with a substrate for a well-defined period, under controlled temperature conditions. The required supersaturation for deposition is generally achieved by lowering the temperature of the solution. The three techniques of tipping, dipping and sliding have developed as the principal methods of establishing and then terminating contact between the solution and the substrate.

2.2.1 Tipping apparatus

The first experiments using LPE were conducted by Nelson [6] in 1963 for the growth of GaAs epilayers. These initial experiments used a tipping technique. Fig. 1 shows a typical growth apparatus ("boat") used for growing layers by the tipping technique. This is slightly more

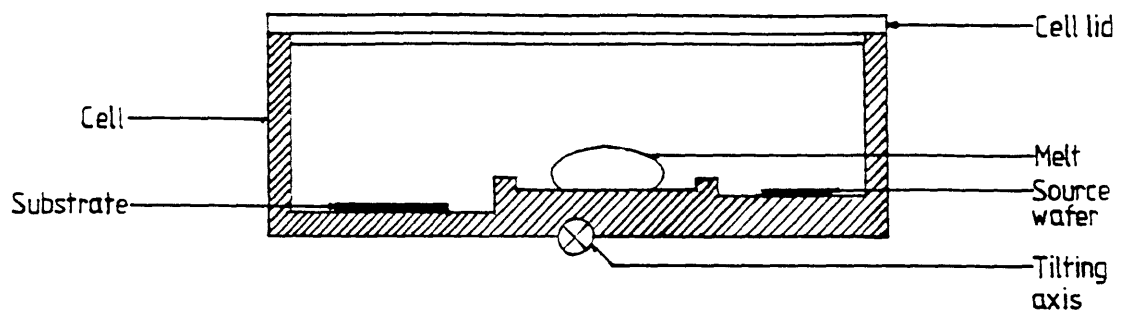


Fig. 1 A growth boat for LPE by the tipping technique.

complex than that used by Nelson [6], in that it is possible to keep the melt separated from both the source wafer and the substrate. The boat is placed inside a tube that permits growth to be carried out under a protective atmosphere. The tube is placed in a furnace that can be tipped to elevate either end of the boat. Initially the substrate end is raised so that the melt is in contact with the source wafer, forming a saturated solution. To bring the solution in contact with the substrate the furnace is simply tilted the other way, permitting the solution to flow down and cover the substrate. Finally, to terminate the growth, the furnace is tilted back to its original position. Any remnants of the solution adhering to the film surface are removed by wiping and dissolution in a suitable solvent.

Layers which were grown using the tipping apparatus described, were found to suffer from poor surface morphology. This resulted from a fundamental design defect, in that, the geometry of the boat, allowed the melt to be cooler than the substrate, (Minden [7]). This resulted in a phenomenon known as constitutional supercooling, (this topic is covered in greater detail in section 2.6.1). As a consequence of

constitutional supercooling, a growing surface can become unstable allowing protuberances to grow rapidly outward into a melt. This leaves a non-uniform surface, containing inclusions from the melt.

Another problem with the standard tipping apparatus was that the tipping angle was limited, and it was found that the melt sometimes became stuck and did not come into contact with the substrate. To overcome both these problems Donahue and Minden [8], designed a new boat. In its simplest form it consisted of a cylindrical crucible which lay horizontally in a tube furnace. The substrate was fixed to the roof or the end wall of the crucible and thus held above the melt which rested in the base. Fig. 2 illustrates a boat of this type. When growth is to commence the boat is rotated through 180 degrees, submerging the substrate. A further rotation of 180 degrees terminates the growth.

The tipping technique, although very simple and easy to operate, suffers from two important disadvantages. Firstly it is extremely difficult to alter the equipment to allow for the growth of multiple layers, and secondly it is difficult to remove the solution completely when the growth is terminated.

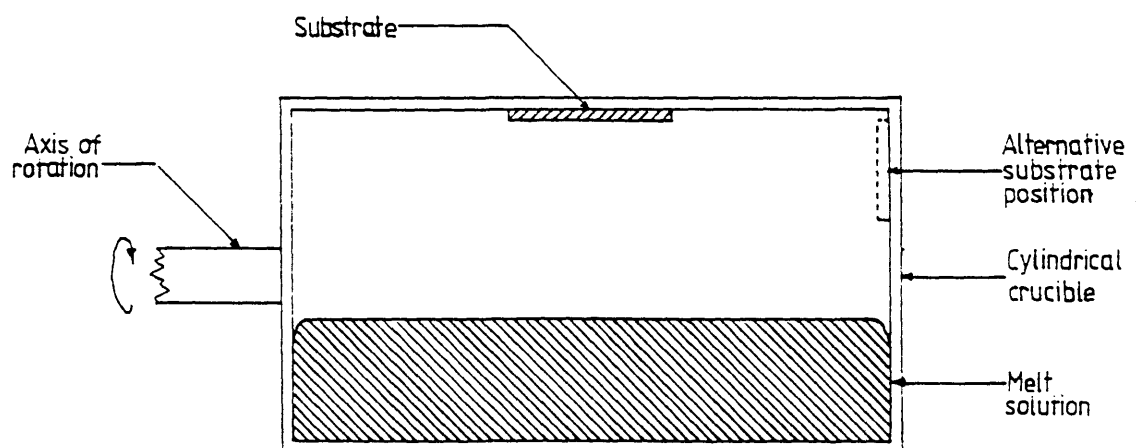


Fig. 2 An alternative design of tipping LPE apparatus which uses rotation to initiate and terminate epilayer growth.

2.2.2 Dipping apparatus

Dipping was first introduced by Linares et al. [9] in 1965 to grow layers of yttrium iron garnet (YIG) on gadolinium gallium garnet (GGG) substrates. Fig. 3 shows a typical LPE dipping apparatus. This consists basically of a vertical furnace and growth tube, with a crucible containing the growth solution at the lower end of the tube and the substrate fixed in a movable holder. It should be noted that the apparatus is also equipped with an isolated pre-heat furnace. This allows the substrate to be heated rapidly, away from the melt, preventing the condensation of material on the substrate.

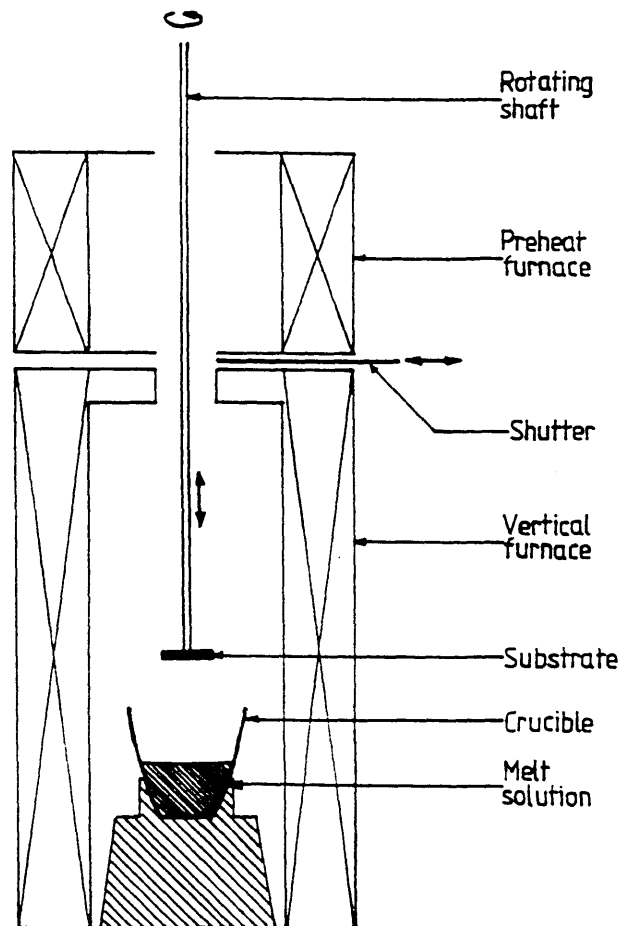


Fig. 3 Dipping LPE apparatus with a rotating substrate.

In the original dipping equipment, growth was initiated by lowering the holder to immerse the substrate in the solution. The melt contact was terminated by raising the holder to its original position. An improvement of this technique using rotation of the substrate during growth greatly enhanced the uniformity of the grown films, and also permitted the removal, by fast rotation, of any residual solution, that adhered to the slice upon its withdrawal from the melt, (the effect of rotation on growth will be dealt with in greater detail in following chapters, as this is the basis of the technique of this work).

The various dipping techniques are very simple and easy to operate. High-quality single layers have been obtained by this technique. However, once again it is extremely difficult to adapt the design for the growth of multiple layers. The ability to grow only a single layer is a major drawback. However, where the growth of one layer only is needed, dipping has been found to be an excellent technique, producing very good uniform films over large areas. Dipping has thus been used extensively for the growth of rare earth magnetic garnet films.

2.2.3 Sliding boat apparatus

The breakthrough in the design of LPE equipment occurred when Nelson [10] designed what is known as a graphite linear sliding boat. The major improvement over other designs was that it permitted the easy growth of a number of layers. The original design has proved so successful that it is still used, and in a form which differs little from the original. Fig. 4 shows a schematic diagram of a typical LPE graphite sliding boat. In its simplest form it consists of a number of wells cut into a graphite block. The block slides on a graphite baseplate, into which a recess has been made for the substrate to sit. The wells are filled with material to give melts of the desired

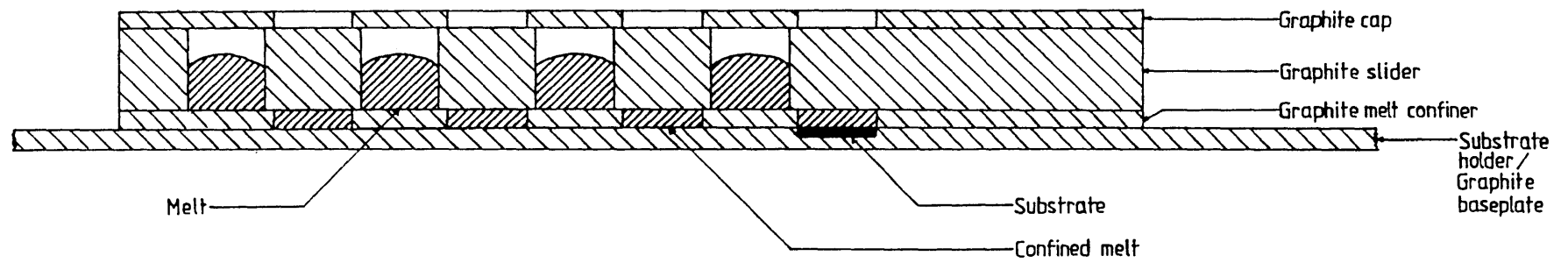


Fig. 4 A cross section through a typical LPE graphite sliding boat.

composition for epitaxial growth of layers of the correct electrical properties. The boat is held in a furnace at an elevated temperature. Lowering this temperature provides the necessary driving force for nucleation and growth of the epitaxial layer. Thus by pushing each well successively over the substrate and pausing for an appropriate period each time, a multilayer structure can be grown.

The apparatus shown in fig. 4 has several additional features to those already described. These are a graphite cap, which is used to suppress the loss of volatile components from the melt and an additional graphite slider which allows the original melt volumes to be reduced considerably (producing what is known as a confined melt). The latter is one technique for improving the uniformity of epilayers. The use of confined melts will be discussed again later in sections 2.7.1, 2.7.3 and 2.7.4.

2.3 FUNDAMENTAL ASPECTS OF LPE GROWTH

Early experimentation with LPE, found that layer growth rates observed were considerably higher than the rates predicted by theory (which assumes ideal solid behaviour, and the melt to be a simple solution). To explain these differences Tiller [11] pointed out that solute transport by convection and diffusion, surface attachment kinetics and constitutional supercooling can all be expected to play a role in determining LPE growth rates. The growth conditions and geometry of modern LPE equipment is such that the growth is limited to the diffusion of solute to the growing interface. This dependence simply on solute diffusion has allowed the growth rates to be predicted with reasonable agreement to theory. However, the other effects mentioned can still have considerable impact under certain conditions, e.g. convective currents when pushing the melt onto the substrate.

These effects are also applicable to the results obtained in this work and hence they will be considered in more detail later.

In the absence of convection, the only mechanism to transport the required material to the growing interface is diffusion. However, this leads to one of the worst limitations of the LPE technique, this being the impossibility in growing a ternary or quaternary epilayer with uniform composition throughout its thickness. The reason for the variation in composition, is that when the melt is brought into contact with the substrate, growth commences and the solution adjacent to the surface is rapidly depleted. The rate of depletion is dependent upon the segregation coefficients (i.e. the ratio of the concentration of a solute in the solid material grown, to that in the solution at the interface), supercooling, growth rate and diffusion coefficients of the various species present. This initial process is known as the transient stage. Following this, a stage known as the pseudo-steady-state condition occurs, this is where the diffusion of constituents of segregation coefficient $k > 1$, matches the loss due to incorporation in the growing epilayer. Conversely if $k < 1$, the pseudo-steady-state occurs when the diffusion of solute away from the growing interface matches the rate at which the solute is rejected by the growing epilayer. Ultimately as the melt volume is limited, the whole melt will become depleted and the composition of the epilayer will begin to drift. It can therefore be seen that in order to reach the pseudo-steady-state condition, the composition of the melt in front of the growing interface will have varied.

For the growth of binary compounds variation in solute concentration will have little effect on the epilayer composition, and will only alter the supersaturation and hence the growth rate. However, for the

growth of ternary and quaternary compounds, the effect will be to vary the composition of the growing material as well as the growth rate and therefore it is impossible to get an abrupt junction. The variation in interface concentrations is depicted in fig. 5 for both the case where $k < 1$ and $k > 1$. Initially it has been assumed that the composition of the melt is uniform and equal to C_0 . This concentration rapidly changes to C_t and C_p as growth proceeds. For the case of $k < 1$ the concentration of the solute in the solid will be increasing as the interface concentration increases. The converse will be true for the case of $k > 1$. Here the layers adjacent to the interface will become depleted.

The concentration profiles are dependent on the rate at which the species can interdiffuse. Thus if the growth rate is changed, it is obvious, that the concentration profiles will change, and hence the composition of the growing epilayer. This is shown in fig. 6.

The surface attachment kinetics are fundamental to crystal growth. As mentioned previously diffusion limitations generally dominate other effects in an ideal sliding boat apparatus. However, Rezek et al. [12] found that with extremely short growth times (less than 100ms), the

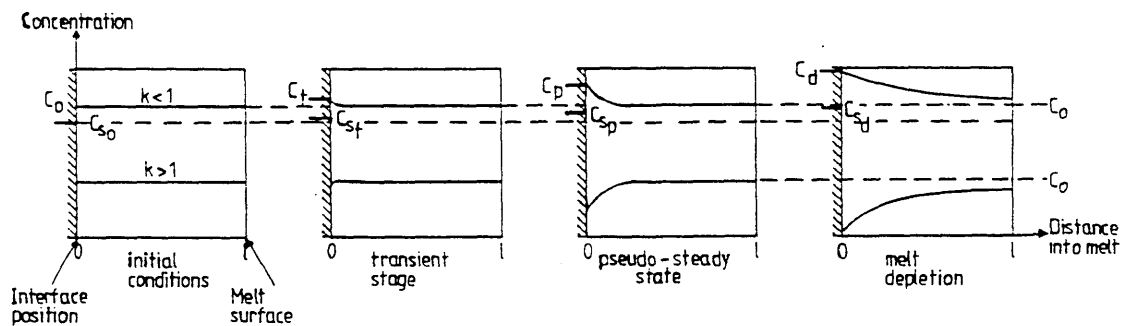


Fig. 5 Variations in solute concentration in the vicinity of a growing layer, for constituents of segregation coefficient < 1 or > 1 , for various stages of LPE.

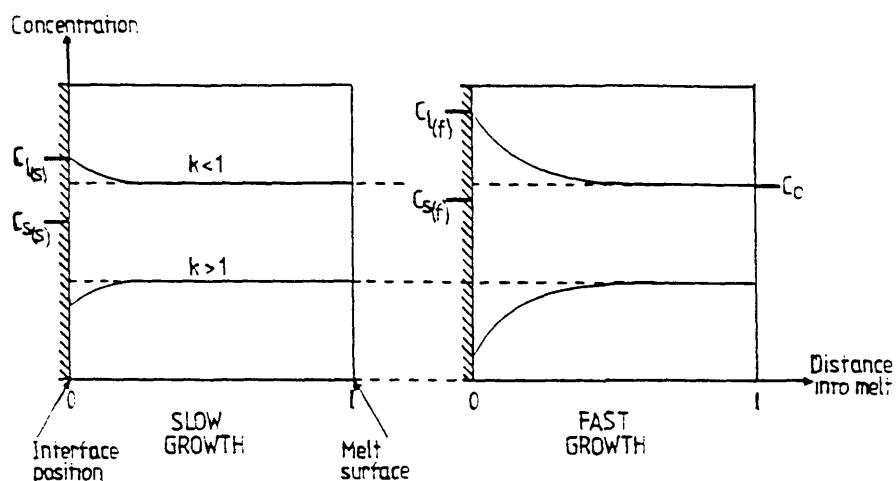


Fig. 6 The dependence of epilayer composition on the growth rate.

growth rate is less than predicted by theory and thus this growth can no longer be diffusion limited. To explain this they suggested that the attachment kinetics of the solutes on the surface of the substrate limit the process.

It has also been suggested by Nelson and White [13] that the greater crystallographic perfection of the layers obtained by LPE, compared to those grown by vapour phase techniques, is due to the higher surface mobility of the species which is trying to attach itself to the substrate surface. This high comparative degree of mobility results from the fact that, for an atom to be incorporated into the growing crystal from the vapour phase, a number of discrete bonds have to be broken with each step possessing an activation energy. In the case of LPE, each solute atom will be surrounded by a sheath of solvent species, and the removal of this sheath can be achieved easily, as it can be done in a comparatively large number of steps, requiring only a very small amount of energy for each step.

The large number of solvation states available in solution growth, was therefore thought by Nelson and White [13] to give the solute

species a higher degree surface mobility, to those in vapour growth, where bond formation with the surface effectively reduces the atom's mobility.

2.4 METHODS OF PRODUCING SUPERSATURATED SOLUTIONS AND LAYER GROWTH

As mentioned previously, the basis of the LPE process, is that the solubility of a solute in a dilute solution decreases as the temperature is decreased. This temperature decrease can be generated by a number of different methods. These are described in the following sections.

2.4.1 Steady-state growth

This technique is used when a thick epilayer is required of uniform composition. A "source crystal" is placed in the melt at a fixed distance away from the substrate. A temperature gradient is imposed between them, with the substrate being the coolest. During the entire growth the furnace temperature is not varied.

Growth occurs, because as one moves away from the source crystal towards the substrate, the solubility of the solute in the solution decreases, thus the solution in contact with the substrate will be supersaturated. When steady-state is established, dissolution from the source slice will equal the rate at which the epilayer is growing, with the concentration gradient in the solution providing the driving force for transportation of the solute from the source to the substrate. The advantage of this technique is that the composition of the layer is uniform (apart from the initial transient stage, (see section 2.3)), with no depletion of the melt possible as long as a sufficiently large source slice is used. The technique does, however, produce layers which tend not to be uniform in thickness due to convection effects.

2.4.2 Equilibrium-cooling technique

In this technique the solution and substrate are not initially in contact, and the system is heated to a temperature above the liquidus temperature of the initial solution. The solution is then cooled at a constant rate. When the temperature reaches the liquidus temperature (i.e. when the solution just becomes saturated), the substrate and solution are brought into contact and are thus in equilibrium.

A variation of this technique, using a source wafer is sometimes used. In this, the solution is initially held at a constant temperature in contact with a source wafer. Once the solution has equilibrated, it is moved to contact the substrate and cooling is started.

2.4.3 Step-cooling technique

The system is again, with this technique, initially held at a temperature above the liquidus temperature of the melt. The melt and substrate are then cooled at a constant rate to a temperature that is below the liquidus temperature, but not too low for spontaneous precipitation, and then held at this temperature. Melt and substrate are then brought into contact and kept at a constant temperature until growth is terminated. This is known as step-cooling, as it is equivalent to equilibrating the substrate and the solution at the liquidus temperature and then suddenly dropping the temperature in a step-like manner.

Step-cooling has the advantage that the initial supersaturation provides the driving force and this makes nucleation insensitive to inhomogeneities in the condition of the substrate surface. This therefore insures that simultaneous nucleation occurs over the substrate surface. Thus the surface morphology tends to be better by this technique than the equilibrium-cooling technique. The step-

cooling technique also allows the growth of layers of uniform and accurately controlled thickness, as it is less sensitive to temperature gradients and fluctuations.

2.4.4 Supercooling technique

As with the step-cooling, the substrate and solution are cooled at a constant rate to a temperature below the liquidus temperature, before being brought into contact. However, unlike the step-cooling technique, the cooling is continued at a constant rate after the contact has been made.

Hsieh [14] found that the supercooling technique has all the advantages of the step-cooling technique. In addition it is easier to maintain a constant cooling rate both before and after the melt is brought into contact with the substrate, than to cool at a constant rate before contact and then to have to hold a constant temperature when contact is made.

2.4.5 Transient-Mode Liquid Epitaxy (TMLE)

In this technique the melt is cooled to a temperature at or below the liquidus temperature (i.e. so that the melt is either saturated or supersaturated). The temperature of the system in this region is then held constant throughout the rest of the growth run. The substrate is held at a lower temperature than the melt. Growth is initiated by lowering the substrate into the melt. The cooling of the solution adjacent to the substrate surface creates a high degree of supersaturation. An epitaxial layer grows as the supersaturation is relieved. The growth rate increases rapidly initially and then decreases as the solution temperature adjacent to the substrate surface approaches the average temperature of the solution. After some time the total solution heats up to its original temperature. Thus as time

proceeds and the melt heats up, it will no longer be saturated and the epilayer will be etched-back. If the melt was originally saturated then ultimately no layer will be left, however if the melt was initially supersaturated then an epilayer will remain. Generally with this method, the growth is terminated by separating the slice from the melt before the temperature reaches its original value. This technique was first used by Deitch [15] in 1970 using a vertical dipping apparatus, with temperature differences up to 50 degrees centigrade between the substrate and the melt. More recently Moon and VanderPlas [16] used the technique for the growth of AlGaAs on GaP and GaAs on InP using a horizontal sliding boat apparatus. Both Deitch [15] and Moon and VanderPlas [16] found that this technique gave comparatively good quality epilayers.

2.4.6 Two-phase-solution cooling

In this technique the temperature of the solution is lowered far below the liquidus temperature, resulting in spontaneous precipitation within the melt. The substrate is then brought into contact with the melt and cooling is continued at the same rate without interruption. This method may be considered to be equivalent to the equilibrium-cooling method, except that departures from equilibrium at the start of growth can occur, and also the deposition occurs on both the precipitate particles as well as the substrate. The problem with the technique is that it is impossible to predict with any accuracy what the layer thickness is going to be. This uncertainty results from growth occurring unreproducibly on precipitate particles due to the variation between runs of the size, number, shape and location of these particles. Growth on the precipitates reduces deposition onto the substrate. The variation in precipitate growth is thus reflected by a

variation in the growth on the substrate.

N.B. For clarity the differences between these different techniques can be seen in fig. 7.

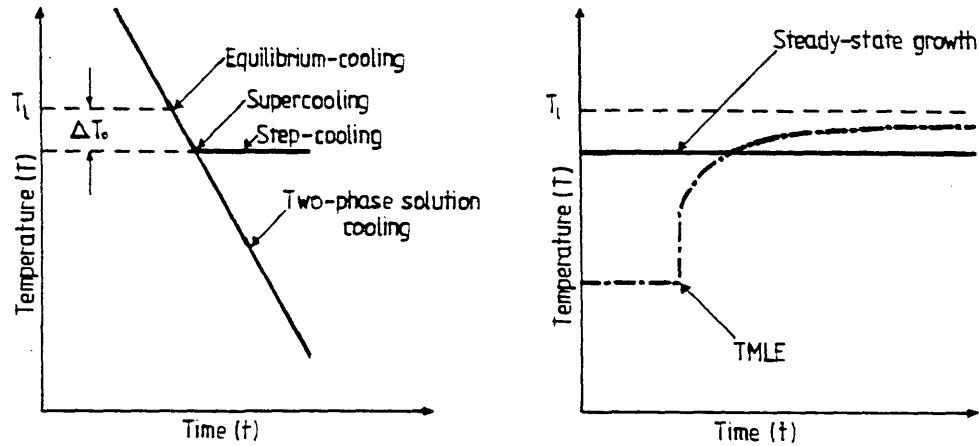


Fig. 7 The variation of substrate temperature with time, when employing the various solution cooling techniques for LPE growth. The arrows indicate the point at which the melt is placed in contact with the substrate. T_1 is the initial melt liquidus temperature and ΔT_0 is the difference between T_1 and the initial growth temperature for the step-cooling and the supercooling techniques.

2.5 CALCULATING EPILAYER THICKNESS

For most device applications the layers required are quite thin, being generally only a few microns at the most. Hence for the growth of these layers, the most applicable of these techniques listed in section 2.4 are equilibrium-cooling, step-cooling and supercooling. The growth rate for two component systems by these techniques have been derived (Hsieh [14]) by calculating the rate at which solute is removed from the growth solution. The following assumptions were made in order to derive the relevant equations:

i) The growth solution is isothermal. This assumption is valid for most growth solutions used in LPE, as the thermal diffusivity is high when compared to the solute diffusivity.

ii) Equilibrium is reached at the growing interface, therefore the solute concentration in the solution is given by the equilibrium phase diagram.

iii) Solute is only removed from the solution by deposition on the substrate (i.e. there are no precipitate particles on which growth can occur).

iv) The growth solution is semi-infinite i.e. melt depletion does not occur.

v) The diffusion coefficient and the slope of the liquidus curve are constant during the growth. Although both parameters are temperature dependent, this assumption is valid with the limited temperature intervals used in these techniques for LPE.

It was explained in section 2.3 that for the growth of LPE layers by the sliding boat apparatus, in the absence of convection, the rate-determining step is the diffusion of the solute to the growing interface. The growth rate (for the diffusion of solute to the growing interface) is thus calculated by solving the one dimensional diffusion equations.

Hsieh [14] solved the diffusion equations for equilibrium-cooling, step-cooling and supercooling techniques, to yield the following equations for the layer thickness:

For the Equilibrium-cooling technique

$$d = (2/C_{sm}) (D/\pi)^{1/2} (2/3) \alpha t^{3/2}. \quad (2.1)$$

For the step-cooling technique

$$d = (2/C_{sm}) (D/\pi)^{1/2} \Delta T_0 t^{1/2}. \quad (2.2)$$

For the supercooling technique

$$d = (2/C_s m)(D/\pi)^{1/2}(\Delta T_0 t^{1/2} + 2/3 \alpha t^{3/2}). \quad (2.3)$$

Where C_s is the concentration of solute in the growing crystalline material (e.g. concentration of P atoms in crystalline InP), m is the slope of the liquidus, (both m and C_s being expressed in terms of atoms per unit volume), D is the diffusion coefficient of the solute in the solvent, t is the growth time (seconds), α is the cooling rate, ΔT_0 is the temperature difference between the liquidus temperature and the growth temperature.

2.6 PROBLEMS ENCOUNTERED WITH LPE

This section will describe the more common problems that have been found to affect LPE growth in general, and which require careful equipment design and experimental procedure to overcome or minimise. The problems encountered are mainly difficulties in achieving uniformity both in composition and thickness of the layer grown. Clearly any variation in either of these two will lead to an alteration in both optical and electrical characteristics of the deposited material. This is particularly the case in thin optically active layers, as present for instance in some laser structures. Existing non-uniformities could also effect the deposition of subsequent layers. Therefore for reproducible manufacture of devices that operate as designed, such variations must be minimized.

2.6.1 Constitutional supercooling

This phenomenon results from the depletion of the solute in contact with the growing interface as described in section 2.3, therefore creating a concentration gradient away from the interface. This variation in concentration is represented in fig. 8 by a plot of

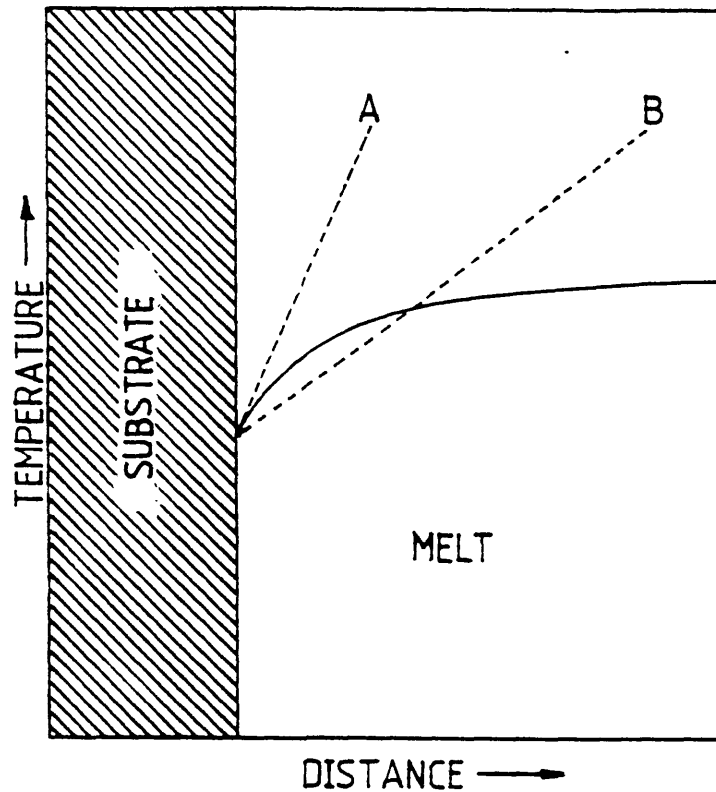


Fig. 8 The occurrence of constitutional supercooling. In this diagram the solid curve represents the liquidus temperature of the melt away from the substrate. Line B represents an actual temperature gradient away from the substrate, which will result in constitutional supercooling. Line A, shows an actual temperature gradient that will result in stable growth.

equilibrium liquidus temperature in the melt taken from a phase diagram. Constitutional supercooling will result if a temperature gradient exists away from the interface such as line B in fig. 8. As one moves away from the substrate, the solution supersaturation can be seen to increase. The result of such a temperature gradient is to make the growing interface unstable. Any protruberance that may develop will

encounter liquid of greater supersaturation than the surrounding flat regions, and will therefore tend to grow at an enhanced rate into the melt. This tendency for instability of the interface can be eliminated if a high enough temperature gradient is imposed. This is shown in fig. 8 by line A which can be seen to be sufficiently steep to avoid passing below the liquidus temperature at any point away from the interface. It is thus common practice, in LPE growth, to introduce a temperature gradient from the substrate into the melt to prevent constitutional supercooling. Experimentally, it is far from clear to what extent constitutional supercooling effects the morphology of LPE epilayers. For instance, Mattes and Route [17] reported that the introduction of a temperature gradient, improved markedly the surface morphology of their GaAs epilayers. However, they noted that the temperature gradient had a secondary beneficial effect on the morphology by increasing the nucleation density. Conversely, Vilms and Garrett [18] found that they were able to obtain smooth epilayers without a stabilising temperature gradient.

The growing interface can therefore be stable even when an apparently unstable temperature gradient exists. This was further demonstrated by Scheel and Elwell [19] who theoretically predicted the growth rate at which constitutional supercooling would occur, (it was explained in section 2.3, that, the depleted region is enlarged by a faster growth rate. Thus, for a given temperature gradient there will be a critical growth rate above which the growing interface will become unstable because of constitutional supercooling).

They found experimentally that the growth rate for instability was in fact much higher than their theoretically predicted value. They explained this discrepancy as a result of the existence of a metastable

region of the supersaturation gradient in which protruberance growth is negligibly slow. This effect is depicted in fig. 9. Line A represents the theoretical minimum temperature gradient for stable growth. T_{eff} represents an actual temperature gradient which gives stable growth and T_{crit} is the metastable limit, the shaded area therefore being the metastable region. A further quantity shown in fig. 9 is the "Concentration boundary layer thickness", δ_c , this is defined as the thickness of fluid in which the concentration of the solute changes from the bulk concentration, or more precisely, from 99% of it.

Layers of good morphology will result as long as the gradient of T_{eff} is higher than T_{crit} . The critical gradient depends on crystal growth rate, solute concentration, the interface temperature, the type of solvent, thermal or mechanical shock, vibration, and impurities. The

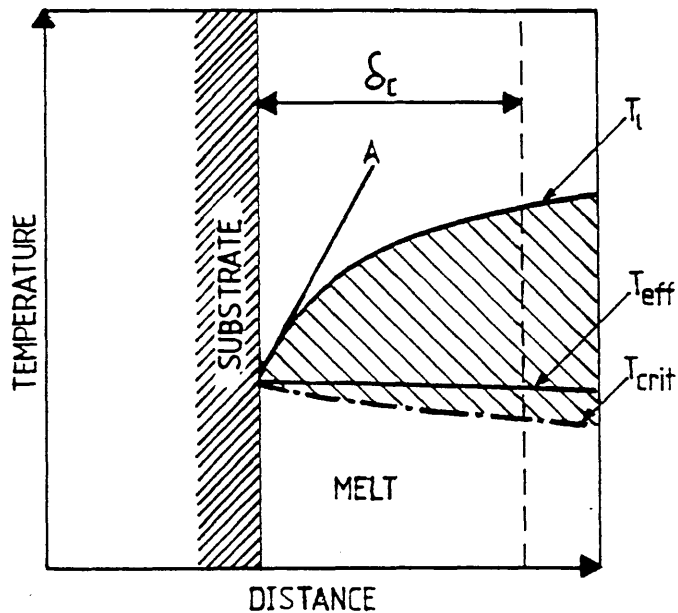


Fig. 9 The temperature distribution in front of a growing crystal. The shaded area under the liquidus temperature curve representing the metastable region.

ability to grow, under what would appear to be, unstable conditions, (i.e. in the metastable region), has been attributed by O'Hara et al. [20] to two factors. Firstly, there is the lower driving force for lateral growth of surface layers, as opposed to normal growth, which suppresses the growth of protrusions, enhancing the growth of layers. Secondly there is a capillarity term, which is the result of low energy being associated with habit planes, that is, the orientation which corresponds to a cusp in the surface energy vs. orientation plot (Wulff plot). Thus, any variation from planar growth (i.e. protrusions) are energetically unfavourable from a surface energy consideration.

2.6.2 Convective currents

There are three sources of convective currents in the melt and they are generally unwanted as they can result in non-uniform growth. These are:

i) **Thermally induced convection:** The presence of temperature variations across the melt can lead to convective flow as the density of a fluid decreases as the temperature increases.

ii) **Solutal convection:** The driving force for this kind of convection is, that the density of a solution depends on the concentration of the solute. Thus at the substrate interface where a solutal gradient exists, there is the potential for solutal convection depending on how the density varies with solute concentration.

iii) **Forced convection:** Convection of this kind results from the melt actually being physically stirred. An example of this is, for instance, when the melts in the wells of a sliding boat LPE apparatus are pushed over the graphite baseplate and as a result of frictional forces the melts roll and hence are stirred.

The effect of these convective currents on epilayer growth can be

understood by considering the distribution of solute away from the interface. This distribution has so far been discussed in terms of diffusion of solute to the growing layer only (section 2.3). However, a convective current will bring new undepleted melt close to the interface. Thus as a result, the depletion of the melt due to the diffusion limitations on growth will no longer extend as far into the melt (i.e. the boundary layer thickness will reduce). This in turn, implies that the melt in contact with the growing interface will be less depleted, resulting in the composition of the growing layer being different to that of the case with no convection. The convective current also has another important effect. Assuming the growth rate is diffusion limited (i.e. fast attachment kinetics), the reduced boundary layer thickness (i.e. thickness through which diffusion has to occur) results in a higher growth rate.

A solution which is stirred by the described convective currents has been found by Jakeman and Hurle [21], to be very unlikely to set up a perfectly stable flow pattern. An unsteady pattern of streamlines will result in any point on the interface being subjected to a varying growth rate and the composition of solid being deposited. The result is the growth of a non-uniform layer both in thickness and composition.

It should be noted, that as stated in section 2.6.1, that for the unstable growth of an interface, where constitutional supercooling is possible, the formation of a protruberance on the growing interface is required and that convective currents provide a mechanism for their formation.

The effects of convection are generally undesirable and therefore one must be careful in positioning the substrates to minimize them. Therefore it is necessary to consider the effects of placing the

substrate in various positions in relation to the melt and thereby discovering the one that is most favourable.

If the substrate is mounted vertically, then a solutal gradient will be set up along a horizontal axis in the solution. In addition a thermal gradient may be applied parallel to the solutal gradient in order to counteract constitutional supercooling. Unless the unlikely event occurs, of the two gradients in combination producing a zero density gradient along a horizontal axis, convection will occur. Thus for the case of the growth of III-V compounds where the solvent is denser than the solution, the material closest to the interface will become depleted and will tend to fall, fig. 10a. The boundary layer through which diffusion has to occur, will have a varying solutal gradient across it from top to bottom of the substrate as the falling solution becomes increasingly depleted. This results in the growth of a wedge shaped layer, which becomes more accentuated with time as the boundary layer also assumes a wedge shape in the opposite sense to the

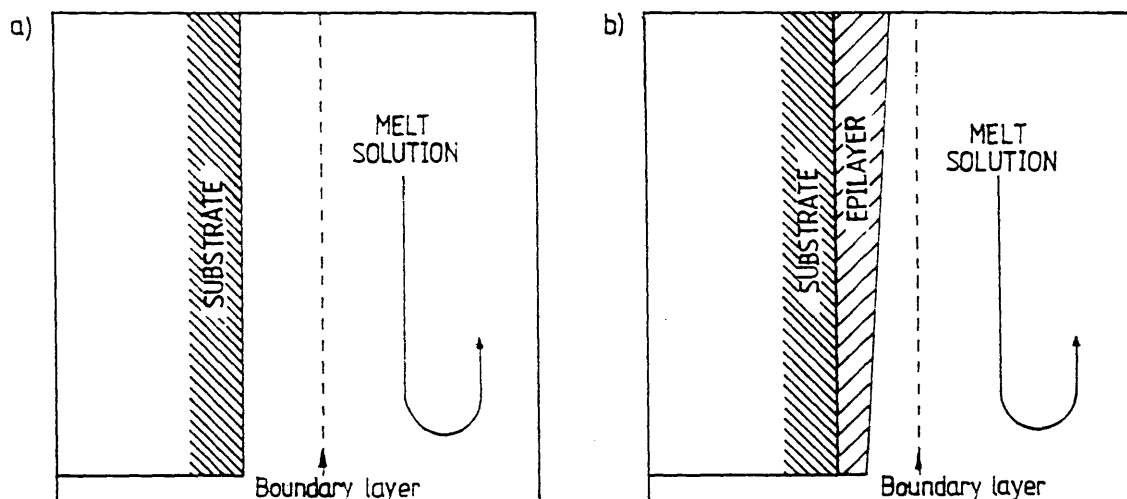


Fig. 10 The effect of using a vertical substrate for LPE. Where the schematic diagram a) shows the convective flow and b) shows the resulting wedge shaped epilayer and boundary layer.

layer, (fig. 10b). Hence a vertical substrate is an unstable geometry and should generally be avoided.

If the substrate is positioned horizontally, then there are two possible locations. Firstly, the substrate can be placed at the top of the melt, this is however unstable, as the density of a depleted melt is, for most solutions used in LPE, greater than the bulk melt density. The depleted melt in contact with the substrate will therefore tend to fall and cause convection. If a temperature gradient is used to suppress constitutional supercooling, then there will be cool liquid above hot liquid, and this also acts to destabilise the system.

The second location for a horizontal substrate is at the bottom of the melt. Here, an imposed temperature gradient and the solutal gradient in the melt near the substrate surface, produces a stabilising density gradient in the solution. Thus, this is the best location for the substrate, to minimize convection, and this is the geometry adopted by the horizontal sliding boat apparatus.

Even after adoption of this optimum geometry, convection is still difficult to eliminate. This is because forced convection from melt rolling, for instance, must be avoided and horizontal temperature gradients must be reduced to negligible proportions. The latter requires not only excellent furnace design and control but also control of the direction of heat flow when the furnace temperature is dropped for growth.

It is possible to overcome the problems, and to use convection to advantage. This is achieved by forced convection, introduced by a mechanical means in a controlled manner, such that the hydrodynamics for the system gives stable flow conditions. An example of this is dipping LPE, where a horizontal substrate is used in conjunction with

rotation. The rotating substrate flings fluid off it due to centrifugal force acting on the fluid. This results in fluid being drawn towards the centre of the substrate to replace that being flung off. The flow resulting from this action, gives a boundary layer which is uniform over the entire substrate. Such rotation, therefore, allows uniform layers to grow over large areas, removing any problems that convection can cause, also, because the boundary layer is dependent on the rotation rate, the growth rate and junction abruptness can also be controlled. As the use of rotation for LPE growth is the basis of the technique covered in this thesis, it will be discussed in greater detail in later chapters.

2.6.3 Diffuse junctions

When a supersaturated solution is brought into contact with a substrate, the solution in contact with it becomes depleted, and as explained in section 2.3 during this transient stage, the composition of this solution changes continuously. The composition of the epilayer will thus also be changing. The junction between the layer and substrate will therefore be diffuse.

This is a fundamental problem, particularly where thin abrupt junctions are required, e.g. multiquantum well structures. The abruptness can be improved by reducing the boundary layer thickness and hence the extent to which the solution has to become depleted before the pseudo-steady-state condition is reached. This can be achieved by controlled forced convection e.g. by rotating the substrate whilst dipping.

2.6.4 Crystal defects

Defects in the crystal structure of either the substrate, or, the epilayer, have in general a deleterious effect on future growth and on

the electrical and optical properties of a fabricated electronic device.

Dislocations are by far the most common form of crystal defect and this section will give a brief summary of their origins. For a more in depth analysis of crystal defects and their effects, the reader is referred to Chin [22].

Dislocations have two main effects on epitaxial crystal growth. Firstly, they can lead to preferential growth and thus uneven epilayers, (Moon and Antypas [23]). Frank [24] 1949, suggested a mechanism to explain preferential growth which requires a dislocation with a screw component to emerge at the surface. Additionally, edge dislocations have also been observed to produce preferential growth and Frank [25] has suggested a further mechanism to account for this.

The second consequence of the presence of dislocations is a degradation in the electrical and optical properties of the resultant device. For instance dislocations emerging at the surface of a substrate or an existing layer, can grow on, into subsequent epilayers. Such dislocations, known as "threading dislocations", act as non-radiative recombination centres, and thus reduce the efficiency of "light emitting diodes" (LEDs) and lasers.

Dislocations can either be present before, or generated during, the epilayer growth. The major causes of dislocations for these two cases and ways of minimizing their generation are as follows:

i) **Substrate dislocations:** These dislocations are present prior to epitaxial growth. They are generated either during the bulk crystal growth, or during substrate preparation.

In bulk crystal growth, where an encapsulant is used (this is common in the growth of III-V substrates, as one of the components is

generally volatile, and thus, requires an encapsulant to prevent excessive loss, and maintain stoichiometry), the dislocations can be generated by a thermal gradient across the encapsulant (boric oxide). Such gradients cause thermal stresses. Dislocations can also be generated around contaminants and inclusions, e.g. Indium inclusions in InP crystals will have a cluster of dislocations associated with them.

Mechanical fabrication, polishing and handling of wafers are the other main mechanisms by which dislocations can be introduced into the substrate.

To remove or reduce the effect of such defects, two techniques are employed in LPE. Firstly, the surface can be dissolved using an under-saturated solution. This is known as "meltback" and will be discussed later in section 2.7.6. Meltback will remove the surface damage from polishing for instance. Secondly a thick layer, known as a "buffer layer", can be grown on the substrate, covering both the substrate surface and most of the defects. Using this technique, defects are separated from the active regions within a device where they might effect its performance.

ii) **Misfit dislocations:** These are generated during the growth of an epilayer, when the periodicity of plane spacing in the substrate surface is significantly dissimilar to the parallel periodicity in the epilayer. The "misfit" can no longer be accommodated as strain at the interface, and results in an array of dislocations. This is depicted in fig. 11.

Choosing a material for an epilayer that has a matching lattice parameter to the substrate and the desired electrical properties, can eliminate this problem. One can use an intermediate layer with a graded composition, such that the lattice parameter matches the substrate

initially, changing gradually in composition and lattice parameter to finally match that of the required epilayer. However, this technique is not easily achievable by LPE.

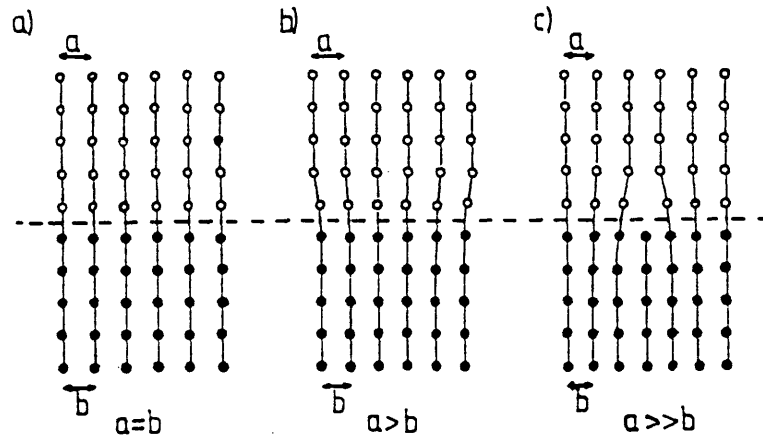


Fig. 11 A simplified view of the atomic planes at the interface between a substrate and an epilayer. Where a) shows lattice matching, b) shows lattice strain accommodating slight mismatch and c) shows formation of an edge dislocation as a result of large mismatch.

2.6.5 Thermal etching of substrate surfaces

The substrates commonly used in LPE usually contain a volatile component. Examples of this include P in InP or As in GaAs. At the elevated temperatures used for LPE such a component vaporises from the surface leaving faceted pits. These pits generally have a droplet of the remaining component in the bottom.

Thermally etched substrates can adversely effect the morphology and the local composition of a subsequently deposited epilayer. As InP was the substrate material used for this work, a detailed description of thermal etching of the material and its effects, will be given in the following chapter.

There are a number of techniques used for either suppressing, preventing or removing thermally induced damage. These include the following:

- i) Meltback of the surface.
- ii) Growing a buffer layer.
- iii) Keeping the substrate at a cooler part of the furnace until it is needed and minimizing the time it is exposed to high temperature.
- iv) Using a protective atmosphere, (e.g. a small amount of phosphine can be used to generate a high P vapour pressure over an InP substrate to prevent decomposition).
- v) For the sliding boat technique, keeping the substrate covered with the graphite slider to suppress decomposition.

2.6.6 Surface terraces and waves

Repetitive patterns of terraces or waves are two common surface morphologies of LPE layers grown onto substrates with orientations closely approximating to those of low-index planes (i.e. substrates with a small misorientation). These patterns are explained below.

i) Terraced surfaces are step-like, consisting of a series of roughly parallel and periodic treads, ("microfacets"). These treads are short sections of singular surfaces with steps in between to accommodate between that surface and the mean surface of the wafer. The terrace edges are lines of intersection of the singular plane with the mean surface.

The formation of terraces has been found to be critically dependent upon the substrate misorientation. It has also been shown that an accurately orientated substrate will show no ripples at all (Bauser et al. [26]). Terraces are formed as a result of minimising surface energy. This is due to the fact, that singular planes have a low

surface energy associated with them, compared to a non-singular surface.

ii) Surface waves can be defined as, a morphological form in which the surface presents a repetitive and generally, continuously variable range of angles to the mean plane of the interface in either one or two dimensions. Their formation, whilst due to similar causes as for surface terraces, has, unlike them, also been linked to constitutional supercooling. The evidence for this, is based on an analysis of the formation of perturbations on a planar interface, growing at a constant mean rate from a dilute solution (Small and Potemski [27]). This analysis predicts that the wavelength of surface perturbations, due to constitutional supercooling, should vary as the reciprocal of the square root of the growth rate. This dependence has been found to occur experimentally (Small and Potemski [27]).

2.7 PROBLEMS ENCOUNTERED WITH THE SLIDING BOAT LPE TECHNIQUE

This section will deal specifically with problems associated with the sliding boat LPE apparatus. The technique as previously mentioned is used almost exclusively for LPE growth and thus when designing a new variation of LPE equipment, and interpreting results from it, a knowledge of the problems associated with the sliding boat LPE technique is invaluable.

Once again, the problems encountered are generally associated with the production of uniform layers, and as explained in section 2.6, it is vital that any variations should be minimal.

2.7.1 Scaling up problems

As mentioned in section 2.6.2, convection can badly affect the uniformity of grown layers. With the sliding boat LPE apparatus, where wells filled with growth solutions are used, growing layers over large

areas obviously requires a sufficient quantity of the melt to cover this area. Preventing convection is difficult in this case, if the volume of the melt is large. This is because excellent temperature uniformity within the furnace is required, if temperature gradients within the melt are to be avoided. This becomes progressively difficult as the volume of the melt increases.

Preventing temperature gradients across the melt is made worse by the high thermal conductivity of the graphite walls of the wells, which impose a temperature gradient at the walls, reflecting any temperature fluctuation or gradient within the furnace. This is particularly problematic when the temperature is lowered for epilayer growth.

The melt volume, therefore, has to be kept small to prevent convection. A small melt volume has added stability, in that friction of the melt with the graphite walls suppresses convection. However, as the melt volume is increased the friction of the melt on the walls has less effect on convection.

A number of alterations have been made by various workers to the original basic design of the graphite sliding boat, in an attempt to give uniform growth over larger areas, (e.g. Tamargo et al. [28] and Leung and Schumaker [29]). These are shown in fig. 12.

The idea of the "confined melt", fig. 12b, with the much reduced height of melt, is to allow growth over a larger area than the original design, whilst only using a small volume of melt. The aspect ratio of the melt (small height to width ratio) and the comparatively large surface area of the walls in contact with the melt, together with the use of a graphite top on the melt and smaller side walls, forms a geometry which significantly reduces convective currents.

Although the confined melt geometry allows growth over a larger area

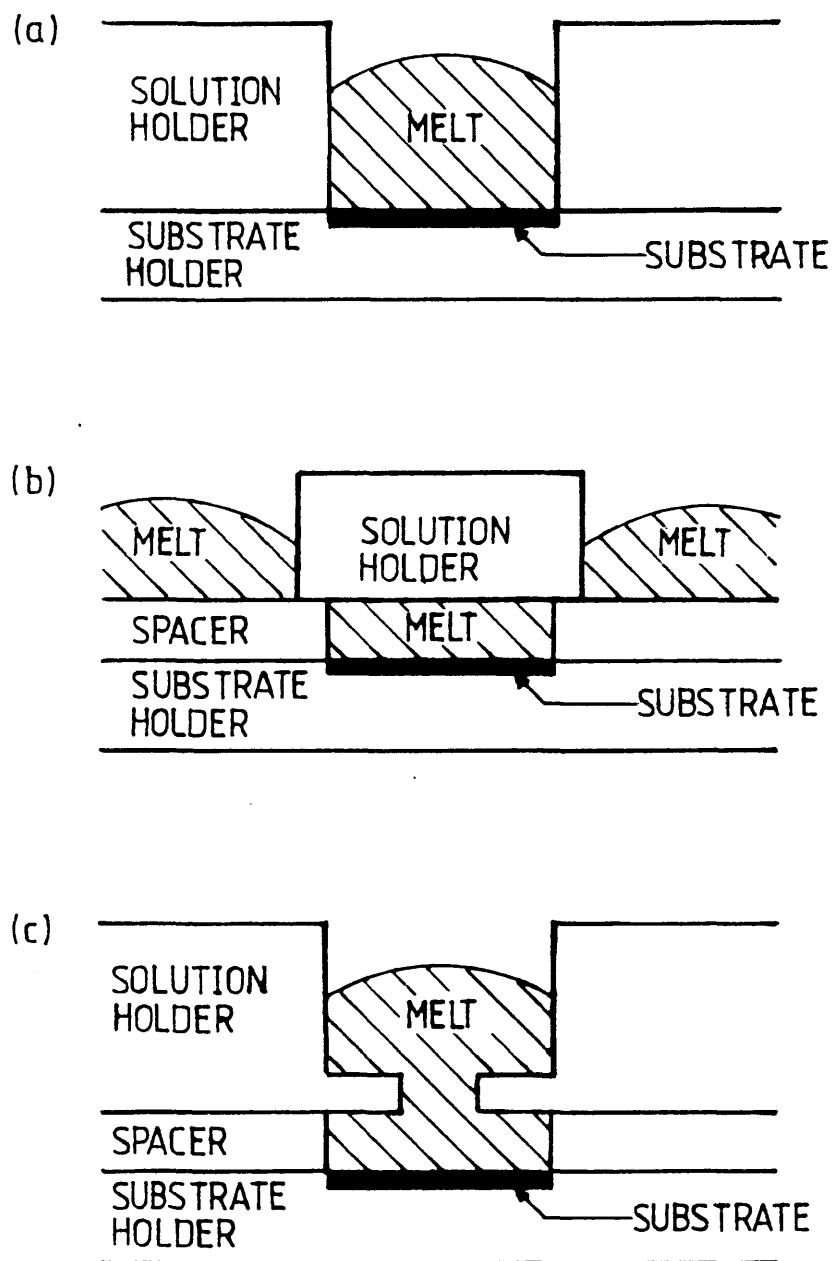


Fig. 12 The various designs for the LPE graphite sliding boat. The original design (a), the confined melt (b) and the baffled melt (c).

than the original design, the limited volume of melt and the large area over which growth is occurring, leads to the rapid depletion of the melt. Only thin layers can thus be grown before the composition and growth rate begin to change. Another consequence of the confined melt, as shown in fig. 12, is that the region at the edge of the substrate over which wetting does not occur, (due to the poor wetting of the graphite by the melt (see fig. 13)), will, increase in size. This is because the confined melt has a low mass and the confining plate cannot assume all the downforce of the original melt. Thus the confined melt will tend to give a larger unwetted region at the edge of the substrate where no growth can occur, unless some means of weighing down the melt is introduced.

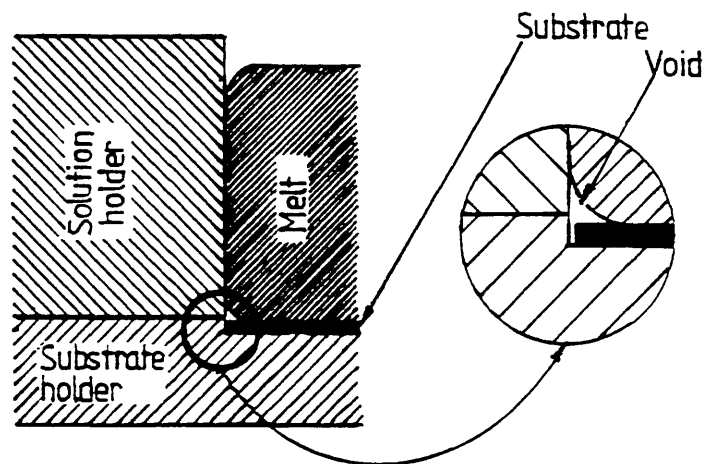


Fig. 13 The void generated at the base of the graphite melt container wall.

The other design for improving uniformity over large areas, shown in fig. 12c, is the baffled melt. The baffle makes the flow of convective currents more difficult in the region of the substrate, and is therefore an improvement on the original design. The baffled melt is

not as good as the confined melt at removing convection, as the volume of fluid below the baffle is still connected to the melt reservoir, and thus, convective currents in the bulk will effect the flow of fluid between and below the baffle. Hence convection still limits the area over which uniform growth can be achieved with this geometry.

However, the baffled melt does have several advantages over the confined melt. Firstly melt depletion, although faster than with the original sliding boat design, will not happen as rapidly as it would with the confined melt design, because, although the melt below the baffle behaves more like the confined melt, it is still supplied to a certain extent with solute from the bulk, and secondly the weight of the melt reservoir will push the melt into the well corners, reducing the voids at the edges. This gives better total coverage of the substrate than the other two geometries.

2.7.2 Melt carry-over

The phenomenon of melt carry-over results mainly from two conflicting requirements on the design of the sliding boat apparatus.

Firstly, there needs to be a clearance between the substrate surface and the sliding well assembly, to allow for increase in wafer thickness caused by the deposition. This also acts to prevent scratching of the epilayer by inadvertent particulate contamination. The latter could occur, for instance, if InP crystallites were broken off by insufficient clearance of the sliding assembly above edge growth, (i.e. preferential growth at the melt periphery, and is described in section 2.7.3). These particles would also scratch the boat, producing particles of carbon which might be incorporated in later layers.

Conversely, it is unfortunately necessary that the clearance between the sliding well assembly and the substrate should be kept to a

minimum, so that the melt is contained and efficiently removed.

The compromise between these requirements means that the gap sometimes is too large for complete removal of the melt when the growth is terminated (known as "poor wipe-off"). Thus the remaining melt, is left on the substrate and incorporated with the next melt which comes into contact with the substrate (i.e. the melt is carried over to the next solution, hence the term "melt carry-over").

Melt carry-over has a number of effects on the grown layer and subsequent layers, (Mahajan et al. [30] and DiGuiseppe et al. [31]). The remaining melt may, if it was originally saturated, allow further growth resulting in "mesas". If the melt was undersaturated, then continued dissolution could occur resulting in pits which may encroach into subsequent epilayers. When the new melt is brought into contact with the substrate the composition and saturation of the solution will be changed, altering the growth conditions from those expected.

This problem is minimized by reducing the unwanted non-uniformity of epilayers, allowing the gap to be as small as possible (obviously allowance for growth, still has to be made). The problem of edge growth will be discussed next, along with methods of reducing it.

2.7.3 Edge growth

It is frequently found in LPE growth, that the growth rate at the extremes of contact of the melt on the substrate is many times higher than anywhere else. Such preferential growth causes problems with melt removal and can result in epilayer scratching if the growth protrudes above the level of the recess in the baseplate.

A number of explanations for the occurrence of this phenomenon have been suggested, these are:

- i) The edges of substrates can become rounded during pre-growth

preparation. This exposes planes on which the attachment kinetics are faster than on the substrate plane. In the case where the melt reaches the boundaries of the substrate, it results in faster growth at the edge. This effect was observed experimentally by Astles et al. [32], who also found that by depositing a film of SiO_2 at the edges of the substrate, edge growth was reduced considerably.

However, when the melt contact area is the same or smaller than the substrate, surface tension effects, create voids at the well edges, (see fig. 13). Under these conditions the substrate edges will not be in contact with the melt. However, edge growth can still be observed, and may be up to thirty times the growth on the rest of the substrate. It is clear, therefore, that a further mechanism, resulting in preferential edge growth must be occurring.

ii) Small et al. [33], postulated that edge growth occurred because the solution present on the wafer, changed the shape of the deposited layer. This took place at the edges of the solution, and resulted in the establishment of the equilibrium contact angle, between the layer, solution and ambient phases. This effect is known to result in a feature known as "meniscus lines" and is explained in section 2.7.5. The resultant surface, has a characteristic S shape cross section. However, edge growth does not show this characteristic shape and Astles et al. [32], postulated that because of the long growth times involved, (when compared to the formation of meniscus lines), the edge growth is dominated by other effects.

iii) A number of authors, Astles et al. [32], Pak et al. [34], Mikawa et al. [35], have shown experimentally that two dimensional diffusion in the solution surrounding the edges results in edge growth, and that this is the dominant mechanism.

This is most easily understood by considering the case where the melt overlaps the substrate, fig. 14a. Over the substrate, solute is transported to the surface by diffusion vertically through the solution, in a one dimensional manner, (region 1 of fig. 14a). Hence the diffusion conditions are the same all over the surface of the substrate, and growth should be uniform (assuming convection does not occur). However at the edges of the substrate conditions are different, (region 2 of fig. 14a), where adjacent to the edge is a region which is not being depleted by the substrate beneath it. A solutal gradient will exist from the adjacent liquid to the substrate and therefore, the solute in this region will diffuse to the edge, adding to that diffusing vertically down onto it, (i.e. two dimensional diffusion). This leads to an enhancement in the observed growth rate.

The common geometry of the substrate extending to the well edges, or even beyond, will also result in two dimensional diffusion and hence edge growth, this is due to the surface tension void generated at the melt corners, fig. 14b. The fluid supported above this void, being undepleted by growth directly beneath it, will enhance the growth at

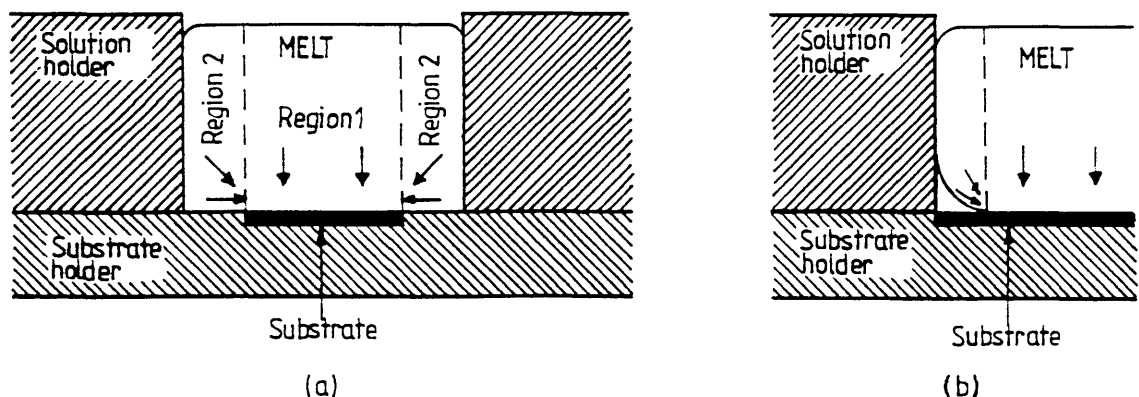


Fig. 14 The occurrence of two dimensional diffusion, for the case of an overlapping melt (a), and near a surface tension supported void (b). The arrows showing the direction of solute diffusion.

the edge of contact of the melt on the substrate.

Pak et al. [34], solved the diffusion equations for this growth mechanism in order to predict the height of the edge growth and they found that their theory was in reasonable agreement with their experimental growth. Conversely, Tamargo et al. [28] and Reynolds and Tamargo [36] found that convective flow and not 2D diffusion, was the dominant edge growth mechanism.

iv) Convective currents near the melt walls, resulting from the graphite walls being cooler than the melt (as explained in section 2.7.1), has been found by Tamargo et al. [28], Reynolds and Tamargo [36] and Rode and Sobers [37] to result in the production of edge growth.

The walls will cool the melt in contact with them. Locally, the cooler melt will sink, thus setting up a convective current. This undepleted supersaturated liquid will enhance the growth at points where it first impinges on the substrate, i.e. at the edges. Thus for the melt geometry depicted in fig. 14b the supersaturated melt above the surface tension void will be brought into contact with the substrate at the melt edges.

v) The cooler well walls, generate a horizontal temperature gradient in the melt. The melt near the substrate edges will be cooler than anywhere else on the substrate and thus this solution will have a greater degree of supersaturation, giving a higher growth rate.

This obviously contributes to edge growth but has been found not to influence it greatly.

There are thus several explanations for the phenomenon of edge growth. Whichever is the cause, it is always undesirable and there have been a number of different approaches to reduce its effect. Examples of

these are given below:

i) **Use of a baffle**, which covers the edge area and is only a small distance above the substrate. The melt between the baffle and the substrate will behave as a thin melt and will therefore deplete faster than the bulk. The growth rate will therefore be reduced at the edge so that its height will be lower than it would be without the baffle, allowing easier melt removal. However, the edge will, with this technique still be an area of variable thickness. This technique was used by Leung and Schumaker [38].

ii) **Use of a confined melt**. As explained in section 2.7.1 a confined melt reduces horizontal temperature gradients, and the dimensions of the melt prevent convection. Tamargo et al. [28] found that the use of a confined melt could give a 30 fold reduction in the height of edge growth and they attributed this large reduction to the removal of convective currents.

iii) **Use of a boat with a lower thermal conductivity than graphite**. This approach was adopted by Reynolds and Tamargo [36] who used both a sliding boat constructed of sapphire, and the confined melt geometry to reduce edge growth. The use of a material with a low thermal conductivity, such as sapphire, reduces thermal variations at the melt well walls. When combined with the confined melt technique, convective driven edge growth becomes unlikely. Reynolds and Tamargo found that the use of sapphire as opposed to graphite (with the confined melt configuration) led to a further reduction in edge growth height.

iv) **Use of a high supersaturation and short growth time** (i.e. step-cooling with a large temperature drop) was found by Pak et al. [34]; to reduce edge growth. Their experiments found edge growth to be 2D diffusion dependent. However, if the solution was supersaturated,

the initial growth was dominated (even at the edges of the substrate) by diffusion occurring perpendicularly. Two dimensional diffusion becomes dominant only after the initial supersaturation is relieved.

2.7.4 Melt rolling

When a melt is pushed along onto a substrate, frictional forces between the melt and the underlying baseplate result in the transfer of momentum. This causes the melt to roll. This is shown schematically in fig. 15.

Leung and Schumaker [29] studied the resultant flow achieved by pushing fluids over a baseplate. Experiments were performed using the original LPE melt geometry, baffled melts and confined melts. They found that the convection that occurred could continue for a considerable period of time, (in the order of minutes for the original

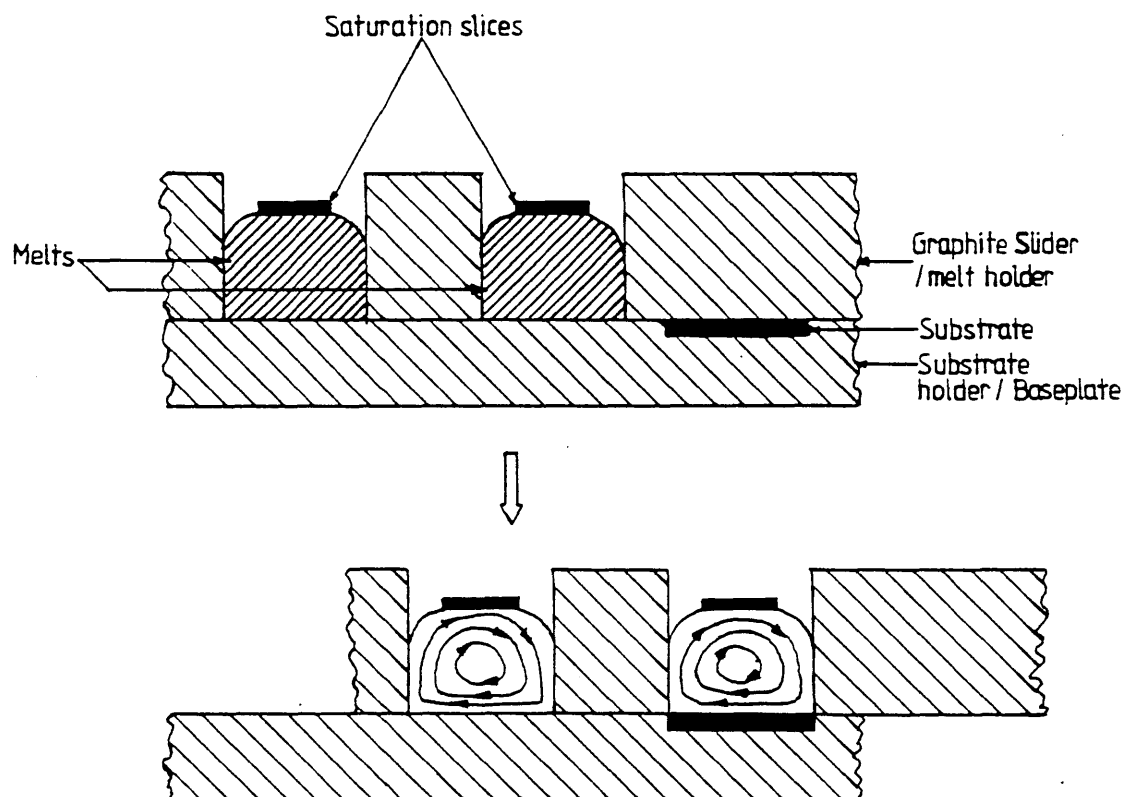


Fig. 15 The production of convection as a result of pushing the melt over the baseplate.

geometry), dependent on the velocity with which the melt was pushed over the baseplate.

The duration of the convection for the different melt geometries was found to decrease in the order original > baffled > confined. The reasons for this have already been discussed in section 2.7.1.

The convective currents thus generated, bring higher level supersaturated solution down to the substrate surface. This disturbs the concentration profile, and results in an enhanced growth rate as described in section 2.6.2. Thus, initially, the growth is dominated by convective mass transport, as opposed to diffusive mass transport. This gives a rapid initial growth until the convection has died down. This initial growth prevents accurate layer thickness calculations to be made when using the equations given in section 2.5.

Another consequence of melt rolling is that the mixing of the solution will almost certainly be non-uniform, making growth conditions on the substrate variable. This results in thickness and composition variations.

This problem can be reduced, but not eliminated, by the use of a confined melt, where the convection dies out rapidly. However, it is found that convective mass transport still dominates initially. Tamargo et al. [28] found that with a confined melt, for approximately the first ten seconds, growth was dominated by such convection.

2.7.5 Meniscus lines

When the melt is removed from the substrate, a series of lines is produced on the surface parallel to the direction in which the melt was pushed off the substrate. These surface lines have a characteristic cross section, having an "S" like shape. Fig. 16 shows a representative cross section through a meniscus line.

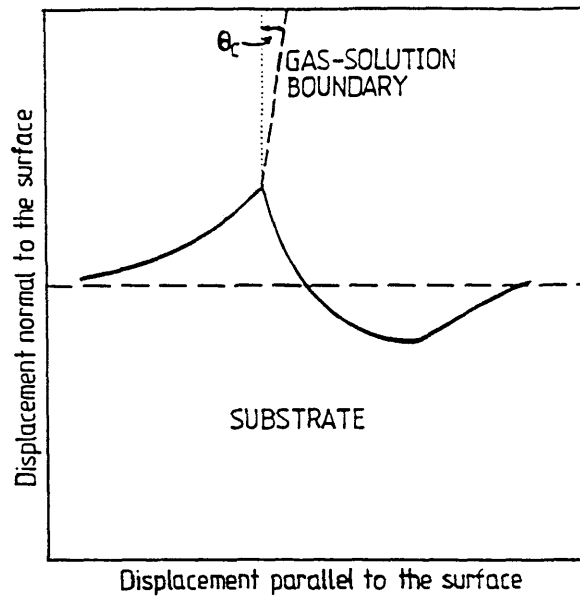


Fig. 16 A typical cross section through a meniscus line.

Small et al. [39], showed that the meniscus lines resulted from a vibratory motion of the three phase boundary that exists at the leading and trailing edges of the melt when it is moved. This has been described as "slip-stick" motion. They also [33], postulated that the behaviour of this three phase boundary, was the same as that observed occurring when a moving grain boundary intersects the surface. Such a boundary also moves with a slip-stick motion leaving a set of grooves on the surface. A further comparison with the motion of a grain boundary is that the line where this occurs is the junction of three interfaces, the equilibrium angle between them being determined by the relative free energies of the surfaces involved.

Mullins [40] described and analysed the case of the moving grain boundary and Small et al. [33] suggested that the explanation for meniscus lines was the same.

The theory of formation of meniscus lines can be summarised as

follows:

At the three phase boundary the formation of equilibrium angles between the surfaces produces a curvature in the solid surface (i.e. a perturbation). This provides the driving force for the transport of material. For the short times involved in the formation of meniscus lines, surface diffusion on the solid-solution and the solid-gas surfaces provide the mechanism for material transport.

Mullins and Small et al. had thus initially assumed that the phase boundary moved across the surface with an associated perturbation at its root (which as explained above, resulted from the formation of equilibrium angles between phases by surface diffusion). The size of this perturbation was calculated as being extremely small. Mullins had predicted the shape of this perturbation, solving the equation for surface diffusion within a moving reference frame and Small et al. noted that the shape was extremely similar to that of a meniscus line.

Mullins' analysis concluded that the shape of the perturbation was independent of conditions for a given equilibrium angle between the two solid-liquid interfaces, and that the perturbation would propagate across the surface with a steady velocity. This velocity is proportional to the reciprocal of the cube of the peak height of the perturbation above the substrate.

Under these conditions the moving phase boundary makes a critical angle, θ_c , with the vertical. Should the angle, θ become less than θ_c then the analysis shows that the perturbation decelerates and grows larger, while maintaining its shape. As a result of this deceleration any continued forward motion of the phase boundary will be pinned to the surface perturbation which can no longer move as fast. Thus θ will increase until the moving phase boundary can reduce its area, and

hence its surface energy, by breaking away. Then the root of the boundary can travel again across the surface carrying a new small surface perturbation. As the meniscus catches up with the bulk of the solution it will again decelerate and grow a new feature, too large to move, pinning the boundary at a new position. The cycle then repeats.

This particular problem of the sliding boat technique cannot be readily overcome. However, Reynolds and Tamargo [36], found that the size of the meniscus lines could be reduced by the use of sapphire liners in the melt wells. They suggested that this was a result of better wetting by the melt, on sapphire, than on graphite. This would affect the slip-stick motion of the melt.

2.7.6 Meltback

Dissolution of the substrate or "meltback" can cause problems in LPE in two main ways, these are:

i) **Production of an uneven surface:** The presence of residual surface films, thermal damage or mechanically introduced substrate damage, often causes severe problems during the growth of an epilayer. In order to overcome these and to present the growth solutions with a clean surface, the normal procedure employed is to use an in-situ "wash melt". This consists of an undersaturated solution, usually of the pure solvent, which is pushed over the substrate at an elevated temperature. The melt will not be in equilibrium with the substrate, since it is not saturated with solute, and thus the surface of the substrate will be dissolved away.

The process of dissolving the surface of a substrate, leads to contacting solution becoming richer in solute. As mentioned in section 2.6.2, for the majority of solutions used in LPE (particularly those used for the growth of III-V based compounds), the richer the solution

is with solute, the lower its density becomes. Thus in the sliding boat LPE geometry, the growth of epilayers is stabilised by density gradients within the solution. With a meltback step the density gradients are destabilising, leading to solutal convection and, therefore, uneven growth (as explained in section 2.6.2).

Nishinaga et al. [41], pointed out that although uneven surfaces are produced by meltback, there is a stabilising action opposing their formation. This is best understood with the aid of fig. 17. As the substrate is richer in solute than the solution, the solute will diffuse out into the melt. This diffusion occurs perpendicular to the surface and thus it can be seen that the solute tends to concentrate at dips in the surface (e.g. region A fig. 17). The melt in these dips in the surface will have a higher liquidus temperature resulting in a decrease in the meltback velocity, when compared to that of the surrounding peaks (e.g. region B fig. 17).

The effect of meltback on surface morphology can be reduced by using solutions with a small undersaturation (e.g. an In-P wash melt as opposed to a pure In wash melt). In the particular case of meltback

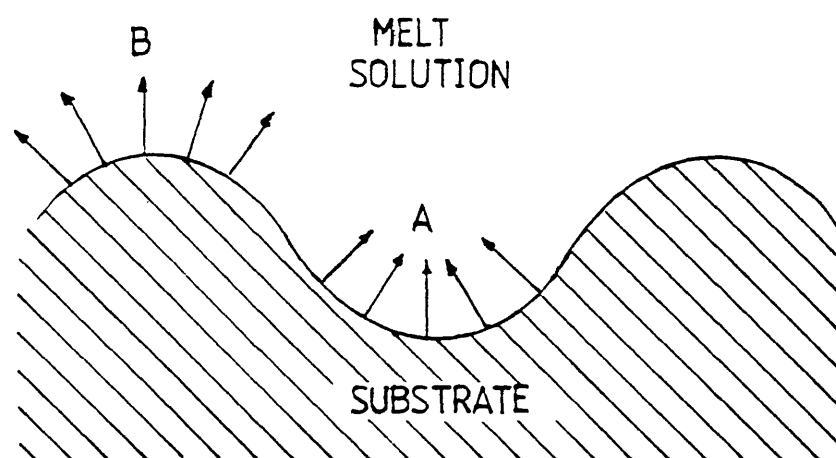


Fig. 17 The concentration of solute between peaks during meltback.

of InP, Nelson et al. [42], found that large improvements in the surface flatness could be achieved using an In-Ga-As melt. Here the flux of P atoms from the surface is low compared to an In wash. This is due to a small undersaturation and also because using this solution, the surface quickly becomes passivated with a composition in equilibrium with the melt.

ii) **Difficulty in growing certain layer combinations:** When a melt is brought into contact with a substrate surface, containing different elemental components, the two phases cannot be in equilibrium with one another (e.g. a GaAs substrate cannot be in equilibrium with a melt containing Al as well as GaAs). As a consequence, meltback of the substrate occurs. However, this meltback is usually limited since the dissolution rapidly produces a locally supersaturated solution that results in the deposition of a thin alloy layer. This prevents further dissolution (e.g. Panish et al. [43] found this to be the case for the growth from a Ga-Al-As melt onto a GaAs substrate).

The degree to which meltback occurs, is dependent on the solubility of the substrate components in the growth solution, since this determines how much dissolution is required to achieve a local supersaturation. For example, because of aluminium's low solubility in Ga-As solutions, only a small amount of meltback occurs when a GaAs layer is grown on a GaAlAs substrate, but a much larger and significant amount results when a GaAlAs layer is grown on a GaAs substrate. Only certain layer orders or combinations can therefore be grown without causing excessive meltback.

The problem is generally made worse the greater the number of dissimilar elements between melt and substrate.

The need to grow certain layer combinations has led to the

development of a technique to prevent the melt back of the important substrate layer. In this technique a thin "anti-meltback" layer is deposited on the substrate, then the melt for the desired layer is brought into contact with it. This dissolves the anti-meltback layer, thereby saturating the contacting melt with the elements required to prevent dissolution of the important underlying substrate.

2.7.7 Problems associated with the use of graphite as a boat material

The majority of LPE equipment is fabricated from machined high purity graphite. Graphite is used for several reasons. Firstly, it is readily obtainable in a highly pure form. Secondly, it can be machined to close tolerances, and thirdly, it has a low sliding frictional coefficient. However, there are also several problems associated with using graphite. It readily absorbs gases and desorbs them at high temperatures. Intimate contact between contaminated graphite and melt solutions allows the incorporation of impurities into the epilayer. Sulphur desorbed from the graphite wells has been found to be a major donor impurity species in the growth of InP and carbon itself, has also been found to be a principal acceptor impurity (Rhee and Bhattacharya [44]). As the surfaces of the graphite components rub over one another, carbon particles can become detached. These can also degrade epilayer morphology. Such particles have been reported to cause pin holes in layers leading to the meltback of the underlying layers (Kondo et al. [45]).

Attempts have been made to overcome the problems associated with graphite. These include constructing the equipment out of silica (Aylett et al. [46]). However, the necessity for accuracy and ease of fabrication rules silica out for the majority of uses. The problem of absorbed gases is usually reduced by heating the graphite to

very high temperatures, often in a vacuum, for a long period of time. This drives out absorbed gases prior to using the graphite for growth (Rhee and Bhattacharya [44]).

2.7.8 Melt preparation

In order to obtain close tolerances in the electrical and optical properties of a fabricated device, it is necessary to achieve accurate compositional control of the various layers that are deposited, and to maintain good reproducibility between growth runs. The small melt sizes used in LPE, (often only a few grammes), means that the quantity of the components used is extremely small. The reproducible weighing of such small amounts, accurately on a run-to-run basis is rather difficult.

This problem can be simply solved, as suggested by Nelson and White [47], by the use of a modified sliding boat apparatus that casts melts for future runs, from a large reservoir. This allows the composition of the melts to be fixed with a greater accuracy as well as improving the run-to-run reproducibility.

2.8 CONCLUSION

LPE has developed into one of the most important methods for growing epitaxial layers. However, rapid advances in the other growth techniques such as MOVPE and MBE, and the need for further improvements in material quality, has necessitated further development of the LPE technique, in order to overcome some of the limitations and inherent problems.

This thesis describes the work which was carried out using the Rotating Disk Liquid Phase Epitaxy (RDLPE) technique, in the expectation that many of the problems discussed above could be overcome.

CHAPTER 3. InP, PROPERTIES AND CONSIDERATIONS FOR LPE

3.1 INTRODUCTION

InP has many desirable electronic and physical properties. These have made it invaluable as a material that can be used actively in electronic devices and also as a substrate for thin film growth.

The work described in this thesis, has been carried out entirely using InP as the substrate material. This chapter gives a very brief summary of some of the more important properties of InP, and indicates the type of devices which have been made using it. Detailed consideration is also given to the use of InP as a substrate material for LPE.

3.2 PROPERTIES OF SINGLE CRYSTAL InP

This section describes briefly important properties of InP. For a detailed review the reader is referred to Bachmann [48].

3.2.1 Crystal structure

In common with the majority of III-V compounds, InP has a zincblende crystal structure, as shown in fig. 18. A common structure is of significance for the growth of heteroepitaxial layers. The lattice constant of InP, a_0 , at 291 K and 1 atm. pressure is 5.8688 Å.

3.2.2 Physical properties

InP single crystals have the following physical properties:

i) The melting point of InP, at an equilibrium decomposition pressure of phosphorous $p_m = 27.5$ atm., is $T_m = 1335$ K.

ii) The thermal expansion coefficient (α_t) at 755 K or less, is approximately constant and equal to $3.97 \times 10^{-6} \text{ K}^{-1}$. However, between 773 K and 1250 K;

$$\alpha_t = 3.97 \times 10^{-6} - 8.25 \times 10^{-9}(T-755) \text{ K}^{-1} \quad (3.1)$$

Where T is the temperature in kelvin.

iii) The density of InP, as a result of the change of the lattice constant described in ii), decreases as the temperature is increased. At the melting point the density is 4.638 g/cm^3 . This increases by approximately 9% upon melting.

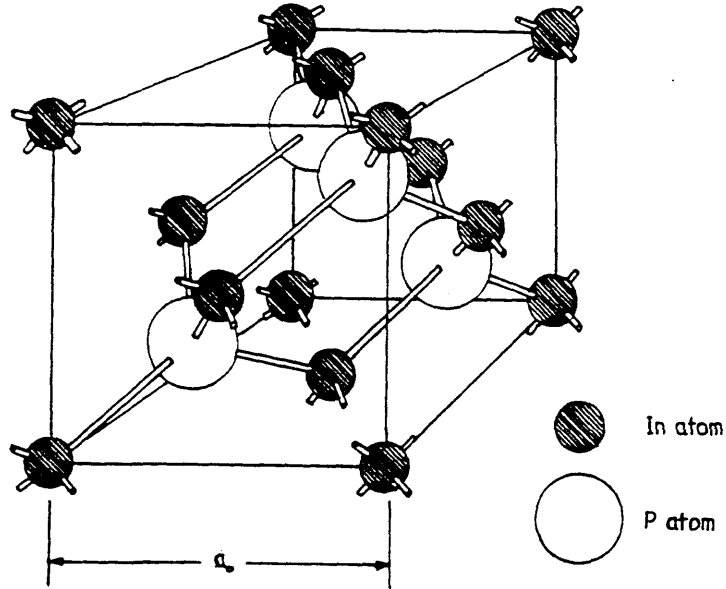


Fig. 18 The zincblende lattice structure of InP; a_0 is the lattice constant.

3.2.3 Band structure

There are a number of important features to the band structure for InP:

i) The fundamental band gap E_g , between the valence band maximum and the conduction band minimum is $E_g (300\text{K}) = 1.351 \text{ eV}$.

Its temperature (T) dependence is given by:

$$E_g = 1.421 - 6.63 \times 10^{-4} T^2 / (T + 162) \text{ eV.} \quad (3.2)$$

ii) The valence band maximum and conduction band minimum occur at the same point in k -space (defined as " Γ "). InP has a direct energy bandgap.

iii) There are two conduction band minima at different positions in k -space, they are at different energies and also the curvature of the E vs. k curve is different. This is a necessary requirement for microwave devices.

iv) The bandgap is close to the optimum value for the efficient conversion of solar radiation into electrical power by means of a single-junction photovoltaic cell.

3.3 InP BASED DEVICES

To give an idea of the uses for InP substrates and epilayers, this section will give a brief summary of the type of devices which have been made. For a detailed discussion of these uses the reader is referred to Bachmann [48], Foyt [49] and Bachmann et al. [50].

3.3.1 Microwave devices

InP is used for many different microwave devices. Although GaAs has the correct band structure to exhibit the Gunn effect, InP is used in preference, as it has a higher peak-valley ratio in the velocity-field characteristics, with a weaker temperature dependence. In addition, the electron diffusion coefficient is smaller than that for GaAs at the same normalised field. The result of these advantages is that InP devices can operate at higher frequencies (60-100 GHz), and at a higher power density than GaAs.

Examples of devices using InP are transferred electron devices (TEDs), transferred electron amplifiers (TEAs), transferred electron oscillators (TEOs), impact ionization avalanche transit time (IMPATT) diodes, barrier injection transit time (BARITT) diodes, metal semiconductor field effect transistors (MESFETs), and metal insulator field effect transistors (MISFETs).

3.3.2 Opto-electronic applications

InP is used extensively as a substrate material for semiconductor opto-electronic devices, both for light emitting devices and for detectors. These devices are generally designed for fibre optic communication systems.

The reason for choosing InP as the substrate material for such devices can be best understood with the help of fig. 19. This shows the lattice constant and bandgap, for two of the more important III-V semiconductor compounds, $\text{Al}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{Sb}_y$ and $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ solid solutions. The range of these parameters possible using these compounds is given by the area enclosed by the solid and dotted lines and the corner points of the constituent binary compounds. Lattice matched

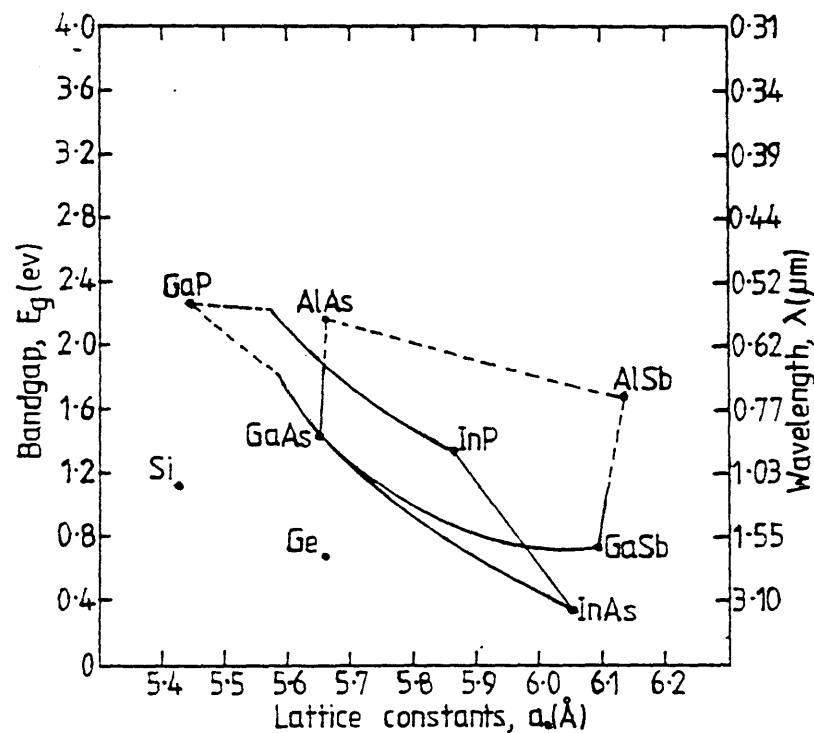


Fig. 19 The bandgap (E_g) and corresponding wavelength as functions of lattice constant for some important semiconductor elements and compounds.

compositions on this diagram will lie along a vertical line at a particular lattice constant. To choose the correct substrate and active layer for fibre-optic applications, it is necessary to know the optimum requirements for transmission via fibres. Currently the best optical fibres are silica-based and these exhibit zero light dispersion at $1.3\text{ }\mu\text{m}$ and lowest signal loss at $1.55\text{ }\mu\text{m}$. Examination of fig. 19 shows that of the available III-V semiconductor substrate materials, InP is the only one which is lattice matched to compounds which can act as emitters and detectors in this range of wavelengths. Of the two quaternary compounds, the GaInAsP system is the one normally used, as it has a wider range of wavelengths over which a direct bandgap exists. GaAs can be used as the substrate material for the GaInAsP quaternary, even though a large mismatch exists. However, it is necessary to initially deposit a graded intermediate layer. This complicates the structure and using LPE it is not practical. Thus the lattice matched combination using InP is generally used.

Devices using the latter substrate include; light emitting diodes (LEDs), lasers (of numerous different designs), PIN photodiodes, avalanche photodiodes, opto-electronic switches and photocathodes.

In addition to devices employed in fibre optic communications InP has been used for solar cells (Bachmann et al. [50]). InP allows complete absorption of solar light and efficient minority carrier collection within thin film device structures. This is because it possesses excellent electrical transport properties and direct absorption edges.

3.4 PRACTICAL CONSIDERATIONS WHEN USING InP IN LPE

3.4.1 Phase diagram of the In-InP system

Growth of InP by LPE, requires a suitable solvent to form the growth solution. The obvious choice is indium (In) as InP dissolves in the molten metal to a limited extent. Also since In is a constituent of InP, unwanted doping, by the solution will not occur.

A knowledge of how the liquidus temperature varies as a function of the composition of the solution is required (i.e. a phase diagram), in order to predict how much InP to add to the indium and at what temperature the solution becomes saturated.

Generally, for the solutions and temperatures used in the growth of III-V semiconductor compounds, the liquidus curve (i.e. the variation of the liquidus temperature with composition) can be represented by an expression of the form:

$$x = A \exp(-T'/T_1). \quad (3.3)$$

Where x , is the atom fraction of the non-metal in the saturated solution (i.e. the solubility of the non-metal), T_1 is the absolute liquidus temperature, A is a dimensionless constant, and T' is a temperature parameter which is a constant for a given system.

For the case of InP dissolved in In, Sol et al. [51] found the above equation to be:

$$x = 1.77 \times 10^3 \exp(-11431/T_1). \quad (3.4)$$

This equation has been found experimentally to allow predictions of the solubility of InP in In at different temperatures to within 1°C.

3.4.2 Dopants used in the growth of InP by LPE

For the majority of semiconductor devices, the pure intrinsic semiconductor is not used, but instead impurities are introduced into the semiconductor to give it the required electrical properties. These

impurities are known as "dopants" and they can act in one of two ways. In the first case, the impurities can "donate" electrons into the conduction band, and are known as n-type dopants. In the second case, the impurities "accept" electrons from, and hence introduce holes into, the valence band. These are known as p-type dopants. The concentration of these impurities is very low, being generally less than 10^{20} atoms/cm³.

In LPE growth, an epilayer is doped by adding a small amount of the impurity to the melt. The concentration of the dopant in the epilayer can be calculated using the distribution coefficient for that dopant. The distribution coefficient is defined as, the ratio of the atom fraction of the dopant in the epilayer to the atom fraction of the dopant in the melt. For a list of distribution coefficients the reader is referred to Kuphal [52].

The main n-type dopants used for InP are tin, germanium, silicon, tellurium, selenium and sulphur. For p-type doping, zinc, cadmium, magnesium, and beryllium are generally employed.

High resistivity, semi-insulating layers are sometimes required for devices. This can be achieved by doping the InP with either iron or cobalt.

3.4.3 Contact angles

The angle at which the melt meniscus touches a surface, such as the substrate, is known as the contact angle. The lower the angle, the better the melt wets the surface.

A low contact angle on the substrate or the well walls in a sliding boat apparatus can lead to problems of melt removal at the end of a run (i.e. melt-carry over). Conversely, a high contact angle of the melt on the substrate will give poor coverage of the surface.

Konig et al. [53] determined experimentally the contact angle of various melts on different substrates. They found that for a saturated solution of InP in In, that the contact angle of this melt with an InP substrate was approximately 48 degrees. However, the contact angle of this melt on a graphite surface was 144 degrees.

It should be noted that these contact angles allow reasonable coverage of the substrate surface and good melt wipe-off compared, to say, the same melt on a GaInAs substrate where the contact angle is as low as 18 degrees.

3.4.4 InP surface decomposition

One of the problems associated with using InP, arises from the relatively high, partial pressure of P over InP at rather low temperatures. This results in a preferential loss of P from the InP surface. The effect is that at the temperatures used in LPE, an unprotected InP substrate surface will degrade. This degradation occurs as pits, which are bounded by walls of well defined crystallographic planes. These pits contain the In that results from the decomposition process.

The thermal degradation and the presence of decomposition pits on a substrate surface can have severe effects on the growth of subsequent layers. It has been found by Sartorius et al. [54] and Temkin et al. [55], that, even at the early stages of degradation where no surface deformation has occurred, the effect of the decomposition is to introduce dislocations into the surface and to produce areas of high vacancy concentration. As mentioned in section 2.6.4 dislocations can propagate into subsequent layers and if such defects are in the vicinity of an active layer of a device, they will effect its optical and electrical properties. Dislocations can act as places where

preferential growth can occur (section 2.6.4). Sartorius et al. [54] and Temkin et al. [55] found these defects, even in samples which had been protected against decomposition and in which no visible signs of it could be seen on the surface.

Without protection, and under LPE growth conditions, the degradation can develop into decomposition pits. Chu et al. [56] studied the morphology of the pits and they found that the surface decomposes on (111) plane faces. The (111)In surfaces are chemically stable, as compared to the (111)P surfaces, which have two unpaired bonds associated with each P atom. Thus for example, for substrates with a (100) surface, these pits will be rectangular, growing most rapidly at the (111)P ends, (see fig. 20). Chu et al. found that the indium droplet associated with the pits enhanced the decomposition in the rapid growth direction, further elongating the pits.

Mahajan and Chin [57] found that dislocations and internal strain are associated with the formation of such pits and this will effect subsequent growth and device performance. The decomposition pits, with their associated In droplet, can lead to the formation of holes in subsequent layers (Mahajan et al. [30]), and generation of stacking faults (Takahashi and Nagai [58]). The exposure of surfaces of different orientation in the pit, will lead to different growth rates across a degraded substrate, as well as the possibility of varying compositions and lattice constants for the growth of certain compounds e.g. GaInAsP - whose composition depends on the growth direction.

Thus the elimination of thermal decomposition is desirable. Techniques which have been developed to overcome this problem are:

- i) Use of lower growth and pre-growth temperatures and also minimizing the time the substrate is exposed to high temperatures. This

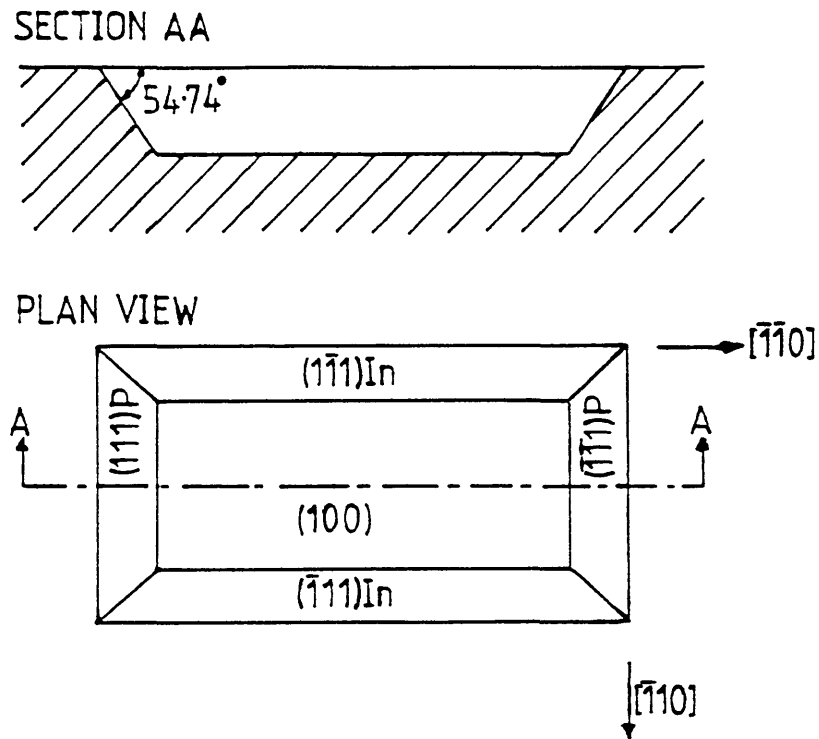


Fig. 20 A typical thermal decomposition pit, on a (100) InP surface.

will reduce the rate and extent to which decomposition can occur.

ii) **Covering the substrate with the graphite slider prior to growth.** This prevents rapid evaporation of P from the surface by reducing the volume which has to be saturated with P vapour. Sartorius et al. [54] investigated this technique and found that it did reduce decomposition compared to an unprotected substrate, but there was still a significant amount of decomposition occurring.

iii) **Covering the substrate with another InP slice to generate a saturated P pressure above the substrate.** Sartorius et al. [54] found that with this technique, surface deformation was reduced drastically compared to graphite protected samples, but decoration of defects due to decomposition was still seen.

iv) **Covering the substrate with a GaAs substrate.** This produces a thin intermediate arsenide layer to minimize evaporation of P. Sartorius et al. [54] investigated this and found that this protective measure yielded very similar results to the use of an InP cover wafer.

v) **Using a Sn-InP based melt.** With this technique, a melt consisting of InP dissolved in tin is held in a basket in the vicinity of the sample. The vapour pressure of P produced by this melt is higher than the pressure of P over the InP wafer and thus this suppresses decomposition. Sartorius et al. [54] found that of all the techniques so far discussed, this technique yielded the best surfaces, maintaining a mirror like finish on the substrate surface.

This technique does however complicate the construction of the equipment.

vi) **Using a mixture of argon and hydrogen gases in the furnace.** Generally hydrogen gas is used for the furnace environment during growth because of its reducing properties and the ease with which very high purity gas can be produced. With the addition of argon it was found (Pak and Nishinaga [59]), that a significant reduction in the decomposition was achieved due to the lower diffusivity of P in argon than in hydrogen.

vii) **The use of phosphine gas.** This is often the technique used to prevent decomposition. With this technique a small amount of phosphine is introduced into the hydrogen furnace atmosphere, this will subsequently decompose due to the high temperatures, producing phosphorous vapour which will prevent decomposition. Lum and Clawson [60] found, that using this technique the substrate surfaces could be kept at high temperatures for a long period of time, with no signs of decomposition having occurred.

However, the phosphorous vapour in the furnace can diffuse into the melt, and hence, change its composition (Yamauchi and Susa [61]). Thus care must be taken to use a very low phosphorous pressure to prevent this but it must be high enough to stop decomposition. For the growth of certain compounds, this may not be possible, so an alternative technique must be used.

viii) **Meltback of the substrate surface.** By using an undersaturated solution, the surface and any thermal damage may be dissolved away (as explained in section 2.7.6). However an uneven surface often results from this technique.

ix) **Growth of a thick buffer layer.** If a thick enough buffer layer is grown on the substrate, then a smooth surface will ultimately result. This can only be used where decomposition of the substrate and not the epilayers is the problem. This very often is not the case. For example, similar decomposition occurs on InGaAsP layers and other techniques, such as vii) must be used.

3.4.5 Crystal defects

As mentioned in section 2.6.4, dislocations originating from the substrate or from lattice mismatch affect device performance. However the degree to which these defects degrade device performance varies from material to material (Chin [22]).

A consideration of the role of dislocations in InP based devices reveals another advantage in the use of InP. It was found that although threading dislocations act as nonradiative recombination centres in InP and InGaAsP, they do not significantly affect device performance and reliability. The nonradiative recombination rate at dislocations is much smaller in InP relative to GaAs. Also, in laser structures, if there are any misfit dislocations, these are in the "confining layer"

and not in the active layer (the confining layer in a laser structure, bends the path the light takes, confining it to a narrow region around the "active" or light emitting layer), hence light emission is not strongly affected. These results are much better than for GaAs devices, where performance and reliability are much more strongly affected by the presence of dislocations.

CHAPTER FOUR: ROTATING DISK LIQUID PHASE EPITAXY (RDLPE)

THEORETICAL APPROACH

4.1 INTRODUCTION

This chapter describes the theoretical background to the novel technique which is the subject of this work.

Rotating Disk Liquid Phase Epitaxy (RDLPE) requires a supersaturated melt to be dropped onto a substrate which is rotating. The melt is then flung outwards due to centrifugal forces. The reason for adopting this particular method will be explained in detail later in this chapter, but briefly from a hydrodynamic point of view the fluid flow over such a rotating disk can reasonably be expected to form a uniform, controllable and reproducible growth conditions at all points on the substrate.

RDLPE is hydrodynamically very similar to the Dipping LPE technique described in section 2.2.2 and also to a technique of bulk crystal growth known as "Czochralski growth" (a technique in which a rotating seed crystal is slowly pulled out of a molten semiconductor). Dipping LPE with rotation has been used for the growth of magnetic garnet films (Giess et al. [62]), GaAs layers (Astles et al. [63]), GaP layers (Mottram and Peaker [64]) and for the growth of mercury telluride layers (Bylander [65]).

In all the above examples, it was found experimentally that the fluid flow associated with a rotating substrate allowed uniform layers to be grown over large areas and the rotation rate gave an added means for controlling the growth. As mentioned in section 2.2.2, a major drawback with dipping is the inability to grow multilayers. This should not be encountered in RDLPE as there are not the same difficulties in designing equipment for the purpose.

RDLPE is also analogous to the preparation of "Spun-on" thin films, commonly associated with the semiconductor industry (Washo [66] and Meyerhofer [67]). In this technique, a fluid, generally fairly viscous, is placed on the middle of the substrate. This is then spun for the required time and speed to achieve the necessary very uniform coating and thickness. This method is used in the semiconductor industry, for such applications as applying thin films of photoresist (a masking material), and polyamide (an interlevel and overcoat insulator). The technique has also been used for thin film deposition of paint, varnish, asphalt and the preparation of conformal films of phosphor impregnated photoresist for television screens.

4.2 HYDRODYNAMICS

The hydrodynamics for the fluid flow occurring in RDLPE has never been mathematically analysed and is a very complex system. However, comparisons can be made with the techniques listed in section 4.1. A particularly close comparison can be made with the dipping LPE method, which involves the rotation of a substrate (disk) whilst submerged in a fluid. Equations for the flow of the fluid on such a substrate have been determined (e.g. Karman [68] and Cochran [69]). In this system the rotation of the disk causes fluid near it to be carried by friction and consequently the fluid is flung from the disk by centrifugal forces. This loss of liquid is compensated by the flow of liquid in an axial direction to the disk, the majority of the flow being towards the centre, see fig. 21. Hence the flow is very similar to RDLPE, where a stream of liquid falls onto a rotating substrate and is flung off. The fluid flow in RDLPE and the equations relating to its behaviour, can reasonably be expected to be similar to the case for dipping LPE. Because of the similarity, RDLPE has the potential

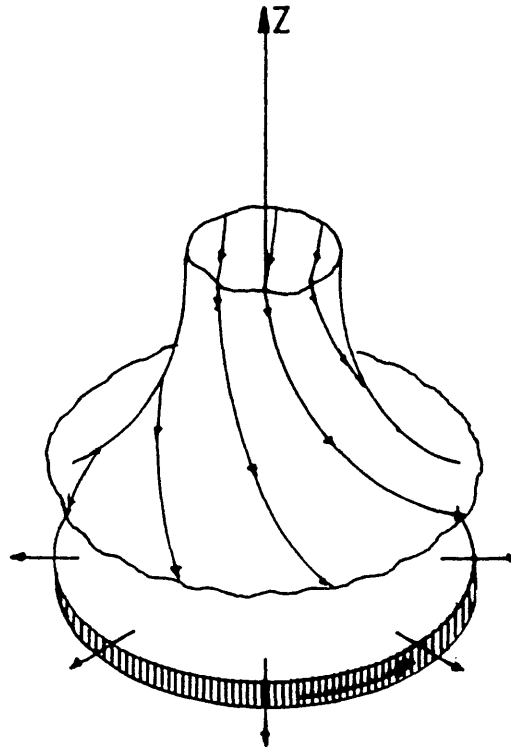


Fig. 21 The flow of fluid resulting from the rotation of a submerged disk.

to give all the advantages of the rotating dipping LPE technique, (particularly the uniform and controllable boundary layer conditions, over large areas), plus additional advantages over the sliding boat technique.

The following sections will derive the equations relating to the flow near a rotating disk for the two cases which have currently been analysed. These are directly applicable to RDLPE. Firstly, where axial flow results from the flinging of fluid off the disk, as explained above and secondly, for the case where an additional axial flow impinges on the disk (i.e. more liquid arrives at the disk surface than would be normally flung off by the rotation of the disk).

4.2.1 Hydrodynamics of a disk rotating in a fluid at rest

This situation is the most studied of the two. It is exactly analogous to the situation encountered in Dipping LPE (with rotation) and also to that in Czochralski crystal growth.

In the following equations the motion has been described in terms of cylindrical polar co-ordinates r, ϕ, z , (see fig. 22). Thus v_r, v_ϕ, v_z are the radial, circumferential and axial components of the velocity vector respectively.

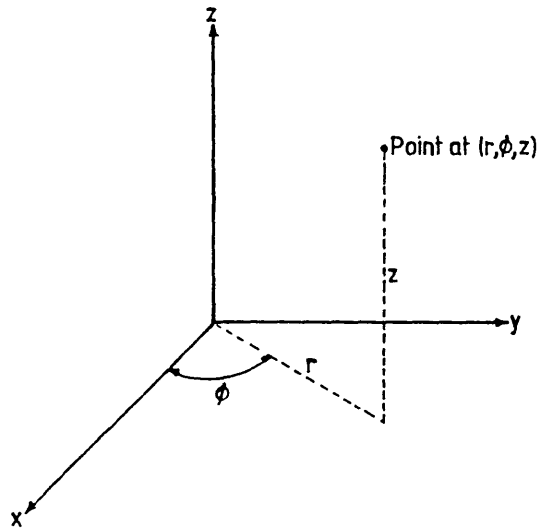


Fig. 22 Cylindrical polar co-ordinate system.

The situation can be considered to consist of an infinite plane disk at $z = 0$, rotating in a viscous medium around the axis $r = 0$ with a constant angular velocity ω .

For calculating the flow on the disk, a consideration of the half space $z \geq 0$ is required. The boundary conditions for the problem are as follows:

$$\left. \begin{aligned} v_r &= 0, \quad v_\phi = r\omega, \quad v_z = 0 && \text{for } z = 0, \\ v_r &= 0, \quad v_\phi = 0 && \text{for } z = \infty. \end{aligned} \right\} (4.1)$$

The value of v_z will be negative at infinity and there will be a motion away from the centre, particularly near the disk. This results from fluid being sucked onto the rotating disk to replace that which is flung off by the rotating action.

In order to derive expressions for the hydrodynamics, the first step is to obtain an estimate of the velocity boundary layer thickness, δ . This is the height of fluid over the surface of the disk in which the flow velocity changes from its free-flow magnitude (or more precisely, from 99% of it) to being stationary on the surface itself.

The fluid flow along the disk will be parallel to the shearing stress, τ_w , at this wall. Let χ be the angle between this flow direction and the direction of the rotational velocity of the disk at this point. The radial component of the shearing stress will be $\tau_w \sin \chi$. This will be balanced by the centrifugal force of the flow thrown off by the disk, i.e. proportional to $\rho r \omega^2 \delta$ (where ρ is the liquid density). But the circumferential component of the shearing stress, $\tau_w \cos \chi$, must be proportional to the velocity gradient of the circumferential velocity at the disk surface, i.e. $\sim \mu r \omega / \delta$ ($\sim$ denotes proportionality and μ is the viscosity). The following equations then apply:

$$\left. \begin{aligned} \tau_w \sin \chi &\sim \rho r \omega^2 \delta, \\ \tau_w \cos \chi &\sim \mu r \omega / \delta. \end{aligned} \right\} (4.2)$$

Eliminating τ_w from the equations (4.2) and assuming that the angle χ is independent of the radius (confirmed by observation), we obtain:

$$\delta \sim \sqrt{\frac{\nu}{\omega}}. \quad (4.3)$$

Where ν is the kinematic viscosity, ($\nu = \mu/\rho$). From equation (4.3) it is clear that the layer of fluid carried by the disk is uniform at all radii (hence, in terms of crystal growth, the growth conditions will be uniform at all radii and controllable by the rotation rate).

From equations (4.2) it also follows that the shearing stress is

$$\tau_w \sim \rho r \omega^2 \delta \sim \rho r \omega \sqrt{\nu \omega},$$

and the resistive torque of a disk of radius R , which is a product of shearing stress, area and arm will be

$$M \sim \tau_w R^3 \sim \rho R^4 \omega \sqrt{\nu \omega}. \quad (4.4)$$

To get a precise description of the fluid flow, one must integrate the Navier-Stokes equations (equations which describe the flow of any viscous fluid, see appendix A). The Navier-Stokes equations for the axially symmetric motion of an incompressible viscous fluid for which density (ρ), viscosity (μ), and heat conductivity (λ) are constant, in the absence of body forces, in cylindrical polar co-ordinates, take the form:

$$\left. \begin{aligned} \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + v_z \frac{\partial v_r}{\partial z} - \frac{v_\theta^2}{r} &= - \frac{1}{\rho} \frac{\partial p}{\partial r} \\ &+ \nu \left(\frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r} \frac{\partial v_r}{\partial r} - \frac{v_r}{r^2} + \frac{\partial^2 v_r}{\partial z^2} \right), \end{aligned} \right\} (4.5)$$

$$\frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + v_z \frac{\partial v_\theta}{\partial z} + \frac{v_\theta v_r}{r} = \nu \left(\frac{\partial^2 v_\theta}{\partial r^2} + \frac{1}{r} \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r^2} + \frac{\partial^2 v_\theta}{\partial z^2} \right), \quad (4.6)$$

$$\frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} = -\frac{1}{\rho} \frac{\partial p}{\partial z} + \nu \left(\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r} \frac{\partial v_z}{\partial r} + \frac{\partial^2 v_z}{\partial z^2} \right), \quad (4.7)$$

where p denotes pressure.

An additional equation of continuity must be considered in order to obtain a solution. This is as follows:

$$\frac{\partial v_r}{\partial r} + \frac{v_r}{r} + \frac{\partial v_z}{\partial z} = 0. \quad (4.8)$$

In order to integrate the equations for the case of the rotating disk, it is appropriate to replace z by a dimensionless measure of the distance from the disk $\zeta \sim z/\delta$ i.e. to put

$$\zeta = z \sqrt{\frac{\omega}{\nu}}.$$

The components v_r and v_θ are proportional to $r\omega$ where the factors of proportionality are functions of ζ , while the component v_z must be proportional to $\delta\omega = \sqrt{(\nu\omega)}$, owing to the equation of continuity.

Karman has proposed the following changes to the variables v_r , v_θ , v_z and p :

$$v_r = r\omega F(\zeta), \quad v_\theta = r\omega G(\zeta), \quad v_z = \sqrt{\nu\omega} H(\zeta), \quad p = -\rho\nu\omega P(\zeta). \quad (4.9)$$

Equations (4.5), (4.6), (4.7) and (4.8) take the following form, when using the values of v_r , v_θ , v_z and p given in (4.9):

$$\left. \begin{aligned} F^2 - G^2 + F'H &= F'', \\ 2FG + G'H &= G'', \\ HH' &= P' + H'', \\ 2F + H' &= 0, \end{aligned} \right\} (4.10)$$

where primes denote differentiation with respect to ζ .

The boundary conditions become

$$\left. \begin{aligned} F = 0, \quad G = 1, \quad H = 0 & \quad \text{for } \zeta = 0, \\ F = 0, \quad G = 0 & \quad \text{for } \zeta = \infty. \end{aligned} \right\} (4.11)$$

N.B. By making this substitution the viscosity terms on the right hand side of equations (4.5), (4.6) and (4.7) reduce to their last member, which represents derivatives in the direction normal to the plane of the disk. Therefore the equations of motion are identical with the boundary layer equations.

From the boundary conditions, (4.11), and the additional fact that H must tend to some negative limit, say $-c$, at infinity, then to a first approximation, we have, for large values of ζ ,

$$-cF' = F'', \quad -cG' = G'', \quad (4.12)$$

$$\text{giving} \quad F = Ae^{-c\zeta}, \quad G = Be^{-c\zeta}, \quad H = -c + (2Ae^{-c\zeta})/c, \quad (4.13)$$

where A , B and c are constants.

To obtain a more accurate solution, Cochran [69] went on to determine expansions in powers of $\exp(-c\zeta)$ for F , G and H which satisfy the differential equations and the conditions at infinity. The first few terms of these expansions are:

$$\left. \begin{aligned} F = Ae^{-c\zeta} - \frac{(A^2 + B^2)}{2c^2} e^{-2c\zeta} + \frac{A(A^2 + B^2)}{4c^4} e^{-3c\zeta} \\ - \frac{(A^2 + B^2)(17A^2 + B^2)}{144c^6} e^{-4c\zeta} + \dots, \end{aligned} \right\} (4.14)$$

$$G = Be^{-c\zeta} - \frac{B(A^2 + B^2)}{12c^4} e^{-3c\zeta} + \frac{AB(A^2 + B^2)}{18c^6} e^{-4c\zeta} + \dots, \quad (4.15)$$

$$H = -c + \frac{2A}{c} e^{-c\zeta} - \frac{(A^2 + B^2)}{2c^3} e^{-2c\zeta} + \frac{A(A^2 + B^2)}{6c^5} e^{-3c\zeta} - \frac{(A^2 + B^2)(17A^2 + B^2)}{288c^7} e^{-4c\zeta} + \dots \quad (4.16)$$

Cochran also derived expansions for F, G and H which satisfy the differential equations and the boundary conditions when ζ is near 0.

These are:

$$F = a_0 \zeta - \frac{1}{2} \zeta^2 - \frac{1}{3} b_0 \zeta^3 - \frac{1}{12} b_0^2 \zeta^4 - \frac{1}{60} a_0 \zeta^5 + \left(\frac{1}{360} - \frac{a_0 b_0}{90} \right) \zeta^6 + \left(\frac{b_0}{315} + \frac{a_0 b_0^2}{1260} \right) \zeta^7 + \dots, \quad (4.17)$$

$$G = 1 + b_0 \zeta + \frac{1}{3} a_0 \zeta^3 + \frac{1}{12} (a_0 b_0 - 1) \zeta^4 - \frac{b_0}{15} \zeta^5 - \left(\frac{a_0^2}{90} + \frac{b_0^2}{45} \right) \zeta^6 + \left(\frac{a_0}{315} - \frac{b_0^3}{315} - \frac{a_0^2 b_0}{252} \right) \zeta^7 + \dots, \quad (4.18)$$

$$H = -a_0 \zeta^2 + \frac{1}{3} \zeta^3 + \frac{1}{6} b_0 \zeta^4 + \frac{1}{30} b_0^2 \zeta^5 + \frac{1}{180} a_0 \zeta^6 + \dots, \quad (4.19)$$

where a_0 and b_0 are unknown constants.

Cochran determined the values for A, B, c, a_0 and b_0 from equations (4.14), (4.15), (4.16), (4.17), (4.18) and (4.19) using the fact that the functions F, G, H and their derivatives defined by these equations, join on continuously. Thus Cochran obtained the following values:

$$\left. \begin{aligned} a_0 &= 0.510; & b_0 &= -0.616; \\ c &= 0.886; & A &= 0.934; & B &= 1.208. \end{aligned} \right\} \quad (4.20)$$

With these results it is possible to determine F, G, H, F', G' and P as a function of ζ .

Experiments by Gregory et al. [70] found their results were very close to the theoretically predicted results given by Cochran [69]. Their measurements also confirmed that the values of F and G are the same at all radii, i.e. the boundary layer thickness is independent of radius.

The solution obtained strictly applies only to an infinite disk. Nevertheless, it remains applicable if it is assumed that the radius is large compared to the thickness of the fluid layer carried by the disk. Thus for a disk of radius R it is possible to calculate the moment of the frictional forces.

A ring of width dr and of radius r gives a resistive torque

$$dM = - 2\pi r dr \tau_{z\theta},$$

where
$$\tau_{z\theta} = \mu \left(\frac{\partial v_{\theta}}{\partial z} \right)_0 = \rho r \nu^{1/2} \omega^{3/2} G'(0) \quad (4.21)$$

is the circumferential component of the shearing stress. Therefore, the torque over the entire disk, of radius R, wetted on one side is given by:

$$M = - 2\pi \int_0^R r^2 \tau_{z\theta} dr. \quad (4.22)$$

Inserting the value for $\tau_{z\theta}$ we obtain:

$$2M = 0.616 \pi \rho R^4 (\nu \omega^3)^{1/2}. \quad (4.23)$$

The dimensionless moment coefficient is defined by the equation

$$C_m = \frac{2M}{(\rho \omega^2 R^5)/2}, \quad (4.24)$$

and is thus equal to

$$c_m = - \frac{2\pi G'(0) \nu^{1/2}}{R \omega^{1/2}} \quad (4.25)$$

or, using the Reynolds number (a dimensionless number, useful for predicting the onset of turbulence, discussed in greater detail later in section 4.3.2)

$$R = \frac{R^2 \omega}{\nu},$$

we get

$$c_m = \frac{3.87}{R^{1/2}}. \quad (4.26)$$

Experimentally this equation has been found to hold for R less than 3×10^5 , above which the flow becomes turbulent.

Finally, one can calculate, Q , which is the volume of fluid pumped outwards from one side of the disk, per second, as a result of the centrifugal effect (i.e. the quantity being sucked axially onto that side per second). This is described by the following equation

$$Q = 2\pi R \int_{z=0}^{\infty} v_r dz.$$

Evaluating the integral we obtain:

$$Q = 0.886 \pi R^2 \sqrt{\nu \omega} = 0.886 \pi R^3 \omega R^{-1/2}. \quad (4.27)$$

Whilst the velocity components have been obtained exactly, the boundary layer thickness has only been determined as being proportional to $\sqrt{\nu/\omega}$. Targ [71] approximately solved the equations of motion for a disk, only partially taking account of inertial terms. In so doing he obtained an equation for the boundary layer thickness.

In his analysis he accounted for the fact that the flow in the boundary layer, at the disk, is smooth. He thus replaced the components of acceleration of the fluid particles on the left hand side of equations (4.5), (4.6), (4.7) and (4.8), with their averages across the boundary layer. Equations (4.5), (4.6), (4.7) and (4.8) can thus be written as:

$$\left. \begin{aligned} \frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial (rv_r)}{\partial r} \right] + \frac{\partial^2 v_r}{\partial z^2} &= \frac{1}{\mu} \frac{\partial p}{\partial r} + rA(r), \\ \frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial (rv_\theta)}{\partial r} \right] + \frac{\partial^2 v_\theta}{\partial z^2} &= rB(r), \\ \frac{1}{r} \frac{\partial (rv_r)}{\partial r} + \frac{\partial v_z}{\partial z} &= 0, \end{aligned} \right\} (4.28)$$

where

$$\left. \begin{aligned} A(r) &= \frac{1}{\nu r \delta} \int_0^\delta \left(v_r \frac{\partial v_r}{\partial r} + v_z \frac{\partial v_r}{\partial z} - \frac{v_\theta^2}{r} \right) dz, \\ B(r) &= \frac{1}{\nu r \delta} \int_0^\delta \left(v_r \frac{\partial v_\theta}{\partial r} + v_z \frac{\partial v_\theta}{\partial z} + \frac{v_r v_\theta}{r} \right) dz. \end{aligned} \right\} (4.29)$$

Equation (4.7) has been omitted because it serves only to determine the pressure.

As before, Targ assumed that on the outer limit of the boundary layer there is only an axial component to the velocity due to suction, and that the friction $\tau_{z\theta}$ at the boundary vanishes. Together with the condition of no slip at the disk surface, the boundary conditions become:

$$\left. \begin{aligned} \text{for } z = 0 \quad v_r = v_z = 0, \quad v_\theta = \omega r, \\ \text{for } z = \delta \quad v_r = v_\theta = 0, \quad \frac{\partial v_\theta}{\partial z} = 0. \end{aligned} \right\} (4.30)$$

As previously discussed in this section, the solution is of the form

$$v_r = rf(z), \quad v_\theta = rg(z), \quad v_z = h(z), \quad (4.31)$$

which assumes that δ is constant along the radius; $\delta = \delta_0 = \text{constant}$.

Inserting these values into (4.28), and remembering that in the present situation $\partial p / \partial r = 0$, the following equations result:

$$f''(z) = A, \quad g''(z) = B, \quad 2f(z) + h' = 0. \quad (4.32)$$

For the first two equations, the left hand sides are functions of z , whilst the right hand sides are functions of r . It, therefore, follows that A and B are constants.

Hence, given the boundary conditions of (4.30), equations (4.32) have the following solution

$$\left. \begin{aligned} f &= -1/2 A \delta_0^2 (\xi - \xi^2), \quad g = \omega (1 - \xi)^2, \\ h &= 1/6 A \delta_0^3 (3\xi^2 - 2\xi^3), \quad B = \frac{2\omega}{\delta_0^2}, \end{aligned} \right\} (4.33)$$

where $\xi = z / \delta_0$.

To determine A and δ_0 , equation (4.29) is used. Into this equation the values for v_r , v_θ , v_z and B from equations (4.31) and (4.33) are inserted to give:

$$40\nu A = A^2 \delta_0^4 - 8\omega^2, \quad 20\nu = -A \delta_0^4,$$

whence:

$$A = -\frac{2\omega^2}{15\nu}, \quad \delta_0 = 3.50 \sqrt{\frac{\nu}{\omega}}. \quad (4.34)$$

This solution gives a fairly good approximation to the exact value (equation [4.26]) of the moment coefficient, c_m :

$$c_m = 3.6 R^{-1/2}.$$

The accuracy of this solution is further improved by consideration of the equation (4.6). On the right hand side of this equation, the terms containing $\partial v_\theta / \partial r$ and v_θ / r can be discarded as they are small compared to the derivatives with respect to z . On the left hand side the terms for v_r , v_θ and v_z can be replaced by the values determined from equations (4.31) and (4.33). As all the components in the equation are functions of ξ , a second approximation is then obtained:

$$\frac{1}{\delta_{01}^2} \frac{\partial^2 v_\theta}{\partial \xi^2} = 0.545 \frac{r\omega^2}{\nu} (3\xi - 6\xi^2 + 4\xi^3 - \xi^4),$$

where δ_{01} is a second approximation to the unknown thickness of the boundary layer.

Thus by integrating this equation with the boundary conditions for v_θ given by (4.30), it is found that

$$v_\theta = \omega r - 0.01816r \frac{\omega^2 \delta_{01}^2}{\nu} (9\xi - 15\xi^3 + 15\xi^4 - 6\xi^5 + \xi^6). \quad (4.35)$$

The condition $v_\theta = 0$ at $\xi = 1$ then gives:

$$\delta_{01} = 3.71 \sqrt{\frac{\nu}{\omega}}. \quad (4.36)$$

The quantity c_m is thus found to be equal to

$$c_m = 3.82 R^{-1/2}, \quad (4.37)$$

and this value differs only by 1.3 per cent, from the exact solution.

The preceding analysis of the hydrodynamics has allowed determination of the flow velocities and the "velocity" boundary layer thickness for a disk rotating in a fluid at rest. However, of more importance to crystal growth from a solution, is the quantity known as the "concentration" boundary layer, δ_c . This is the height of liquid above a surface in which the concentration varies from the bulk concentration, to the depleted concentration at the substrate surface. The formation of this boundary layer was discussed in section 2.3 and is shown graphically in fig. 9. It was also shown that the growth rate and concentration of solute species at the growing interface (i.e. the composition of the growing layer) was dependent, on how fast solute could diffuse to the interface, to replenish the solution which was being depleted by the growth. The fluid motion generated by the rotating disk, unlike a stationary melt, physically brings undepleted melt to near the growing surface. However, because of the effect of the velocity boundary layer, on approaching the substrate this replenishing action becomes less effective and diffusion, once again, predominates as the method for transportation of material to the growing layer. Consequently, the size of the concentration boundary layer will be directly related to the size of the velocity boundary layer. The formation of the concentration boundary layer under such conditions was analysed by Burton et al. [72], as follows.

The continuity equation, for the conservation of solute in the melt is given by:

$$\frac{\partial C}{\partial t} = - \nabla \cdot (CU - D \nabla C), \quad (4.38)$$

where C is the concentration of the solute in the melt, U is the velocity vector and D is the diffusion coefficient of the solute in the solvent (assumed to be independent of concentration in the dilute solutions which are encountered).

Burton et al. considered the problem to be one dimensional, as experimentally they found the concentration to be radially independent. Hence, taking also into account that the liquid is incompressible, equation (4.38) reduces to:

$$D \frac{d^2C}{dz^2} - V_z \frac{dC}{dz} = 0 \quad (4.39)$$

where V_z is the sum of the normal fluid velocity v_z and the growth velocity f . The latter is chosen to be positive for growth, and negative for melting. The boundary conditions for steady-state growth are:

$$\left. \begin{aligned} C &\rightarrow C_0 \quad \text{as} \quad z \rightarrow \infty, \\ (C_p - C_{sp})f + D \frac{dC}{dz} &= 0 \quad \text{at} \quad z = 0, \end{aligned} \right\} (4.40)$$

where C_0 and C_p are the concentrations of the solute in the bulk of the liquid and at the growing interface respectively. C_{sp} is the composition of the solid being deposited.

From Cochran's [69] analysis, for small values of z , Burton et al. used the following approximation for v_z (i.e. substituting the first term of equation (4.19), as z is small, into the equation for v_z , (4.9), and also substituting for ζ using $\zeta = z \sqrt{\frac{\omega}{\nu}}$):

$$v_z = 0.51 \omega^{3/2} \nu^{-1/2} z^2 \quad \text{for} \quad z < \nu^{1/2} \omega^{-1/2}. \quad (4.41)$$

Using this approximation Burton et al. found a solution to equations (4.39) and (4.40) of the form:

$$\frac{C_p - C_o}{C_p - C_{sp}} = \int_0^{\infty} e^{-(Z + \psi Z^3)} dZ, \quad (4.42)$$

where $\psi = 0.17 f^{-3} \omega^{3/2} D^2 \nu^{-1/2}$ and $Z = fz/D$.

For practical purposes a further approximation is used, where it is assumed that the fluid motion keeps the concentration uniformly equal to C_o beyond a distance of δ_c from the growing surface. Within δ_c the normal flow velocity is merely f , and here diffusion likewise contributes to the transport. Thus equation (4.39) becomes

$$\frac{Dd^2C}{dz^2} + f \frac{dC}{dz} = 0 \quad (4.43)$$

and (4.40) is replaced by

$$C = C_o \quad \text{at} \quad z = \delta_c. \quad (4.44)$$

Therefore the following solution results for the concentration at the interface.

$$\frac{C_p - C_{sp}}{C_o - C_{sp}} = e^{\Delta}, \quad (4.45)$$

where $\Delta = f \delta_c / D$. The somewhat arbitrary quantity δ_c , may be characterized by defining it to yield the same dependence of the composition upon the growth parameters that is given by equation (4.42), which is the more exact solution. Thus, δ_c is required to vary in a manner such that

$$e^{-\Delta} = 1 - J, \quad (4.46)$$

where J is the integral on the right of equation (4.42).

Consequently δ_c is given by the following equation:

$$\delta_c = 1.6D^{1/3}J^{1/6}\omega^{-1/2}. \quad (4.47)$$

Therefore it can be seen that the concentration boundary layer thickness is the same at all points on the disk, and is proportional to $\omega^{-1/2}$.

The growth rate is determined by two factors, firstly the attachment kinetics and secondly the rate at which solute can diffuse to the interface. The growth rate is therefore dependent on the size of the concentration boundary layer thickness. Thus for growth which is diffusion limited (i.e. fast attachment kinetics), Brice [73] determined the growth rate to be equal to:

$$f = \rho^{-1}D(C_o - C_p)/\delta_c. \quad (4.48)$$

Because of the inverse proportionality with δ_c , the growth rate is proportional to $\omega^{1/2}$. This dependence has been confirmed experimentally, (e.g. Astles et al. [63]).

4.2.2 Hydrodynamics of a disk rotating in a fluid with an additional impinging flow.

This can be considered to be comparable to a situation in RDLPE, where the rate at which the melt is dropped onto the rotating substrate, is greater than that at which it is flung off by the centrifugal action, as described by equation (4.27).

The flow around a disk under such conditions was solved by Tifford and Chu [74].

They assumed that the impinging flow is axially symmetric and at

right angles to the disk. At the outer limits of the boundary layer, the axially symmetric potential flow in the space $z \geq 0$ can be described by the equations

$$v_r = ar, \quad v_\theta = 0, \quad v_z = -2az \quad (4.49)$$

The kinematic significance of parameter a , is apparent if the flow around a disk of radius R , perpendicular to its surface is considered. Assuming the flow to be uniform and to have a velocity, W_∞ , at infinity the potential along the axis for such a flow is given by (Kochin et al. [75])

$$\phi = \frac{2 W_\infty z}{\pi} \left(-\frac{R}{z} + \tan^{-1} \frac{z}{R} \right). \quad (4.50)$$

In the vicinity of a disk and on the axis $r = 0$ the derivative of the axial flow velocity has the value

$$\left. \frac{\partial v_z}{\partial z} \right|_{z \rightarrow 0} = \left. \frac{\partial^2 \phi}{\partial z^2} \right|_{z \rightarrow 0} = -\frac{2 W_\infty}{\pi} \frac{2}{R}. \quad (4.51)$$

According to equation (4.49) this derivative equals $-2a$.

Thus equating equation (4.51) to the derivative of v_z given by equation (4.49), a , is defined by the following equation

$$a = \frac{2 W_\infty}{\pi R}. \quad (4.52)$$

From this, the ratio of the impinging flow velocity to the rotational velocity is determined by the quantity a/ω as

$$\frac{W_\infty}{R\omega} = \frac{\pi a}{2 \omega}. \quad (4.53)$$

For steady flow, the system of equations (4.5), (4.6), (4.7) and (4.8) have to be solved using the following boundary conditions

$$\left. \begin{aligned} v_r &= 0, & v_\theta &= r\omega, & v_z &= 0 & \text{for } z &= 0, \\ v_r &= ar, & v_\theta &= 0 & & & \text{for } z &= \infty. \end{aligned} \right\} (4.54)$$

Using the equation of continuity (4.8) (and the condition that v_r must be finite at $r = 0$) we obtain, after integration with respect to r :

$$v_r = -rv'_z/2, \quad (4.55)$$

where the prime denotes differentiation with respect to z .

Further, by putting

$$v_\theta = rg(z), \quad (4.56)$$

and using (4.55), equation (4.6) becomes

$$v_z g' - v'_z g = \nu g'', \quad (4.57)$$

and equation (4.7) becomes

$$v_z v'_z = -\frac{\partial p}{\partial z} \frac{1}{\rho} + \nu v''_z.$$

Integration over z leads to

$$\frac{p}{\rho} = \nu v'_z - \frac{1}{2} v_z^2 + P(r). \quad (4.58)$$

Inserting (4.55), (4.56) and (4.58) into equation (4.5) gives:

$$r \left(\frac{1}{2} v_z' \right)^2 - \frac{r}{2} v_z v''_z - rg^2 = -\frac{dp}{dr} - \frac{\nu}{2} r v_z'''_z. \quad (4.59)$$

Since v_z and g are independent of r and for $z \rightarrow \infty$ then $v_z' \rightarrow -2a$, and $g(z) \rightarrow 0$, then:

$$\frac{dP}{dr} = -a^2 r,$$

and equation (4.59) takes on the form:

$$\left(\frac{1}{2} v_z' \right)^2 - \frac{1}{2} v_z v_z'' - g^2 = a^2 - \frac{\gamma}{2} v_z''' . \quad (4.60)$$

To simplify the equation to a dimensionless form the following substitutions are used:

$$\zeta = z \left[\frac{a + \omega}{\nu} \right]^{1/2}, \quad v_z = [\gamma(a + \omega)]^{1/2} H(\zeta), \quad v_\theta = r(a + \omega) G(\zeta). \quad (4.61)$$

As a result, equations (4.57) and (4.60) become the ordinary differential equations (prime denoting differentiation with respect to ζ)

$$\left. \begin{aligned} \left(\frac{H'}{2} \right)^2 - \frac{1}{2} H H'' - G^2 + \frac{1}{2} H''' &= \frac{(a/\omega)^2}{(1 + a/\omega)^2}, \\ H G' - H' G &= G''. \end{aligned} \right\} (4.62)$$

With boundary conditions:

$$\left. \begin{aligned} H = H' = 0, \quad G &= \frac{1}{1 + a/\omega} \quad \text{for } \zeta = 0, \\ H' &= -2a/\omega : (1 + a/\omega), \quad G = 0 \quad \text{for } \zeta = \infty. \end{aligned} \right\} (4.63)$$

Tifford and Chu performed numerical integration on equations (4.62) to obtain the radial, circumferential and axial velocity distributions near the disk for various values of a/ω . The reader is referred to their work for the tables of results.

To obtain an equation for the velocity boundary layer thickness, an approximate solution to the problem of a disk in a current perpendicular to its plane has to be used. The method adopted to achieve this is that due to Targ [71] which was used in section 4.2.1 for the case of a disk rotating in a stationary fluid. The boundary conditions are different from (4.30), in that, at the outer limit of the boundary layer the velocity component v_r will no longer equal zero but instead will satisfy the condition

$$v_r|_{z=\delta} = ar. \quad (4.64)$$

Also the pressure is no longer radially independent, because for the potential flow impinging on the disk

$$\frac{\partial p}{\partial r} = -\rho a^2 r. \quad (4.65)$$

In place of equations (4.32) the following equations are therefore obtained:

$$f''(z) = A - \frac{a^2}{v}, \quad g''(z) = B, \quad 2f(z) + h'(z) = 0, \quad (4.66)$$

where A and B are constants. Applying the boundary conditions for this problem, the following solution to these equations results:

$$\left. \begin{aligned} f &= -\frac{1}{2} \left(A - \frac{a^2}{\nu} \right) \delta_o^2 (\xi - \xi^2) + a \xi, \\ g &= \omega (1 - \xi)^2, \\ h &= \frac{1}{6} \left(A - \frac{a^2}{\nu} \right) \delta_o^3 (3\xi^2 - 2\xi^3) - a \delta_o \xi^2, \end{aligned} \right\} (4.67)$$

$$\text{and} \quad B = \frac{2\omega}{\delta_o^2}, \quad (4.68)$$

where $\xi = z/\delta_o$.

Inserting these expressions into integral (4.29), equations relating the unknowns A and δ_o are obtained:

$$\nu A = \frac{1}{40} \left(A - \frac{a^2}{\nu} \right)^2 \delta_o^4 - \frac{1}{12} \left(A - \frac{a^2}{\nu} \right) a \delta_o^2 - \frac{\omega^2}{5}, \quad (4.69)$$

$$\frac{\nu}{\delta_o^2} = -\frac{1}{20} \left(A - \frac{a^2}{\nu} \right) \delta_o^2 + \frac{1}{6} a, \quad (4.70)$$

whence A and δ_o are found to equal the following:

$$A = -\frac{2\omega^2}{15\nu} + \frac{1}{3} \frac{a^2}{\nu}, \quad (4.71)$$

$$\delta_o^2 = \frac{\nu}{\omega} \left[\frac{-12.5}{(5a/\omega + \omega/a)} + \sqrt{\left(\frac{12.5}{(5a/\omega + \omega/a)} \right)^2 + \frac{150}{(5(a/\omega)^2 + 1)}} \right]. \quad (4.72)$$

Therefore, it can be seen that the velocity boundary layer thickness is the same at all points on the disk and is rotation rate dependent. A theoretical treatment to determine the concentration boundary layer thickness, δ_c , has not been carried out for the case of crystal growth in such a fluid flow situation, but as explained in 4.2.1, δ_c is

determined by the size of δ_0 and thus as δ_0 is uniform over the substrate so will δ_c . Consequently growth conditions should be identical at all points of the substrate and thus epilayers which are flat and uniform in composition should be achievable.

4.3 POSSIBLE CONSEQUENCES OF HYDRODYNAMICS

4.3.1 Advantageous consequences of hydrodynamics

The theoretical analysis of the hydrodynamics which can be considered to be very close to that occurring in RDLPE, indicate that a number of improvements over conventional LPE techniques can be expected.

The equations for the boundary layer thickness derived for the two situations in 4.2.1 and 4.2.2 (i.e. (4.34) and (4.72)) indicate that the growth conditions will be constant at all points on the rotating substrate. Thus, uniform growth should be obtainable, without any problems from convective currents, which would otherwise limit the size of substrate that can be used. This overcomes one of the main problems with sliding boat LPE as explained in section 2.7.1.

It was shown in section 2.6.3 that a fundamental problem of LPE, is that diffuse junctions result from the initial creation of the concentration boundary layer. However, this problem should be minimized with RDLPE. The reduced concentration boundary layer thickness resulting from the fluid motion bringing undepleted melt closer to the substrate surface, will mean a shorter distance for the solute to diffuse to the substrate surface. Consequently, the melt at the substrate surface will be depleted less than with a stationary melt and thus, a smaller variation in composition of epilayer in the initial stages of growth will occur. With the boundary layer being smaller, it will take less time to form and thus steady-state growth will occur sooner.

The junctions between epilayers, formed using RDLPE, would thus be expected to be sharper and show less variation in the composition. The epilayer will also have a composition closer to that predicted by the equilibrium phase diagram for a given melt.

Hydrodynamic theory states that the concentration boundary layer thickness is rotation rate dependent. As the rotation rate is increased the concentration boundary layer thickness decreases. This decrease will lead to the improvements in the area of a junction, as detailed above.

The growth rate is also a function of the rotation rate, (4.2.1). As the rotation rate increases so does the growth rate. The rotation rate, therefore, allows additional control of the growth rate, as well as providing a mechanism for further improvement in the growth of epilayers. However, there is a limit to how fast one can rotate the substrate before turbulence occurs and this is discussed in the following section

4.3.2 Turbulence

At low fluid velocities the motion of a fluid on a rotating disk is stable and orderly and is known as "laminar" motion. As the fluid's velocity is increased by, for instance, increasing the rotation rate of the substrate, a disorderly motion sets in, in which irregular fluctuations begin to play an essential part. This flow is called "turbulent".

The point at which turbulence begins is usually defined using the Reynolds number, the particular value being called the "Transition Reynolds number".

The Reynolds number, R , is a dimensionless number which is a measure of the relative magnitude of the inertial to viscous forces occurring

in a flow. The higher the Reynolds number the greater will be the relative contribution of the inertial effects. The smaller the Reynolds number the greater will be the relative magnitude of the viscous stresses. The Reynolds number is given by the following equation:

$$R = VL/\nu \quad , \quad (4.73)$$

where V is the free stream velocity and L is a characteristic linear dimension, which is taken as the smallest dimension that influences the fluid flow. Thus for a disk rotating in a fluid, $L = r$, (the radial distance) and $V = r\omega$. Thus the Reynolds number equals

$$R = r^2\omega/\nu \quad . \quad (4.74)$$

For RDLPE the height of the fluid on the substrate, h , is taken as the characteristic dimension (clearly the smaller the height, the more difficult it will become for eddies to operate) and hence

$$R = hr\omega/\nu \quad . \quad (4.75)$$

Theodorsen and Regier [76] found experimentally that for a disk rotating in a fluid, the transition Reynolds number was of the order of 300,000.

Observation of the transition to turbulence was conducted by Smith [77] and later in greater detail by Gregory et al. [70]. They found that in the transition zone, between twenty eight and thirty one vortices, forming standing waves relative to the disk, were generated. Beyond this zone, the flow became totally turbulent. Inside the zone it was laminar (fig. 23).

The transition zone is, therefore, composed of periodic areas of fluid, which are stationary with respect to the disk, but whose motion



Fig. 23 Schematic diagram of the transition from the central, laminar flow region (shaded zone), through the transition zone, where there are standing waves, to the turbulent zone.

is different (i.e. different boundary layer thicknesses over the disk). Hence, if crystal growth were occurring on a rotating substrate on which this transition occurs, then periodic variations in growth rate and composition of the epilayer could be expected to occur in the transition zone.

Apart from the growth variations in the transition zone there will be a difference in the growth conditions between the laminar central zone and any turbulent outer zone. Therefore, for the growth of uniform planar layers, the rotation rate should be kept to a rate which, for its radius, is too low for turbulence or transitional turbulence to occur. For dipping LPE Davies et al. [78] found, that for a 16mm diameter substrate (used for the growth of magnetic garnet layers), the maximum rotation rate before turbulence occurred was 240 rpm. The effect of this turbulence on the growth has, however, been found not to

be very significant. For example Davies et al., found that for higher rotation rates, although a change in layer thickness and composition did occur due to the change to turbulent flow, this change was in fact very slight and for their particular end product was very acceptable.

RDLPE can be expected to behave similarly to dipping LPE. However, as the characteristic dimension, L , in equation (4.73) is the height of the fluid above the substrate for RDLPE (which is significantly less than the substrate radius used for dipping LPE), the onset of turbulence on a substrate would be expected to occur at a much higher rotation rate. This is because the limited volume of fluid above the disk makes the formation of eddies difficult. This improvement over dipping LPE might not be as great as would first appear, however, since Theodorsen and Regier [76] found that a small high pressure jet, to the centre of the disk, reduced the transition Reynolds number. If the melt dropping on to the substrate is too concentrated, a similar reduction might occur. However, it is felt unlikely that the dropping melt will approach the high pressure jet condition as used by Theodorsen and Regier.

4.4 EXPECTED ADVANTAGES OF RDLPE OVER THE SLIDING BOAT TECHNIQUE FOR LPE

From a consideration of the hydrodynamic theory, (section 4.3.1) and when compared with the sliding boat LPE technique, RDLPE can be expected to have a number of advantages. These are briefly as follows:

- i) Growth of uniform layers over large areas (discussed in 4.3.1).
- ii) Improved sharpness between layers (discussed in 4.3.1).
- iii) Additional control of growth rate using the rotation rate (discussed in 4.3.1).
- iv) Growth of layers whose composition is closer to that predicted

by the equilibrium phase diagram for the melt composition (discussed in 4.3.1).

v) Reduced edge effects as the melt will totally cover the substrate, with only the curving at the edges of the substrate producing preferential growth (see section 2.7.3 for a discussion on edge growth).

vi) Clean removal of the melt with no problem of melt-carry over. This is because at the termination of the growth, any fluid remaining on the disk will be rapidly spun off due to the large centrifugal forces on the fluid (rapid rotation is used for melt removal off substrates in dipping LPE very successfully).

vii) Because RDLPE uses forced convection to produce a well defined flow on the substrate, there should be no convectional problems such as can occur in the sliding boat apparatus, (e.g. melt rolling).

viii) The melt can be contained easily in a silica container, and thus it need not come into contact with any graphite surfaces prior to growth which would otherwise introduce contaminants.

ix) There are no rubbing graphite surfaces and hence no particulate carbon contamination.

x) As the melt is not wiped from the surface, there is no chance of the epilayer getting scratched by insufficient wiper clearance or foreign particles.

The dipping with rotation technique for LPE, also has most of the above advantages. However, it cannot be adapted for the growth of multilayers, which form the basis of most device structures.

RDLPE should be easily adaptable to allow the growth of multilayers. In addition, faster rotation rates should be possible without the turbulence that is associated with the dipping LPE technique.

CHAPTER 5. RDLPE EQUIPMENT DEVELOPMENT

5.1 INTRODUCTION

Since RDLPE is a new technique, the majority of the work presented here, is concerned with the development of the necessary equipment. This has involved constant improvements to the basic apparatus, using the results from preliminary growth experiments. The final version of the RDLPE apparatus allowed a series of controlled growth experiments to be conducted, which aided in the characterisation of the technique.

This chapter will, therefore, discuss the development of the equipment to its final form. The following chapter will describe the growth experiments undertaken and discuss the results obtained.

5.2 RDLPE EQUIPMENT DESIGN

The technique of RDLPE involves dropping a supersaturated solution onto a substrate which is being rotated at a constant rate. The following basic features have been incorporated into the equipment in order to achieve growth.

- i) A Furnace capable of heating the melt to the elevated temperatures needed to form the saturated growth solutions.
- ii) Control of the temperature and the temperature profile, throughout the furnace.
- iii) A Container (the "melt dropper") which holds the melt, and allows it to drop onto the substrate in a controlled manner.
- iv) Provision of a mechanism to prevent the melt from exiting the melt dropper, until growth is required. This is known as the "stopper rod".
- v) A Turntable to securely hold the substrate.
- vi) Connection of the turntable, via a shaft, to a motor outside the

furnace. This requires a rotating seal, at the point of entry into the furnace, that is capable of sealing the shaft at high rotation rates.

vii) Control of the speed of rotation of the substrate.

viii) A Means of measuring the temperature of the melt, and of measuring the rotation rate of the substrate.

ix) A Container for collecting the melt after it is flung from the turntable, to prevent it spraying haphazardly and possibly damaging furnace components. This is known as the "melt catcher".

x) A Furnace sealed from the laboratory atmosphere, with provision made to allow hydrogen gas to flow through it at a controlled rate.

The initial RDLPE apparatus is shown in fig. 24. This design was found to be far from ideal (as will be explained later), and thus further improvements to the design were subsequently made.

The following sections concentrate on the individual parts of the RDLPE apparatus, describing their evolution in detail.

5.2.1 The Furnace

The furnace used throughout the research was a low thermal mass gold reflector furnace (Transtemp Inc.), see fig. 25. This furnace offered a number of important advantages over conventional, high thermal mass furnaces:

i) The low thermal mass of the gold reflector furnace allowed it to be rapidly heated and cooled. This helped to minimize any damage that could occur to the substrate, by reducing the period over which an InP slice was subjected to high temperatures. The elevated temperatures necessary for growth can easily lead to the decomposition of III-V substrates. The ability of the furnace to drop its temperature quickly, was also advantageous, since the step-cooling technique (section 2.4.3) was employed for growth by RDLPE.

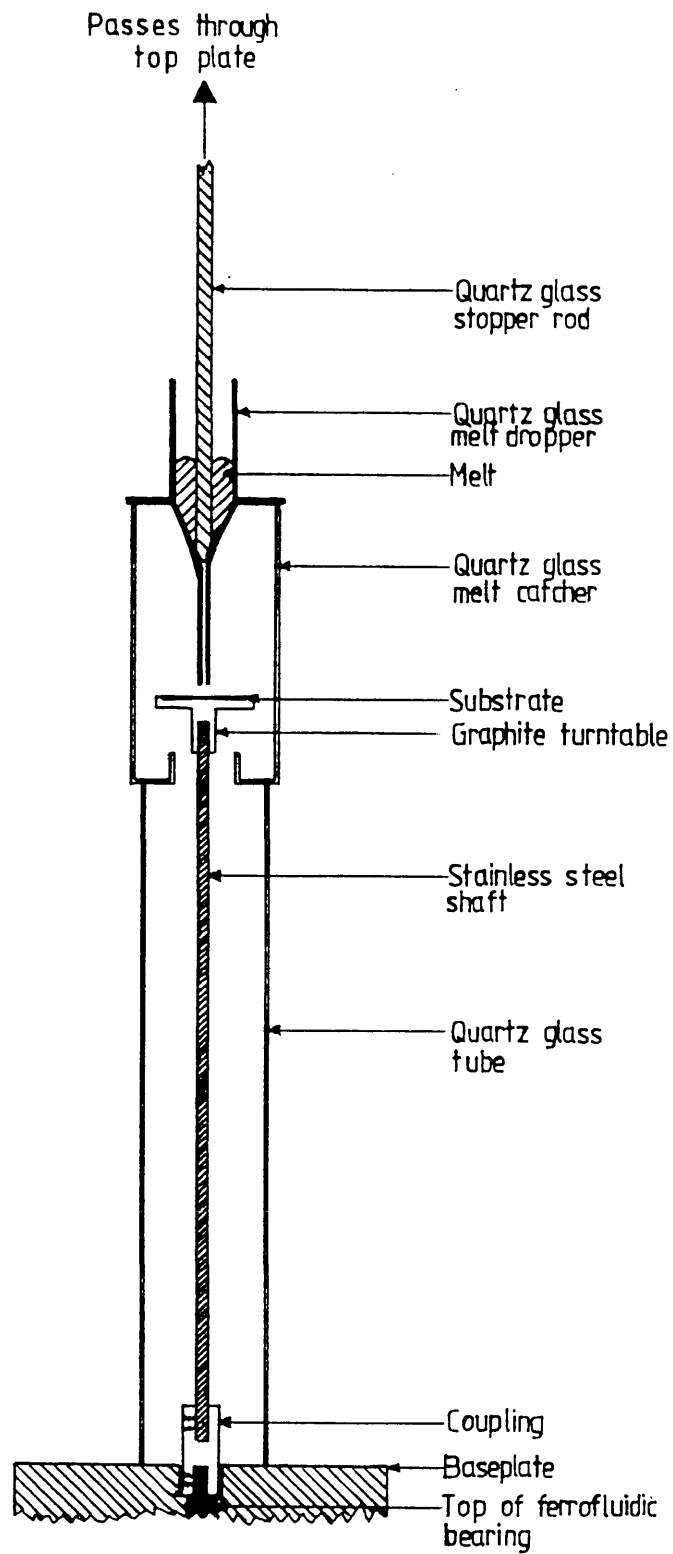
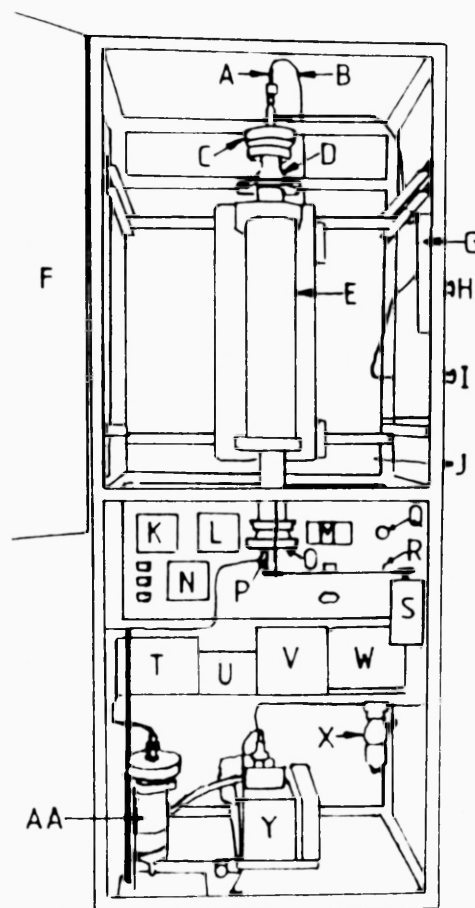
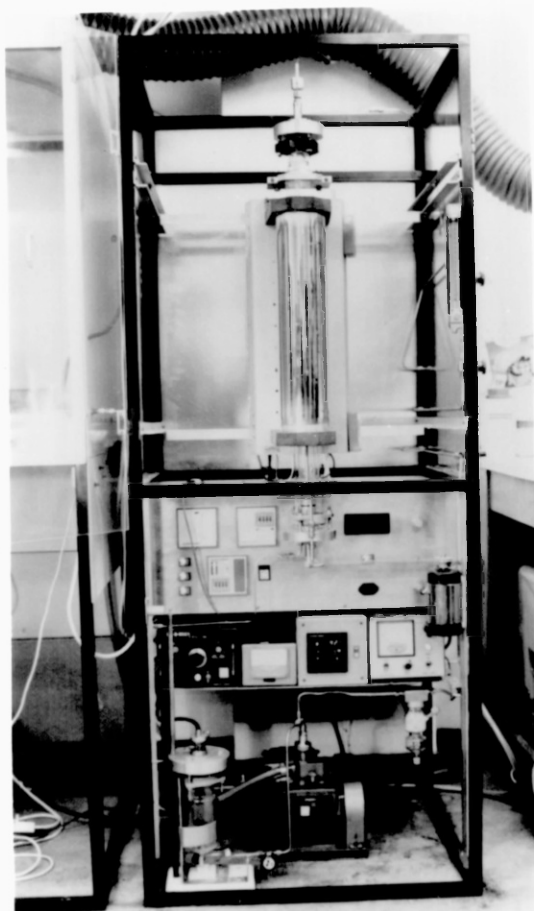


Fig. 24 The original design of apparatus for RDLPE.



KEY

A Melt stopper rod	O Baseplate
B Melt thermocouple	P Ferrofluidic bearing
C Top plate	Q Six way rotary switch
D Inner furnace tube	R Amplifier gain selector switch
E Gold reflector furnace	S Motor
F Perspex door	T Vacuum furnace temperature controller
G Gas flowmeter	U Pirani gauge
H Nitrogen supply valve	V Digital temperature meter
I Hydrogen supply valve	W Motor speed controller
J Vacuum line needle valve	X Zeolite trap
K Slave thyristor stack	Y Vacuum pump
L Slave temperature controller	Z Vacuum furnace line valve
M Digital panel meter	AA Vacuum furnace
N Master temperature controller	

Fig. 25 An external view of the furnace and associated control equipment used for RDLFE, with a simplified diagram and key to facilitate identification of principal components.

ii) The outer tube of the furnace was gold coated on its internal surface. This permitted a highly efficient reflection of infrared energy whilst also being semitransparent, and so allowing observation of the inside of the furnace. This latter fact, was an invaluable aid in the interpretation of the growth experiments.

The gold reflector furnace had three windings (heating elements), having a small winding situated at each end, and a longer winding extending along the remaining length. Each of these windings were connected to separate temperature controllers which regulated the temperature and temperature profile in the furnace, (see fig. 26). The controller for the central zone acted as a master unit, and the controllers of the outer two zones were slave units. Each slave was set to maintain a fixed difference in temperature between its zone and the central zone.

The gold coated furnace functioned faultlessly for only the first few experiments conducted using the RDLPE apparatus. Unfortunately, the top winding of the furnace then burnt out and for the remainder of the work conducted on RDLPE, only the bottom two zones were used to achieve the required temperature and temperature profile. Although this limitation caused some inconvenience initially, it was still possible to achieve the conditions required for growth.

The temperature profile required, for general LPE work, is one in which the substrate is slightly cooler than the melt. This ensures that the occurrence of constitutional supercooling is avoided (section 2.6.1). In order to obtain the optimum temperature profile within the RDLPE furnace, it was necessary to carry out a number of calibration experiments. A thermocouple was lowered down the centre of the furnace, and the temperature profile was measured from the substrate to the melt

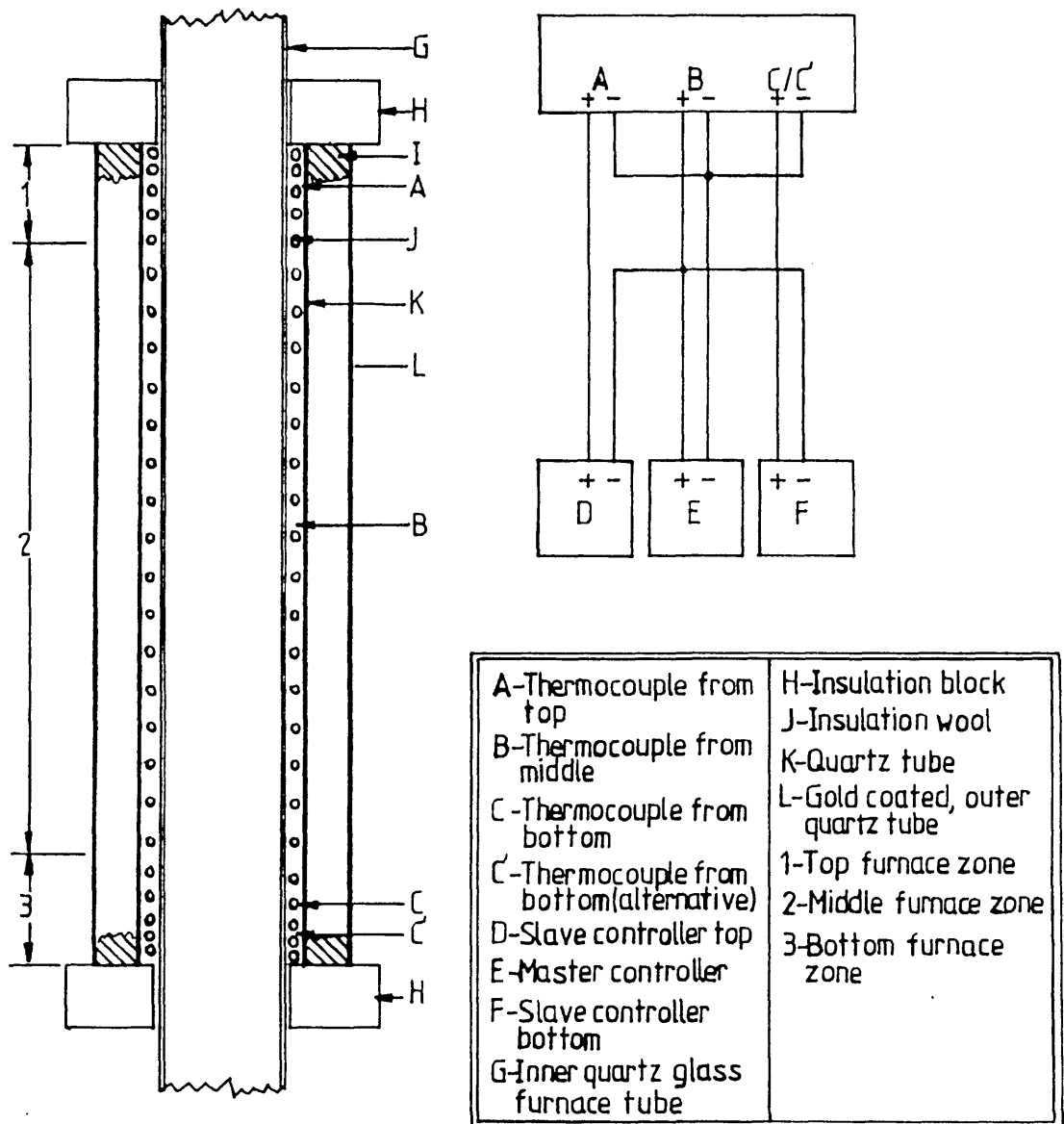


Fig. 26 Cross section through the gold reflector furnace, and the arrangement of thermocouples and temperature controllers which were employed to control its temperature.

position (the bottom and top of the melt being 70mm and 100mm above the substrate respectively). Calibration experiments were conducted throughout the development of the equipment in order to ascertain the best growth condition. The only difference in the conditions, between a growth and calibration run, was that in the latter, the melt stopper rod and the melt itself were not present. Later experiments indicated that this was not significant. The temperature variations in the furnace, for the equipment when used in its final form, are shown in fig. 27 and tabulated in appendix B.

5.2.2 Rotating Assembly

The original design of this particular piece of the apparatus, is partially shown in fig. 24. It consisted of a solid graphite turntable (shown separately in fig. 28) push fitted onto a stainless steel shaft (1/4 inch diameter rod). This was coupled, at the bottom of the furnace, to the shaft of a ferrofluidic bearing (Ferrofluidics Inc.). The latter is a bearing, which has its shaft surrounded by a magnetic liquid. This provides an excellent rotary seal under both pressure and vacuum conditions, up to rotation rates well in excess of those required for the RDLPE experiments. The bearing was connected to a motor directly beneath it, via a flexible coupling.

The turntable, for the first growth experiment, had a circular recess machined into its surface in order to accept a complete 1.5 inch diameter InP wafer. When the turntable was rotated (500 rpm) during a preliminary experiment, it was found to vibrate violently although not sufficiently to dislodge the substrate. Because of the difficulty and expense of procuring a sufficient quantity of InP wafers, the large circular recess was replaced by four smaller rectangular recesses, whose depth was such, that the surfaces of the substrates were flush

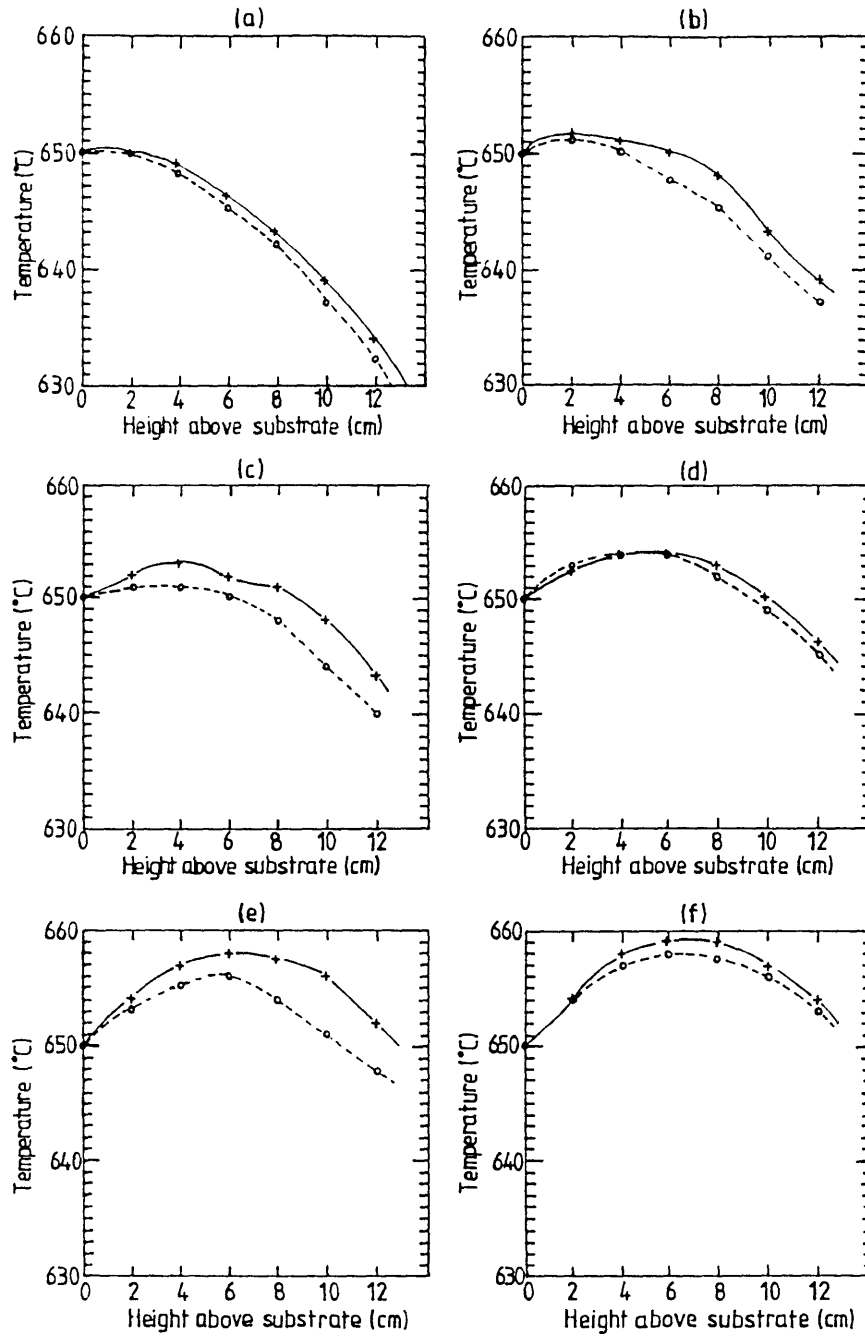


Fig. 27 Temperature variations above a substrate, at 650°C, for slave temperature controller settings of a) 0.0 mV, b) -0.2 mV, c) -0.4 mV, d) -0.6 mV, e) -0.8 mV and f) -1.0 mV. Where the thermocouple for this controller was 65mm ("o" points) and 75mm ("+" points) from the bottom of the furnace. The latter position being used for all of the growth runs.

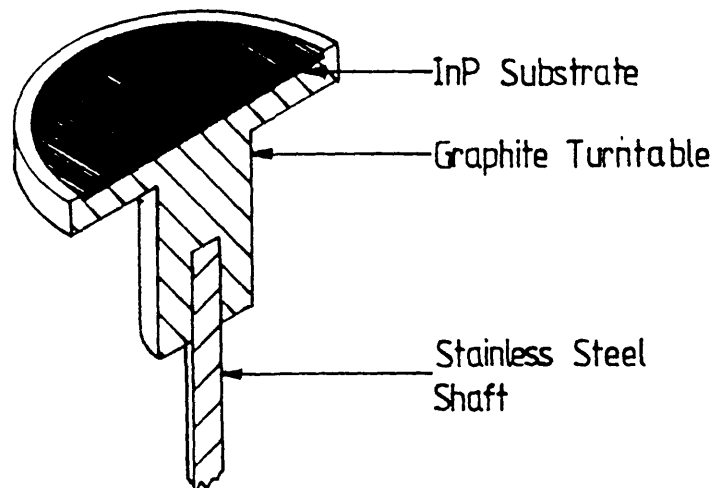


Fig. 28 Cross section through the original turntable.

with the surface of the turntable. The smaller pieces, arranged at various positions on the turntable, were to be used to simulate a complete wafer and give data at different radial distances. However, when attempting to rotate the turntable with the smaller pieces, it was found that they were in fact very quickly flung off. This was thought to be linked to the vibrations mentioned earlier.

The vibration therefore had to be eliminated, not only, to help stop the substrates from being flung off, but also to prevent it from adversely effecting the flow of the melt on the substrate surface.

The source of the problem was thought to be the transmission of vibration from the flexible coupling (used to connect the motor to the ferrofluidic bearing), along the shaft, and then to the turntable. This was ultimately found to be the case.

The origin of the vibration was traced to a misalignment of the motor shaft to that of the ferrofluidic bearing. Small movements at the

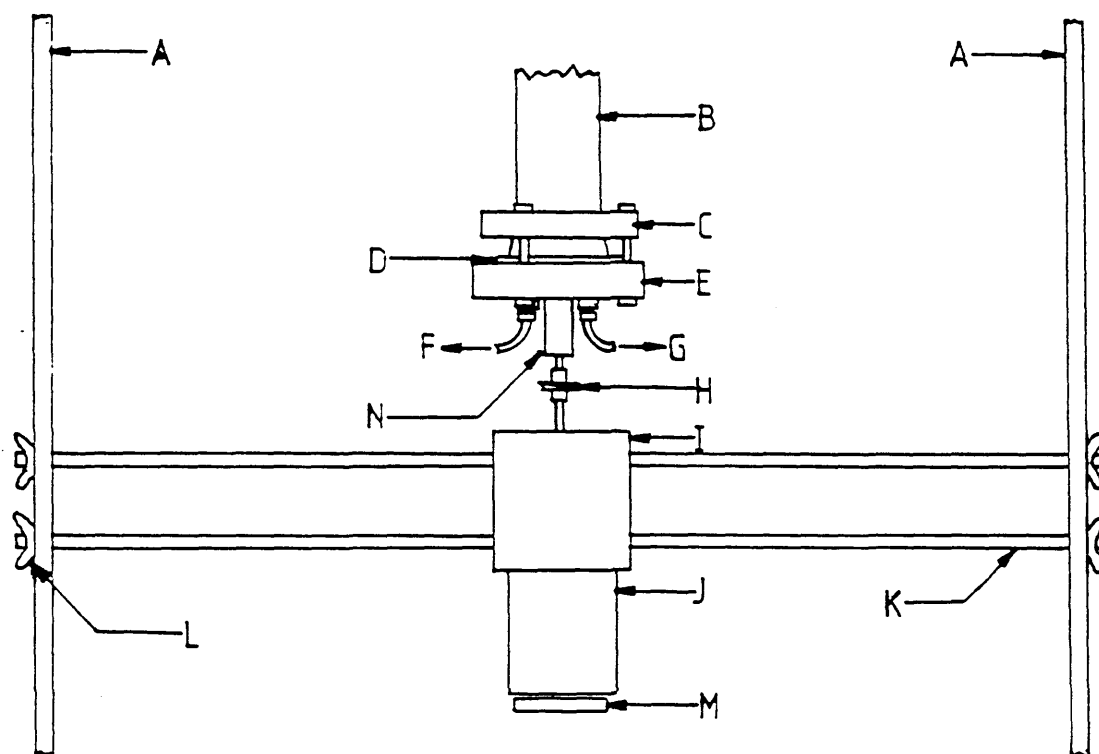
coupling were being transmitted by the flexible O-ring seating of the ferrofluidic bearing, and further amplified by the length of the stainless steel shaft/turntable combination. The vibration was observed to get particularly bad in a certain range of rotation rates (1000-1500 rpm). This was because the turntable and shaft reached a resonant frequency.

Efforts to eliminate the vibration, by using a thicker and hence more rigid stainless steel shaft, served only to reduce it. However, the vibration was still very significant and it was sufficient to dislodge the substrates. It was, therefore, necessary to tackle the problem at its source.

In the initial design, the motor that drove the shaft/turntable combination, was bolted to the apparatus directly below the baseplate. In addition to making loading and unloading of the RDLPE furnace awkward, this arrangement also made alignment of the motor with the bearing shaft very difficult.

The apparatus was changed so that the motor was in a cradle that was attached to parallel bars of studding (fig. 29). The studding travelled along slots at either side of the apparatus (marked A in fig. 29), thus allowing the motor to be raised and lowered whilst maintaining its axial position relative to the ferrofluidic bearing. Clamping of the motor, at a particular height, was achieved by using wing nuts on the ends of the studding. Although these modifications resulted in a marked reduction of the vibration effects, these were not completely eliminated. It was felt that a different mode of coupling the motor to the stainless steel shaft was the only remaining solution.

A belt drive arrangement was designed whereby the motor was fixed rigidly to the frame of the apparatus, and the rotation was transmitted



A-Slot for studding to slide in	H-Flexible coupling
B-Bottom of inner furnace tube	I-Cradle for the motor
C-Clamp	J-Motor
D-Silicone rubber gasket	K-Studding
E-Baseplate	L-Wingnut
F-Gasses out to fume cupboard	M-Motor speed control
G-Vacuum line	N-Ferrofluidic bearing

Fig. 29 The bottom of the furnace, and the use of a cradle to position the motor.

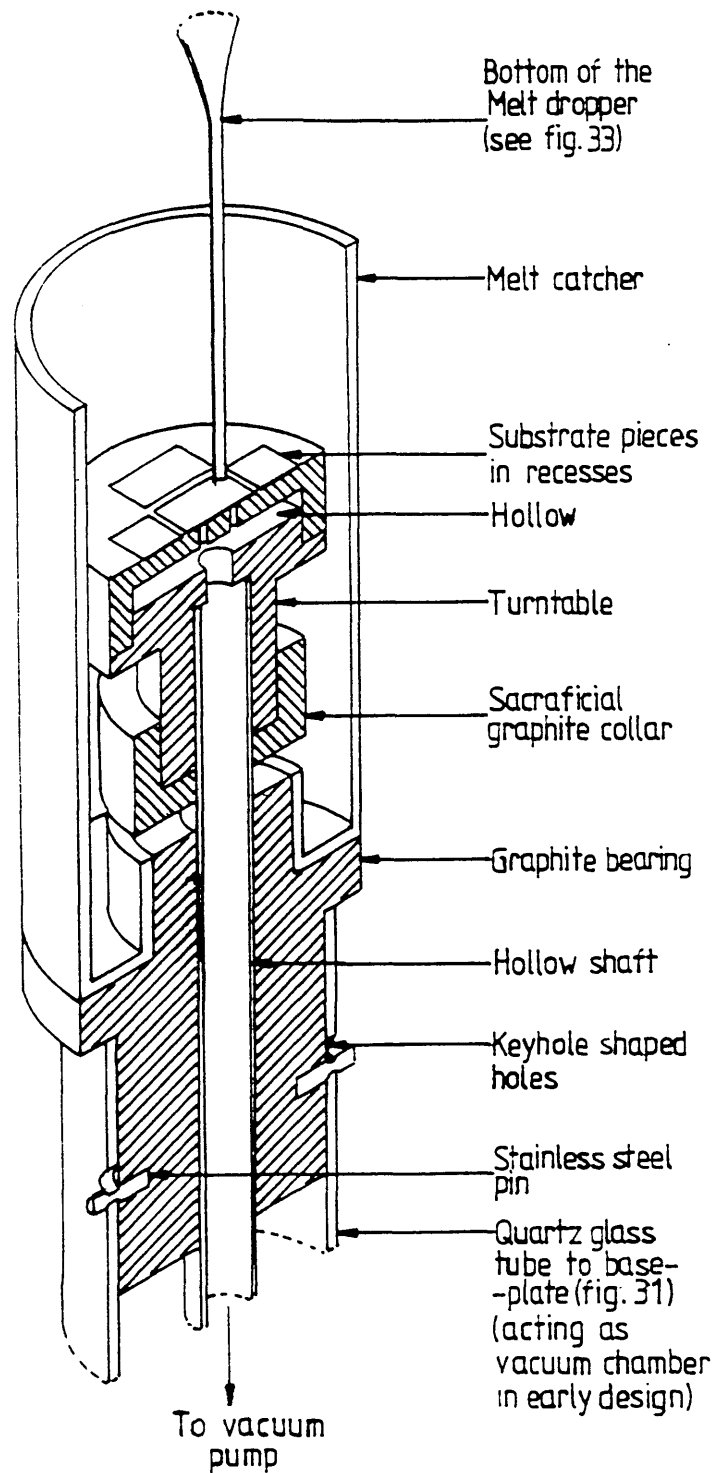
to the turntable via a rubber belt stretched over pulleys. This was found to be very successful, as it effectively eliminated the vibration and also made the assembly and dismantling of the apparatus far easier.

In order to remove any further chance of the substrates dislodging, it was necessary to carry out a further modification to the turntable. This involved the provision of a vacuum within the turntable itself, which acted on the substrate pieces so as to hold them securely down. A large scale redesign of the apparatus was required in order to incorporate this feature. The solid stainless steel shaft was replaced by a hollow version to allow the transfer of the vacuum to the turntable. The resulting design is shown in fig. 30 and fig. 31.

To explain this design it is best to describe parts of it individually:

The turntable itself comprised three main parts; the top platter, the main body, and a sacrificial collar, all machined from graphite. When assembled these created a hollow within the turntable which allowed communication of the vacuum from the hollow stainless steel shaft, through to the holes in the top platter beneath the substrates.

Problems initially arose when the differences in the thermal expansion coefficients between stainless steel ($16 \times 10^{-6} \text{ K}^{-1}$) and graphite ($8 \times 10^{-6} \text{ K}^{-1}$) caused the latter to crack at the base of the turntable, during a growth run. This was overcome by machining the graphite so that it sealed against the stainless steel only at the higher temperatures achieved during a growth run. A further refinement was the incorporation of the graphite sacrificial collar, which if cracked, could easily be replaced, unlike the turntable assembly. The collar formed the main seal between the turntable and the hollow shaft. An additional, backup, seal was formed at the top of the hollow shaft,



(a) The construction of the rotating section.

Fig. 30 The turntable section of the RDLPE apparatus, which first employed a vacuum to hold the substrate pieces on.

Fig. 30 continued...



(b) Photograph of the turntable.

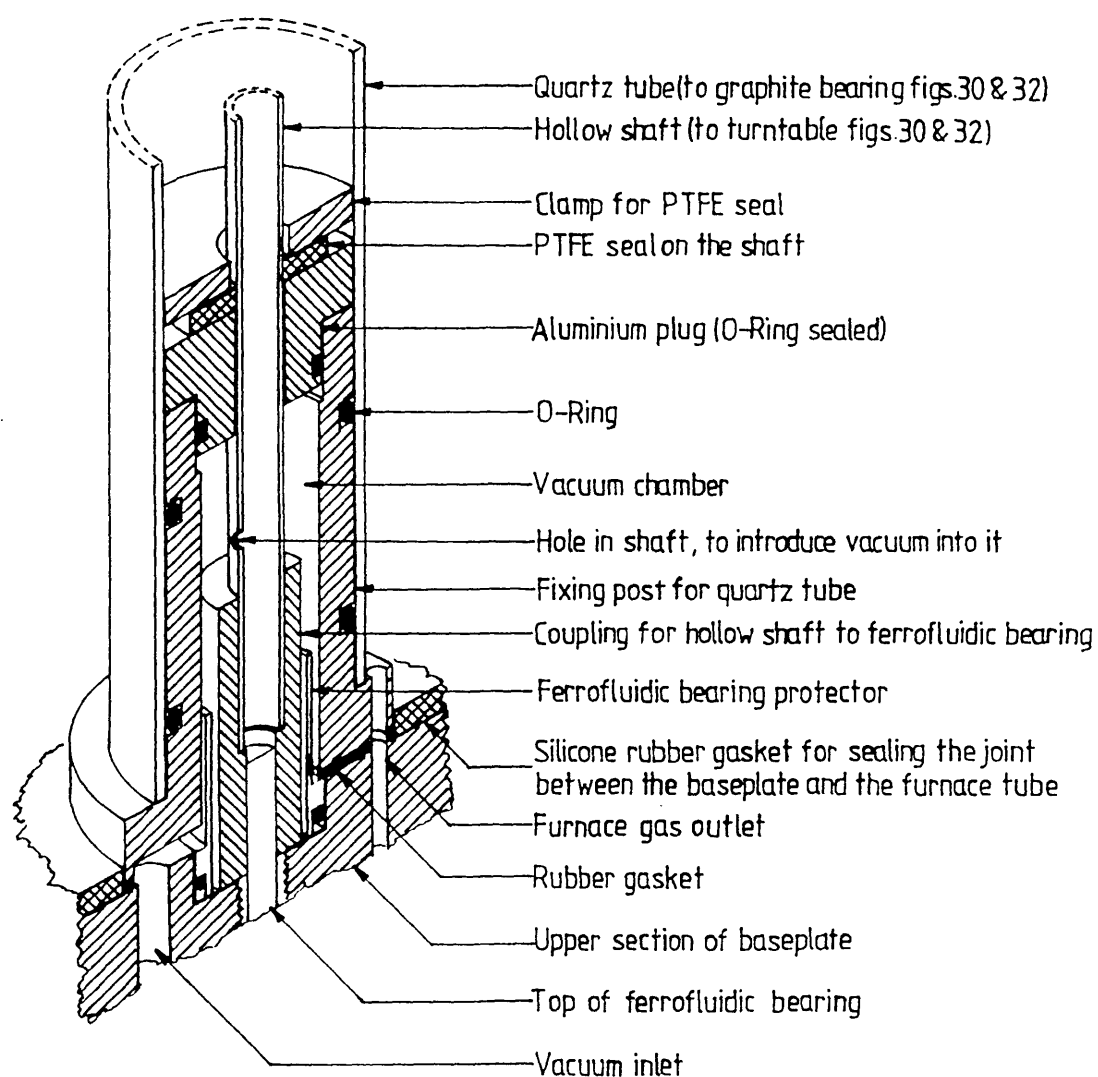


Fig. 31 The construction of the lower part of the rotating assembly.

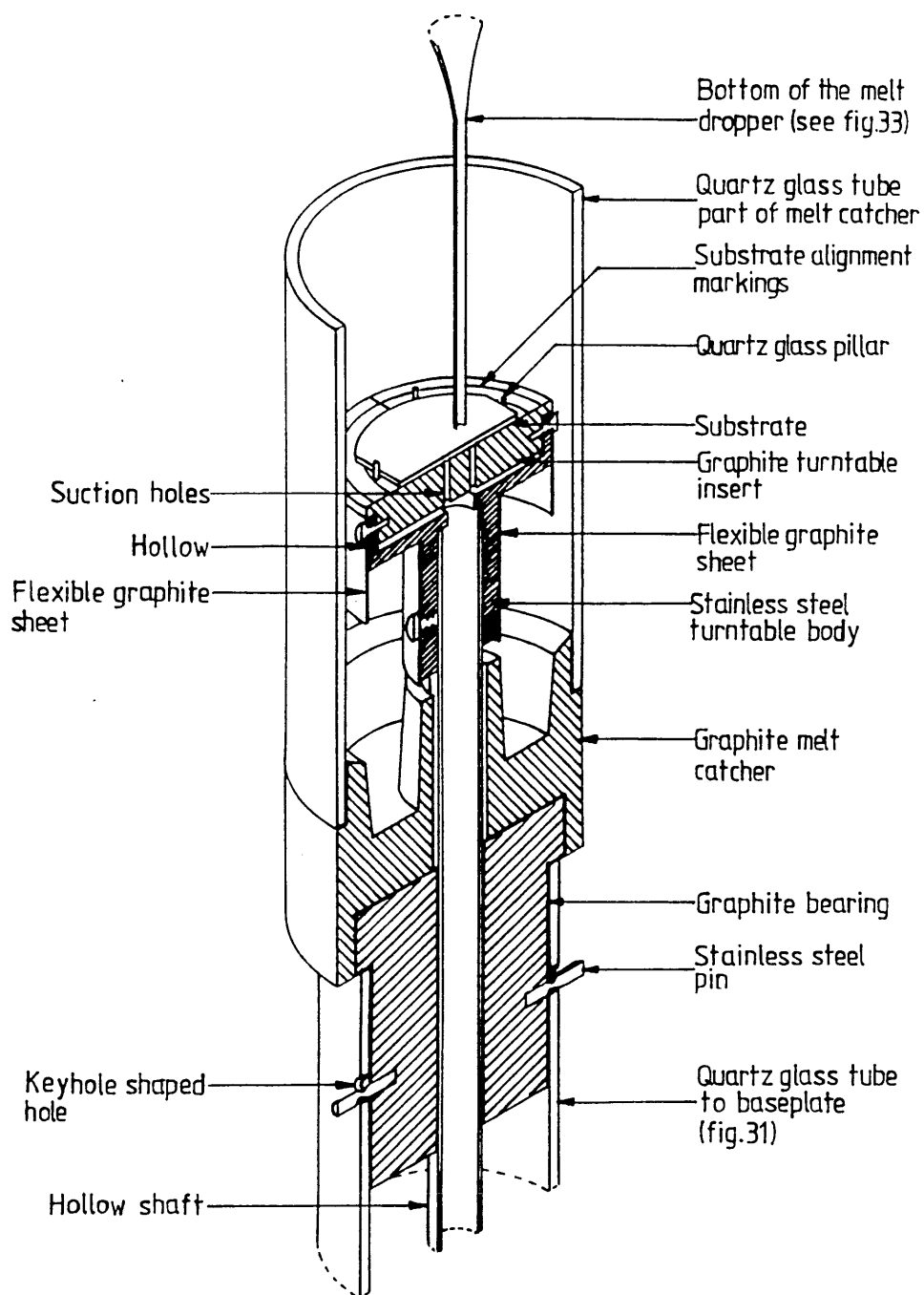
where it contacted the central graphite component. Fig. 30a and b illustrate the design of the turntable assembly.

The problem in maintaining a vacuum through a component, whilst it is also rotating at speeds that can exceed 2000 rpm, required a number of design steps before it was ultimately solved. A vacuum chamber was created around the stainless steel shaft. Initially by using a quartz glass tube (fig. 30). This tube was supported by an aluminium alloy "fixing post", attached to the baseplate of the RDLPE equipment. The graphite component at the top of the vacuum chamber acted as both a bearing and a vacuum seal. Stainless steel pins running through the quartz glass and into the graphite bearing prevented the latter from rotating with the stainless steel shaft. Holes near the top of the shaft allowed communication of the vacuum between the chamber and the interior of the shaft, and ultimately, to the turntable itself. In experiments this was found not to be a viable solution. The differences between the thermal expansion coefficients of the quartz glass tube, the bearing, and the shaft, together with the tolerances in the machined dimensions of the bearing, could result at growth temperatures in a poor seal, or the seizing of the shaft and the bearing. This design was, therefore, modified, and the result of this is shown in fig. 31. A new vacuum chamber was created around the base of the stainless steel shaft using the aluminium alloy "fixing post" together with a PTFE rotary seal. A new shaft with vacuum communication holes at its base was fabricated.

The modifications made to the RDLPE apparatus successfully prevented the substrates from dislodging during a growth run. However, a number of additional problems prompted a further redesign of the turntable. Continual cracking of the sacrificial collar necessitated frequent

machining of fresh components. During growth experiments it was also found that only the central InP slice was completely covered by the melt emanating from the melt dropper. The inadequate coverage of the peripheral slices was observed to be due to the break up of the flow of the melt as it passed out of the central region. This break up was attributed to the differences between the nature of the InP and graphite surfaces as the melt traversed the turntable. The In melt wetted the InP substrates better than the graphite portions that lay between (section 3.4.3 gives the relevant contact angles). This caused balling up of the In melt as it left the central slice and hence poor coverage of the remaining substrates. It was then decided that only one, large, centrally placed slice would be used, which need not be cut to any specific shape. Thereby, maximising the growth area and simplifying the experimental procedure. This necessitated the construction of a new turntable.

The final turntable design is shown in fig. 32. It comprised a stainless steel body (i.e. no expansion problems with the shaft) into which a graphite insert was placed. Four peripheral stainless steel screws secured the insert, and with the screw fixing the turntable to the shaft, also served to attach flexible graphite sheets around the turntable assembly. These sheets protected the stainless steel portions of the turntable from the In melt. This aided the cleaning of the apparatus between growth runs. The substrates were positioned onto the top surface of the graphite insert and held in place by the action of the vacuum (as before) and by the use of quartz glass pins. These were inserted into holes in the graphite located around the periphery of the substrate. To facilitate the alignment of the substrate and the dropper tube, lines were scribed onto the graphite surface.



(a) Cross section through the top part of the assembly.

Fig. 32 The turntable section of the rotating assembly, in its final form.

Fig. 32 continued...



(b) Photograph of the turntable section of the apparatus.



(c) Photograph, as with (b), but without the quartz glass melt catcher tube, for added clarity.

5.2.3 Melt Catcher

This component of the RDLPE apparatus was used to collect spent In melt, as it was flung off the rotating turntable during a growth run. It was designed so as to minimise the amount of cleaning necessary to the inside of the apparatus after a run and also to prevent damage to the O-ring seals and ferrofluidic bearing that might result from droplets of In melt.

As with the majority of the apparatus, the melt catcher evolved in design with the experience gained during experimentation. The initial design is shown in fig. 24. It consisted of a quartz glass tube whose base had been turned inward and upward so as to form an annular container that served to hold the spent In melt. This design was preserved when the turntable assembly was redesigned in order to incorporate vacuum retention of the substrate pieces (fig. 30). The graphite bearing which was a feature of the redesigned turntable assembly, was machined so as to support and locate the melt catcher centrally with respect to the turntable axis.

Further experiments revealed problems associated with the assembly of the apparatus before a growth run, and also, the cleaning and removal of the spent In melt from the melt catcher after the completion of the run. The melt catcher was, therefore, redesigned.

The resultant assembly is shown in fig. 32. It consisted of two components; a graphite base and melt container, and a quartz glass deflector shield that sat on the graphite base. The internal walls of the graphite container were tapered so as to allow easy removal of the solidified In melt, which could then be kept for possible future reuse. The container was capable of holding up to 100g of spent material, this being sufficient to contain melts from future multilayer growth

experiments. The two piece construction of the melt catcher greatly aided the assembly of the apparatus, whilst maintaining the ability to observe the progress of a growth run through the quartz glass deflector. This design proved very successful during growth experiments, and was extremely easy to clean subsequently.

5.2.4 Melt dropping assembly

This assembly initially consisted of the melt dropper and the melt stopper rod. The dropper held the melt, prior to growth, whilst the stopper rod prevented it from exiting through the bottom of the dropper, until required.

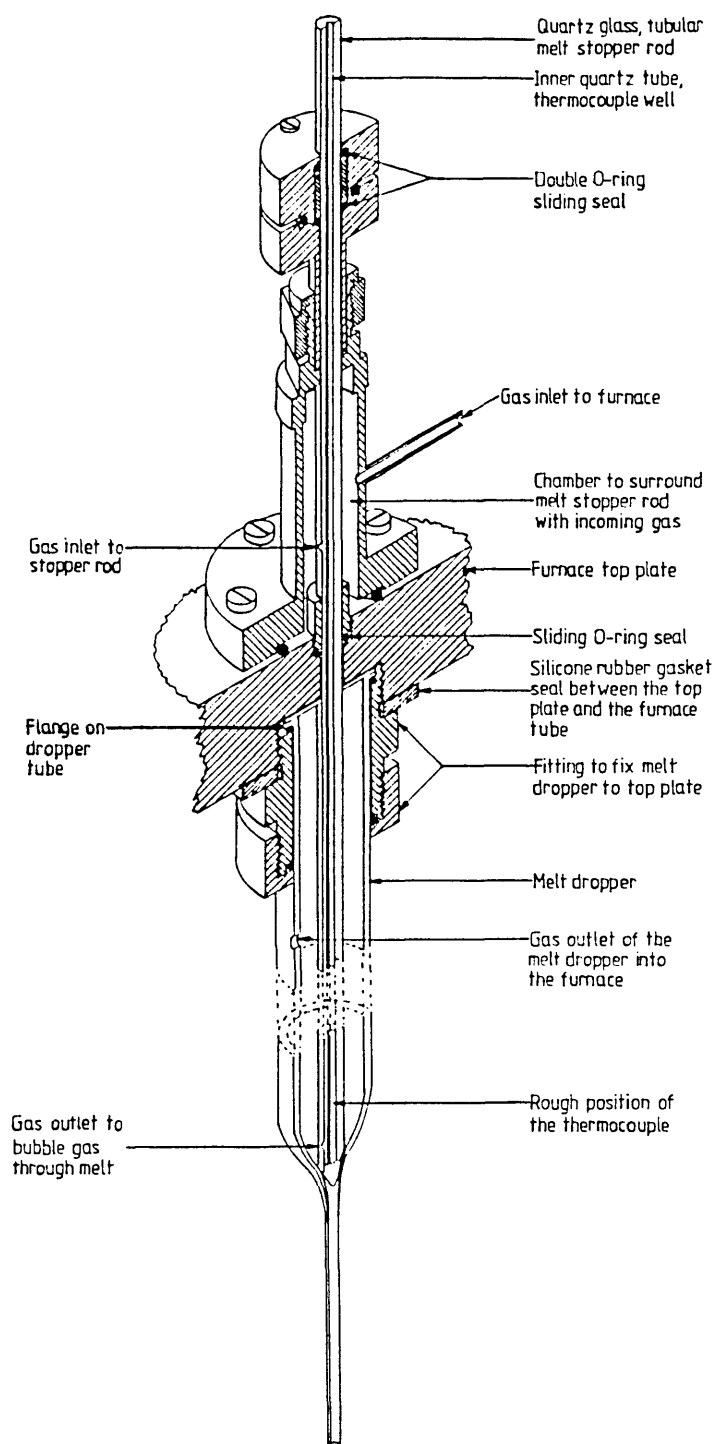
The initial apparatus is shown in fig. 24. The dropper comprised a funnel shaped quartz glass tube, which rested on three quartz arms on the rim of the melt catcher. The melt stopper rod was also fabricated from quartz glass and had a tapered and ground tip. This rod mated with a ground surface in the melt dropper, so as to prevent the contained melt from dropping out. At the top it passed out through a PTFE seal in the top plate of the furnace tube. The dropping of the melt was simply initiated by pulling the quartz glass rod up, allowing the melt to exit from the resultant opening.

It can be predicted from theory (see appendix C), that the rate at which a liquid flows out of a container, is dependent upon the pressure at the outlet (or the "head") exerted by the liquid within it. This depends only on the height of the liquid above the outlet and the area of the outlet. As the level of the liquid within the container drops, so does the rate at which it travels out. This variation was deemed to be undesirable for the growth of epilayers by RDLPE, as it would inevitably affect the boundary layer thickness, and hence the composition and doping uniformity of the deposited layer. Consequently,

the melt dropper was designed, so that it maximized the length of time that a relatively constant head of melt was present after actuation of the stopper rod. This was achieved by tapering the melt dropper down to a narrow tube at its end. The internal diameter of this was approximately 1mm, and its length was twice that of the depth of the In melt in the untapered section of the dropper tube. This design allowed the output flow rate of the In melt to remain fairly constant until exhaustion of the melt reservoir.

Ultimately, if a yet more constant flow rate was required, there was sufficient dimensional leeway to enable further improvement. This would be achieved by either, an increase in the diameter of the melt reservoir (and hence a reduction in its height for a particular volume of melt) or, an increase in the length of the narrow outlet tube, or a decrease in the diameter of the narrow tube. However, for the series of experiments undertaken, these modifications were not found to be necessary.

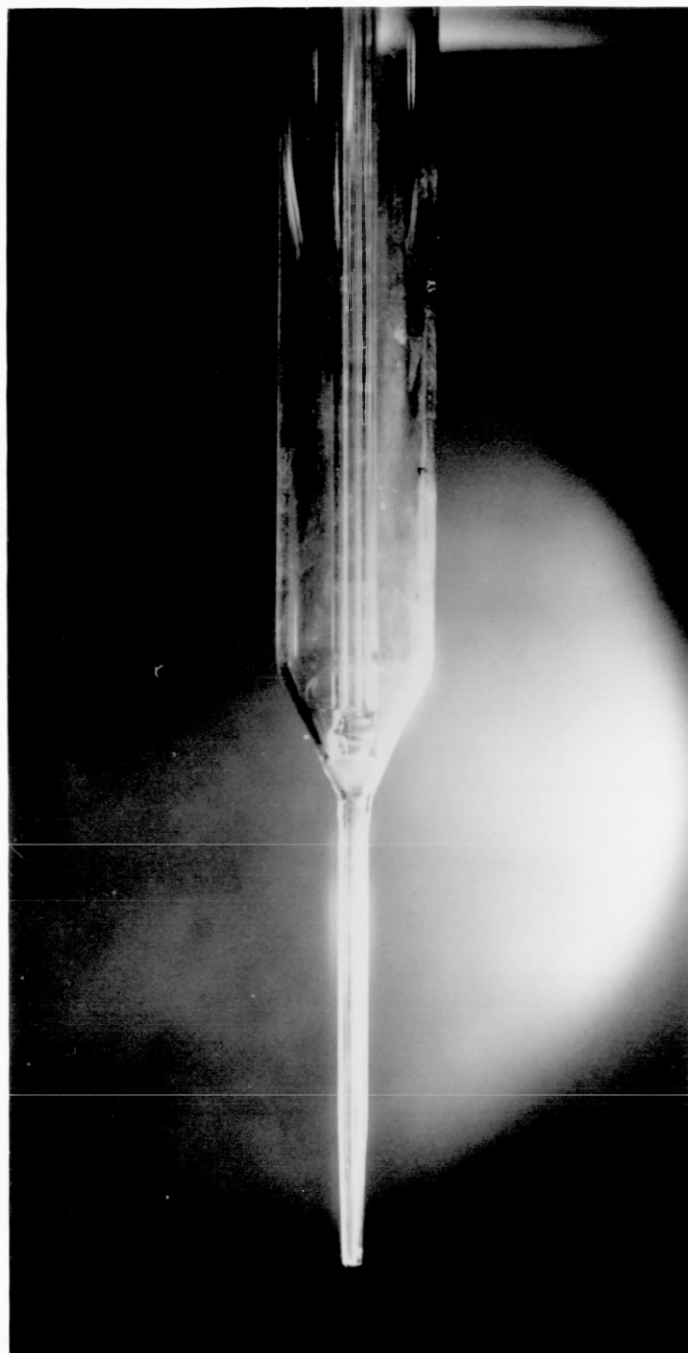
This initial design suffered from a number of failings. Experimentally it was extremely difficult to load the RDLPE furnace, prior to a growth run, and to satisfactorily centralize the dropper assembly over the substrate. In addition, the design as depicted in fig. 24, did not allow any means of monitoring the melt temperature; nor did it provide a method of suppressing the thermal decomposition of the InP substrates used for growth. In order to tackle these limitations, a new melt dropping assembly was designed and built. The design of this was very similar to that shown in fig. 33. [It differed only in that Swagelok compression fittings (employing PTFE ferrules), and a flangeless melt dropper tube, were employed. The reasons for altering these features, in further design modifications, are described



(a) Cross section through the melt dropping assembly.

Fig. 33 The melt dropping assembly.

Fig. 33 continued...



(b) Photograph of the bottom of the melt dropper tube and the melt stopper rod.

in detail later in this section]. The melt dropper was made much longer, and held firmly to the top plate by a compressed O-ring. This made assembly much easier.

The melt stopper rod was designed to be multifunctional. The rod consisted of one tube within another. The outer tube, was bent over and sealed onto the edge of the inner tube at its top. At the base, the two tubes were sealed and tapered. This tapered section was ground on the outside so as to mate with the ground surface at the base of the dropper tube. This design allowed a thermocouple to pass down the inner tube, from the outside of the furnace, right into the melt, without entering the furnace atmosphere. The construction of the melt stopper rod also permitted incorporation of a method of suppression of the decomposition of the InP substrate.

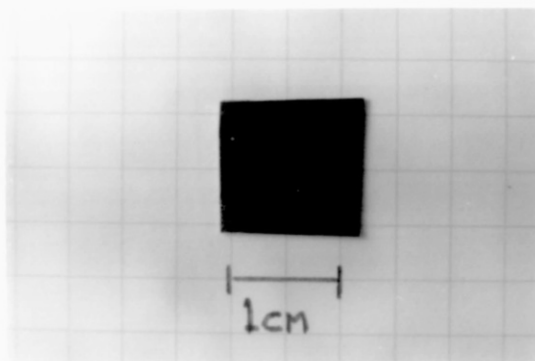
Substrate decomposition was discussed in detail in section 3.4.4 and the techniques for overcoming this problem were outlined. However, from a practical and safety point of view, none of these remedies could be used in the present equipment. The majority of techniques for suppression of decomposition, involved increasing the vapour pressure of phosphorous over the substrates. It was therefore thought that a similar effect could be achieved if the hydrogen gas, which normally flows through the furnace during the run, was bubbled through a melt containing an excess of InP. This would then enhance the pick up of phosphorous by the hydrogen, providing a greater phosphorous over pressure at the substrate.

To achieve this bubbling action in the RDLPE apparatus, the annular gap between the outer and the inner tubes of the melt stopper rod, was employed to provide a means of transporting the hydrogen gas down to where it could pass into the melt. This was accomplished by having a

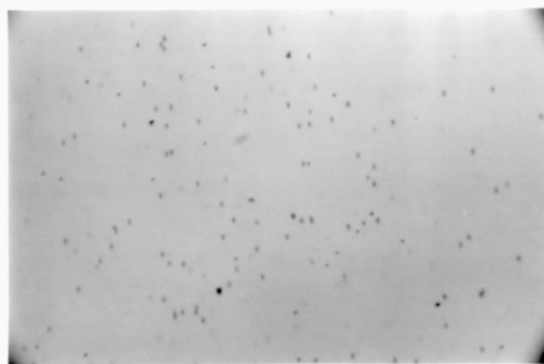
hole in the outer tube, near the top, and having the outer tube surrounded by the hydrogen at this point. Below this hole a sliding seal, around the melt stopper rod, was used to prevent the hydrogen gas escaping directly into the furnace. Near the bottom of the melt stopper rod, below the level of the melt, another hole was made in the outer tube in order to let the hydrogen out. The melt dropper tube, (now a continuous tube up to the top plate), had to be provided with an outlet in order to allow the phosphorous enriched hydrogen to flow into the furnace. This outlet, was made near the top of the dropper tube so as to facilitate the process of flushing the furnace out with hydrogen, prior to a run.

This technique for suppression of substrate decomposition, was found to work very successfully. Fig. 34a and b, shows one half of an InP substrate which was exposed to typical growth temperatures, and experiment times, with the hydrogen bubbling through the melt. Whereas fig. 34c and d, shows the other half of the InP substrate, which had undergone exactly the same experimental procedures, except, that the hydrogen was not bubbled through the melt. It is clear from these photographs that the bubbling action significantly reduced the decomposition, although it was not totally eliminated.

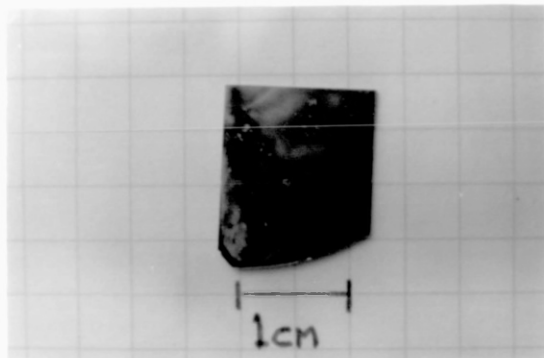
The design as described above, was used for a number of growth experiments. However, during some of these, a change in the surface tension behaviour of the In melt was observed. This resulted in the melt adhering to the quartz glass and the substrate, leaving them completely coated. This change occurred when the vacuum pump was switched on in order to hold the substrate pieces in place, and when simultaneously, the PTFE sliding seal around the melt stopper rod was slightly slackened to allow the rod to be lifted.



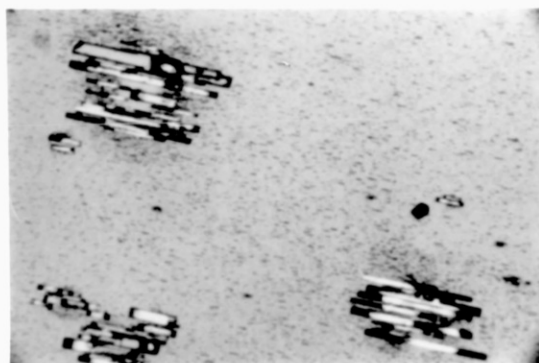
(a) Specimen protected by bubbling H_2 through the melt.



(b) Minor decomposition pits on the sample shown in (a).



(c) Specimen with no decomposition protection.



(d) Decomposition pits on the sample shown in (c).

Fig. 34 Substrate decomposition on specimens heated to 650°C and under identical conditions to those experienced in an actual growth run.

The problem had not occurred in the few experiments, which were conducted before the vacuum pump was introduced. Initially, therefore, it was thought that the vacuum pump might possibly act to contaminate the melt. Thus, a zeolite trap was constructed and placed in the vacuum line (discussed later, in section 5.2.5). However, after several more experiments, the same problem recurred. The only other possible source of this contamination was a leak in the furnace. This would lead to the oxidation of the melt and hence a change in its nature. The source of the leak was finally traced to the PTFE Swagelok sliding seal. If this seal was slackened only slightly more than that required to permit the melt stopper rod to be lifted, a leak would be created, and the melt would be oxidised. Consequently, the seals were replaced with the O-rings shown in fig. 33. This allowed the melt stopper rod to be moved whilst effectively maintaining a seal.

In addition to the problem described above, a number of growth runs had to be aborted when it was found that the melt prematurely exited from the dropper, shortly after it had melted. The cause of this was eventually traced to small pieces of indium becoming trapped between the melt stopper rod and the ground surface of the melt dropper tube. This stopped the latter from sealing and hence allowed the escape of the In as soon as it melted. Trapping of the In pieces was traced to the loading procedure. The In that comprised part of the melt was prepared in the form of small chips. As this was the first component to be loaded into the melt dropper, it was found possible for small pieces to get caught between the rod and the tapered dropper.

In subsequent growth experiments, after loading the melt components into the melt dropper tube, the area around the joint was checked to ensure that there was nothing preventing the melt stopper rod sealing

against the base of the melt dropper tube. This initially solved the melt drop-out problem. However, it recurred during later growth runs (at a different point in the operating procedure), and this was traced to the bubbling of the In melt causing the dropper tube to fall slightly, and thereby unseating the stopper rod. This was prevented, during subsequent runs, by incorporation of a flange at the top of the melt dropper tube. The flange prevented any downwards displacement of the tube. This is shown in fig. 33.

5.2.5 Vacuum system

A single stage, rotary vane vacuum pump was introduced into the apparatus when it was found that suction was required to hold the substrate pieces on the turntable (section 5.2.2). The incorporation of a vacuum line to the furnace proved very useful. It allowed the various graphite furnace components to be "baked out", under vacuum conditions, up to 0.05 Torr as measured in the furnace at 800 °C. Baking out involves heating components to elevated temperatures in order to desorb impurities. This technique is widely used e.g. Rhee and Bhattacharya [44].

As mentioned in section 2.7.7, graphite readily absorbs impurities, particularly sulphur which is a very strong dopant in InP. Clearly, unlike conventional sliding boat LPE, RDLPE does not involve the melt coming into intimate contact with the graphite prior to growth, and so, the problem is not as critical. However, with the newly made graphite components, it was found, that they contained quite a lot of sulphur. It was felt that it was advantageous to reduce the level of such impurities to a minimum.

When the furnace was being used to bake out the various furnace components the ferrofluidic bearing was replaced with a Pirani gauge

head. This allowed the vacuum to be monitored on the Pirani gauge meter which was situated below the control box. The vacuum reading, gave a comparative indication of how well a particular piece of graphite was baked out.

In initial experiments the vacuum line was connected directly to the furnace. However, as mentioned in section 5.2.4, some growth runs resulted in melt contamination. This caused it to coat the glass melt dropper tube, the substrate pieces and the melt catcher. This was first believed to be due to contaminants backstreaming into the furnace through the vacuum line. To eliminate this possibility a zeolite trap was constructed.

The zeolite trap also served to reduce the chances of damage to the ferrofluidic bearing. This had happened during an earlier run, after the vacuum pump failed and pump oil was sucked into the vacuum line, then to the furnace, and finally swamped and destroyed the ferrofluidic bearing.

Fig. 35 shows a schematic cross section through the zeolite trap. It consisted of an upper container, which held the zeolites, and a lower container, which held any oil that might have been accidentally sucked back through the vacuum line.

In addition to the zeolite trap, an aluminium section was made to surround the ferrofluidic bearing, giving added protection against flooding by oil. This "bearing protector" (see fig. 31) also ensured that there was no possibility of the bearing becoming coated with melt solution, should any get sucked down the rotating shaft.

After a series of runs the zeolites were regenerated by baking them out in a purpose built furnace, under vacuum. The furnace was heated by a cartridge heater. The temperature controller for the furnace, was

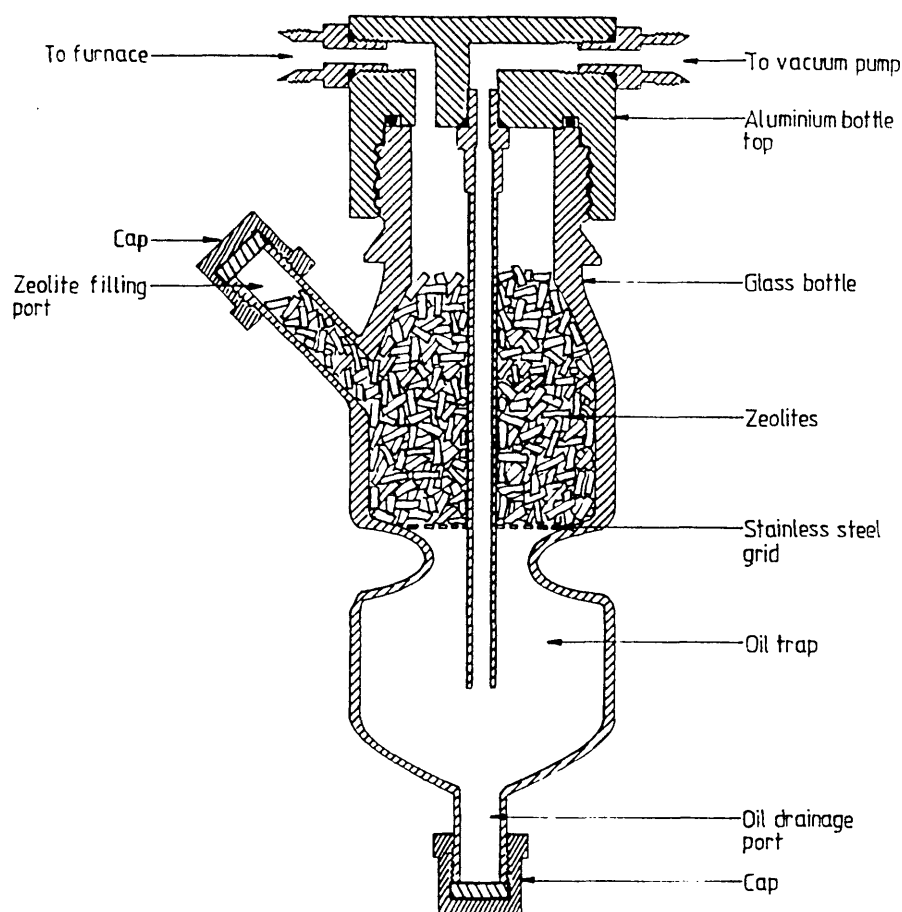


Fig. 35 Cross section through the zeolite trap.

situated on the shelf below the control box.

Fig. 36 schematically illustrates the various vacuum connections and gas supplies to the RDLPE equipment. The exhaust outlet of the vacuum pump was fed into the fume cupboard, and thence into the extraction system.

Initially it was found that using the vacuum system to hold substrate pieces onto the rotating turntable, also caused a partial vacuum in the furnace itself. This was found to be a consequence of the poor seal between a substrate piece and the suction holes machined in the turntable. This effect was not desirable, as a reduced furnace pressure

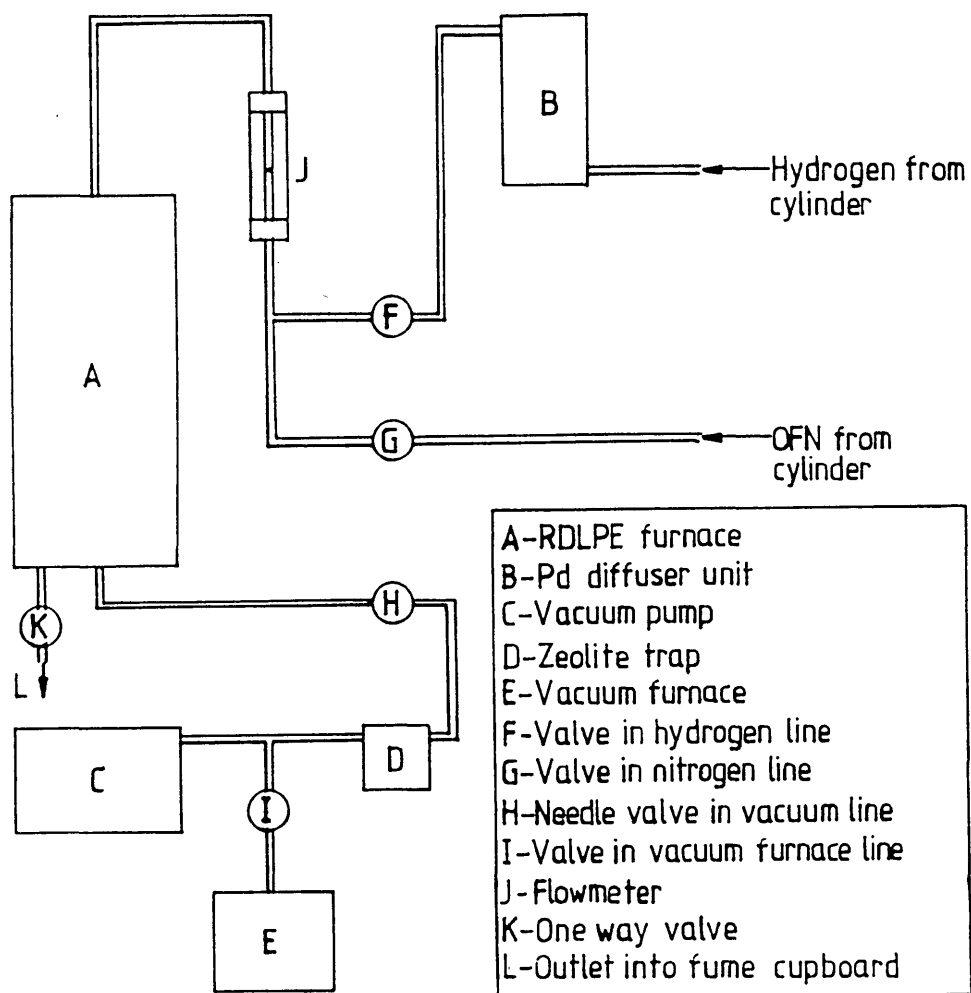


Fig. 36 Schematic diagram of the gas lines and vacuum lines connected to the furnace.

would enhance decomposition of the InP substrates. The vacuum system was therefore only connected to the turntable, upon commencement of the substrate rotation stage of a growth run. This minimized the duration of application of a vacuum to the furnace to a maximum of 60 seconds. Connection was effected using a simple on/off high integrity valve. However, this was found to cause abrupt changes in furnace pressure, resulting in violent bubbling and splashing of the melt within the melt

dropper tube. Replacing the valve with a needle version eliminated this problem.

5.2.6 Gas supplies

As mentioned previously, the gas used in LPE processes is generally hydrogen. This is because of the ease with which hydrogen can be produced in high purity, and because it provides a reducing ambient atmosphere. The original RDLPE apparatus was only supplied with purified hydrogen from a Pd diffuser unit. A supply of oxygen free nitrogen (OFN), was later installed in order to aid leak testing of the apparatus, and to act as a flushing gas prior to the use of hydrogen during a growth run. Fig. 36 shows the arrangement of the gas lines.

Before commencing to heat the furnace, the nitrogen atmosphere was replaced with purified hydrogen. This was fed into the top of the furnace, via the holes in the melt dropper tube. Because of its comparative lightness it filled the furnace from the top, displacing the other gases through the baseplate into the fume cupboard.

The H_2 and the N_2 lines joined upstream of a Brooks flowmeter (type R2 15 AA with a sapphire ball) to form a single gas supply line to the furnace. The flowmeter could measure flow rates up to 8.2 litres/hour.

5.2.7 Control box and associated instruments

The control box instruments are shown in fig. 25, this section will deal with each part in turn, giving a detailed description where applicable.

i) **Master temperature controller:** This was a three term temperature controller and was used to maintain the central zone of the furnace at a preset temperature. The temperature sensor connected to the controller was a type R thermocouple, suitably positioned in the central zone of the furnace. A thyristor stack was built into the

controller and this regulated the amount of power going to the furnace.

ii) **Slave temperature controller:** This was also a three term temperature controller. It was used to control, at a preset value, the difference between the temperature of the lower furnace winding and that of the central furnace zone (see section 5.2.1). The temperature sensor for this controller was again a type R thermocouple. The sensing point was situated in the bottom zone of the furnace.

iii) **Slave thyristor stack:** This controlled the power to the lower furnace winding, dependent on the control signals sent from the slave temperature controller. This particular instrument had an ammeter on the front, giving a visual indication of the current passing through the winding.

iv) **Temperature monitoring:** When designing the equipment, it was obviously very important, that there should be a means of monitoring temperatures in the furnace. At the beginning, temperature profiles were taken through the furnace for various settings on the temperature controllers (only possible, with much of the dropping assembly and the turntable not in place). During initial growth experiments, the temperature profile and the temperature of the substrate, had to be assumed to correspond to the profile measured previously for those settings. The only way of monitoring the temperature at various points in the furnace, during an experiment, was by using the type R thermocouples used by the temperature controllers (the temperature readings from these could be compared with those obtained during profiling). Thus, as well as being connected to the temperature controllers, the thermocouples were connected to a two pole, six way rotary switch (fixed into the front panel of the control box). This allowed the two pole connections to be switched between six inputs

each.

Connected to the rotary switch was a purpose built circuit (see fig. 37). This enabled the thermocouple voltages to be amplified to a suitable level to be displayed on the three and a half digit, digital panel meter (DPM). This was achieved by utilizing an operational amplifier (IC2). To provide the necessary supply voltages for this a hex inverter integrated circuit (IC1) was employed.

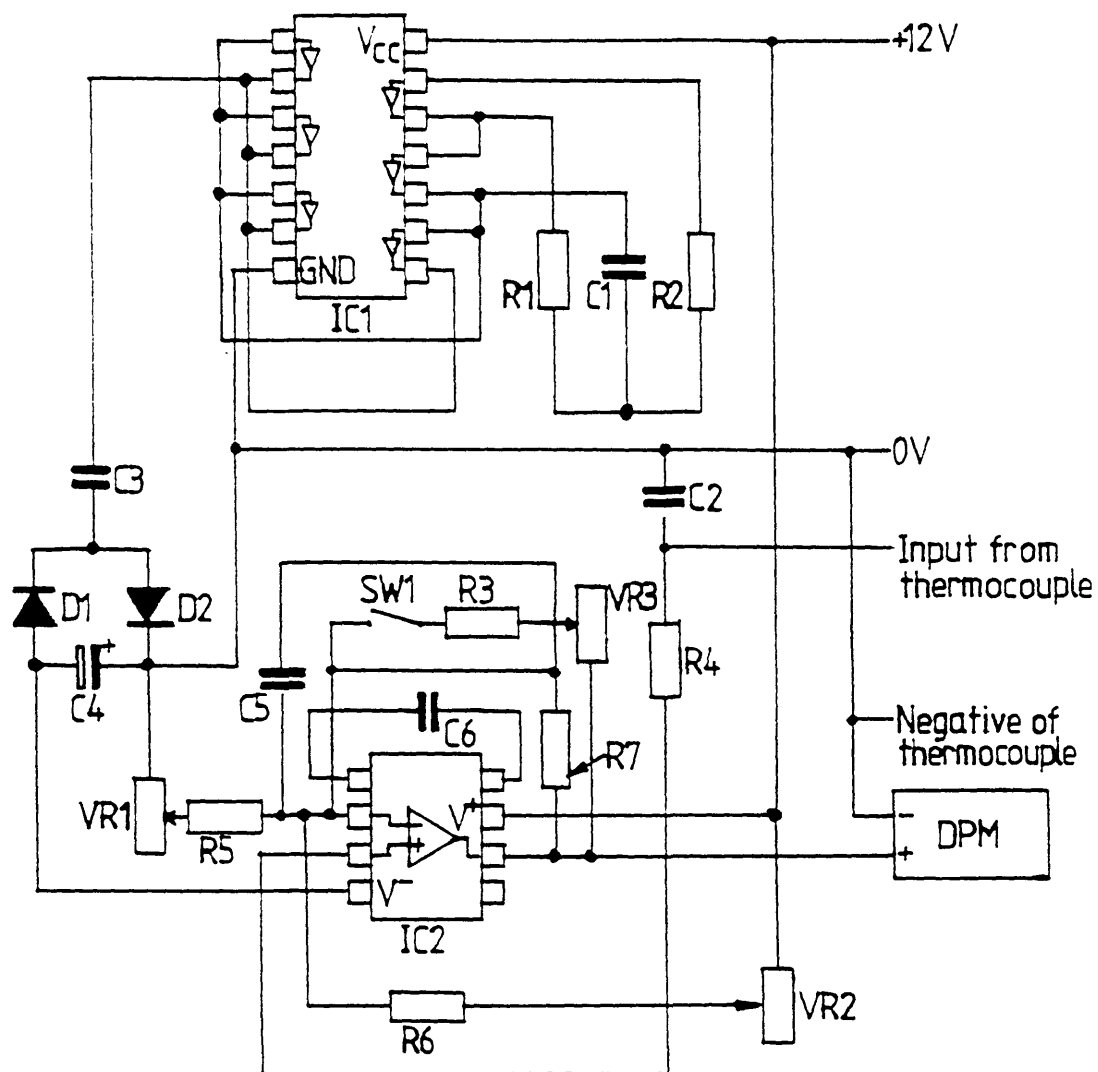
When the melt dropping assembly was redesigned, an improvement was made to the temperature monitoring system. The melt stopper rod was redesigned to allow a type K, sheathed, thermocouple to pass down its centre into the melt area (see section 5.2.4). This thermocouple was also connected to the rotary switch.

The voltage levels produced by the type K thermocouple were different to those produced by the type R thermocouples. Therefore, the circuit was altered so that it could be switched to give suitable amplifications for the different thermocouple types.

This arrangement for monitoring and measuring the temperature of the melt was used for a number of runs. Later runs also employed a more accurate commercial meter to indicate the melt temperature directly. The purpose built circuit continued to be used for monitoring furnace temperatures during growth runs and when the graphite components were baked out.

v) **Motor speed control:** A means of accurately controlling and varying the speed of rotation of the turntable within the RDLPE apparatus was required.

The motor used during initial experiments had a simple speed controller built into its base (see fig. 29). This was found to be unsuitable as it provided little sensitivity, and reduced the torque



Resistors: $R1=47k\Omega$, $R2=10k\Omega$, $R3=56k\Omega$
 $R4=10k\Omega$, $R5=1k\Omega$, $R6=330k\Omega$, $R7=100k\Omega$
 Variable resistors: $VR1=200\Omega$, $VR2=100k\Omega$, $VR3=50k\Omega$
 Capacitors: $C1=470pF$, $C2=0.22\mu F$, $C3=1\mu F$, $C4=100\mu F$
 $C5=0.22\mu F$, $C6=100pF$
 Switch: SPDT toggle switch
 Diodes: $D1 \& D2=1N4007$
 Integrated: $IC1=$ Hex inverting buffer 4069
 Circuits $IC2=$ Op-amp LM308AN

Fig. 37 Circuit diagram of the thermocouple voltage amplifier.

delivered by the motor at lower rotational speeds. This made the motor susceptible to irregular rotation and even stalling. The controller also limited the lowest speed to 200 rpm, which severely restricted the range of experiments possible.

Later runs employed a different motor and control system. This overcame the limitations mentioned above. The motor was controlled from a separate unit, capable of adjusting the rotation speed from stationary up to 3000 rpm. It was also possible to have the shaft rotating at an extremely slow rate, yet still maintaining a high torque.

In order to simultaneously vary the rotation rate and view the substrate during a growth run, a remote control unit was also constructed. This was based on a 10 turn potentiometer connected via a lead to the control unit.

vi) **Motor speed measurement:** It was necessary to know the speed of rotation of the substrate, and for this purpose a tachometer was constructed. To determine the rotation rate, the circuit employed a reflective opto-switch, placed to face the motor shaft. Half of the shaft was masked to prevent reflection, (see fig. 38). Thus, when the infrared light was emitted by the opto-switch, a reflected beam was received by the detector for only half of each revolution of the shaft. Therefore, one electrical pulse was produced by the detector for every revolution, and the frequency of those pulses was directly proportional to the rotation rate of the motor. The pulses from the detector, were fed into a frequency-to-voltage-converter integrated circuit. This produced a voltage directly proportional to the frequency of the input pulses, and thus, directly proportional to the rotation rate.

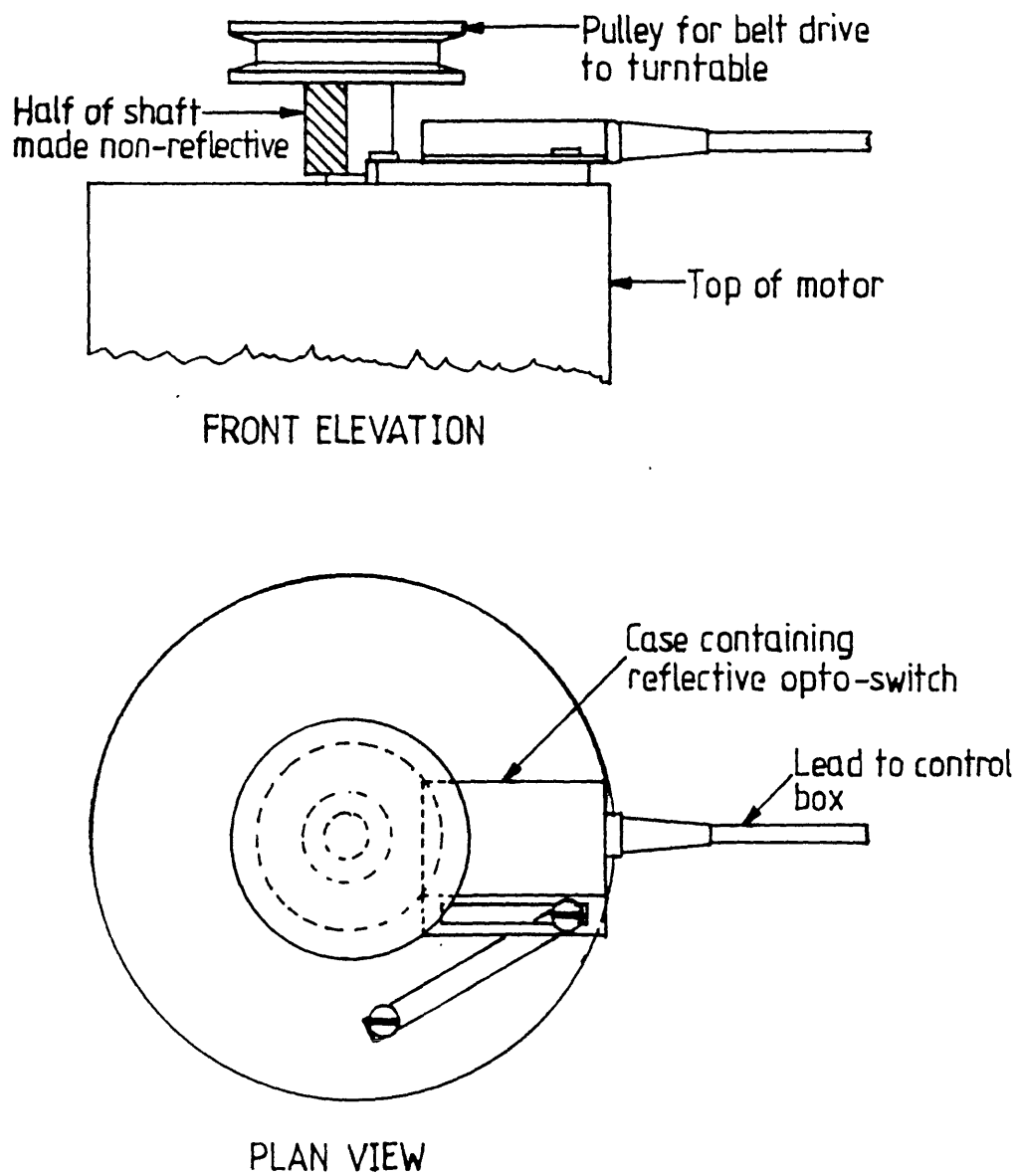


Fig. 38 The top of the motor and the reflective opto-switch.

By carefully choosing the components in the circuit, it was possible, to get an output voltage, which was a direct reading of the rotation rate in revolutions per minute (rpm) e.g. 1000 rpm produced a 1000 mV output from the circuit. The resulting voltage from the circuit, was connected to a spare position on the rotary switch (mentioned previously in part iv of this section) such that, upon selection, the rotation rate was displayed on the DPM.

The tachometer circuit was installed in the main control box of the equipment, and the opto-switch was connected to this via a socket in the front panel. A box was made to house the opto-switch in such a way, that it could be fixed at the appropriate position on the motor, see fig. 38.

The circuit was calibrated, by connecting the output of the opto-switch to an oscilloscope, and adjusting a potentiometer in the circuit until the DPM displayed frequency, equaled the actual frequency.

vii) **Pirani gauge meter:** This unit was situated directly beneath the control box, and was used to give a measure of the vacuum in the furnace when the graphite pieces of the equipment were being baked out. See section 5.2.5.

viii) **Vacuum furnace, temperature controller:** Situated on the shelf directly below the control box, this unit was a combined temperature controller and thyristor stack, and was connected to the cartridge heater in the vacuum furnace. The temperature sensor, for this controller, was a platinum resistance thermometer. See section 5.2.5.

5.2.8 Additional safety features

The original apparatus design for RDLPE, had the furnace and control box fixed to an open framework cabinet. For operator safety, in case of

explosion, the sides and the back were clad with aluminium sheets and a clear perspex door was fixed to the front of the cabinet. This allowed the run to be viewed safely.

In order to reduce the risk of a hydrogen explosion within the RDLPE system, the apparatus was thoroughly checked for leaks under positive pressure before a growth run. In addition, the vacuum pump was prevented from drawing outside air through the furnace outlet, by sealing this off before evacuating the turntable. A one way valve, situated in the outlet line, provided an extra safeguard should the sealing procedure fail.

5.2.9 Apparatus for confining the height of the melt

One of the main limitations and problems with the RDLPE apparatus, as so far described, was the limited coverage of the substrate by the melt. The size of the total coverage, during a growth experiment decreased as the rotation rate was increased (e.g. it decreased to approximately 10mm diameter at 1000 rpm). This is discussed in more detail in chapter 6.

To overcome this limitation, it was necessary to develop a method of spreading the existing quantity of melt over the substrate. The design solution adopted is shown in fig. 39. The apparatus confined the melt to a small gap between the rotating turntable and a stationary graphite surface. The height of the melt being limited by the size of the gap.

The design consisted of a single piece of graphite (the "melt confiner"), the inside of which served as a reservoir to contain excess melt. The under-side of the melt confiner acted as the stationary, top, surface. The centrally positioned hole in the base served to deliver the melt to the substrate. It also ensured that the melt would be

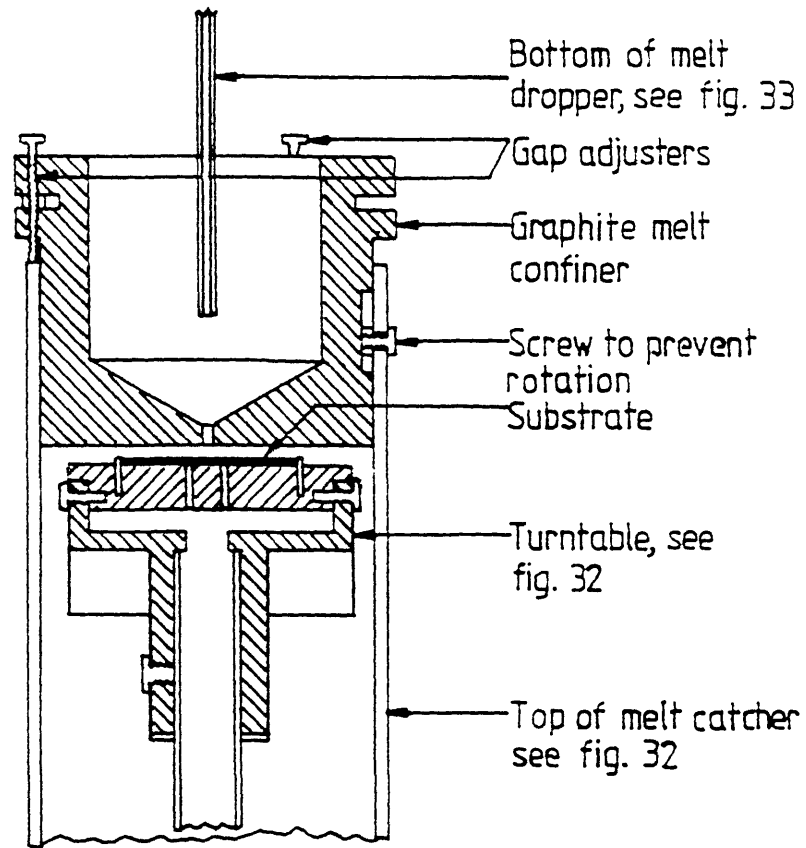


Fig. 39 Cross section through the graphite melt confiner.

delivered directly to the centre of the substrate. This removed the need to perform the difficult alignment procedure of the melt dropper tube with the turntable centre.

The melt confiner, as shown in fig. 39, fitted snugly in the quartz glass melt catcher tube. It rested on the rim of this on its three adjustment screws. By rotating these, the melt confiner could be raised or lowered from the melt catcher, and thereby, an alteration in the gap size could be made. To prevent the possibility of the confiner rotating, due to friction with the melt, a nut and bolt was fixed through the melt catcher tube. The nut, which was on the inside of the melt catcher tube, located in a vertical slot in the melt confiner,

thereby preventing rotation but allowing it to be raised and lowered by the adjustment screws.

The melt confiner was used in one growth experiment only, which had to be abandoned due to thermal expansion problems. These resulted from the shaft and turntable rising, as they expanded, causing the substrate to be forced against the melt confiner. To overcome this problem, it would have been necessary to take account of this expansion when setting the gap between the two components. This could only have been done prior to loading the furnace. This was a very complicated problem, as the expansion would have to be calculated from an integration that took into account the temperature gradients present in the furnace. Also, the change in the positions of the melt confiner and the substrate would have to be accurately calculated. This required a summation of expansions from a number of furnace components of differing properties, at varying positions within the furnace. Consequently, a way of physically measuring the effect of the temperature on the gap was required. Unfortunately, the sideways visibility through the inner furnace tube at this point, was poor, so an optical measurement of the gap was not possible. It was also found that when the melt confiner was in use all visibility of the substrate during a run was lost.

Shortage of resources made it necessary at this time to suspend further investigation into the use of the melt confiner. However, it was felt that with further work, the melt confiner would eventually prove to be a viable solution to the problem of poor melt coverage.

5.3 SUMMARY

An apparatus was designed and built to grow layers by RDLPE, in which a supersaturated solution was dropped at the required time, onto a substrate which was rotating at the desired speed. The original apparatus was altered and added to, as a result of experimentation, to a point at which a reproducible set of experiments could be conducted to investigate the LPE growth of layers by this technique.

The following list contains some of the main design features:

i) Substrates of any shape or size (limited only by the size of the turntable) could be used. These were held on the turntable by suction. The equipment permitted substrate rotations up to 3000 rpm.

ii) The equipment was designed such that different graphite turntable surfaces could easily be used.

iii) The speed of rotation could be accurately and remotely controlled up to speeds of 3000 rpm, and this was measured optically and displayed on a three and a half digit DPM.

iv) The use of a belt drive arrangement for the motor, plus the incorporation of several bearings down the length of the turntable shaft, made vibration negligible at all speeds (i.e. up to 3000 rpm).

v) The temperature of the melt could be monitored and displayed.

vi) The design incorporated a novel technique for suppressing the decomposition of the InP substrate.

vii) The furnace, which was used, allowed visual monitoring of the growth experiments.

viii) By employing a graphite melt catcher, used melt could be simply tapped out and stored for possible future use. This also made cleaning much easier.

ix) The melt dropping assembly was made from an all quartz glass,

construction, which minimized contamination (compared to graphite melt wells used in conventional LPE). This also eliminated any abrading graphite surfaces which can introduce particulate contamination.

x) The melt stopper rod allowed easy and precise initiation of a growth run.

CHAPTER 6. RDLPE GROWTH EXPERIMENTS

6.1 INTRODUCTION

This chapter describes the experiments conducted using the RDLPE equipment. The procedures used for growth, the problems of substrate coverage, the characteristic features resulting from the growth, and finally, the effect on the epilayer growth as a result of conditions present, are all discussed.

6.2 MATERIAL USED FOR THE GROWTH EXPERIMENTS

The substrate material used for the growth experiments was single crystal InP with a (100) oriented surface, and was either n-type (S or Sn doped), or p-type (Zn doped). Due to problems of availability of suitable material, the majority was in fact n-type.

The size of the substrates used in the earlier experiments were one 12mm X 12mm piece, centrally positioned and four outer pieces measuring 12mm X 8mm. These pieces fitted into recesses, machined in the turntable surface, (see section 5.2.2). This was necessary to make the best use of the substrates which were available at the time. With later modifications to the turntable, when quartz pillars were used to restrain the substrate, it became possible to vary the size of the pieces from experiment to experiment. However, generally speaking, the size was at least 12mm X 12mm and sometimes as large as 25mm X 25mm.

In each experiment, the melt was composed of 40g of Indium (99.9999% pure), as the solvent, and an appropriate amount of InP as the solute. To this mixture, a dopant was also added. This was Zn when the substrate was n-type, or Sn, when the substrate was p-type. Consequently, any epilayer grown on the substrate, should have created a p-n junction, making the observation of the grown layer easier (this

is discussed in section 6.4).

The quantity of In used was a compromise, decided by a number of different factors:

i) The melt had to be in contact with the substrate for a suitable period of time (i.e. sufficient for epilayer growth).

ii) The rate at which the melt dropped onto the substrate, had to be high enough to give good substrate coverage (discussed in section 6.5.1).

iii) In order to conduct a reasonable number of growth experiments, the quantity of melt per run had to be restricted.

The amount of In which was chosen, gave a 10 second growth time (with the 1mm hole in the dropper tube), and a reasonable surface coverage at lower substrate rotation rates.

Once the amount of In, had been decided, it was possible to calculate the quantity of InP needed, using equation (3.4) i.e.

$$x = 1.77 \times 10^3 \exp(-11431/T_1).$$

Here x is the atom fraction of the phosphorous in the solution and T_1 is the liquidus temperature.

It was decided to use a temperature of 650°C when conducting the growth experiments, this being the temperature at which a suitable amount of InP would dissolve in the In. Thus $T_1 = 923\text{K}$, making $x = 7.40 \times 10^{-3}$ and consequently, for 40g of In, 0.3788g of InP must be added to form an exactly saturated solution at 650°C (calculation is accurate to $\pm 1^\circ\text{C}$).

For many of the early experiments, more than this quantity was used. One reason for doing this, was that it ensured saturation of the melt, another was, that it did not require accurate weighing. Additionally,

excess InP provided the extra phosphorous to account for that removed due to forced evaporation by the bubbling hydrogen. It was only for the later experiments, that the exact amount of InP required was used (see section 6.5.2 for a detailed explanation).

Finally, the quantity of the dopant, which was to be added to the melt, was calculated by using the distribution coefficient k , which can be defined as the ratio of the atom fraction of dopant in the growing layer, to the atom fraction of dopant in the melt. For Zn $k = 0.7$ and for Sn $k = 2 \times 10^{-3}$ (Kuphal [52]).

The doping was aimed to be approximately 5×10^{18} atoms/cm³ for most of the growth experiments, but during later experiments the doping was increased to ten times this in order to compensate for having to use n-type InP when a p-type melt was required (see section 6.5.2).

6.3 EXPERIMENTAL PROCEDURE

The following section is a description of the step-by-step procedure used for a growth experiment. It is the method used for all the later growth runs and had evolved gradually from the earlier attempts. However, the basic procedure remained the same throughout all growth runs.

The procedure took a number of days to complete and was as follows:

i) An Indium ingot was placed on a cleaned ceramic tile and cut into pieces approximately 3mm X 3mm X 3mm. This enabled the indium to be loaded easily into the melt dropper tube, and stopped any becoming wedged between the melt stopper rod and the melt dropper tube.

ii) Appropriate quantities of the indium, indium phosphide and the dopant for the melt, were weighed out.

iii) The uncut substrates were aligned centrally on the surface of

the turntable, which had holes drilled in it, to take the quartz glass pins. These holes were positioned such that the pins when in place held the substrate centrally onto the turntable.

iv) The indium was cleaned in a 10% HCl solution, followed by a thorough rinsing with de-ionised water. The water was then drained away and the indium was partially dried.

v) Next, the Indium was loaded into the cleaned and degreased melt dropper tube (the melt stopper rod being in place, to prevent any indium getting on the sealing surfaces). Then, the melt dropping section of the apparatus was assembled (see fig. 33) and put in place in the furnace. The base of the furnace was sealed, using the baseplate, with the Pirani gauge head, attached.

N.B. At this stage none of the rotating assembly was placed in the furnace.

The furnace was then heated to approximately 125°C, for three hours under vacuum, to thoroughly dry the indium and to partially bake it out (ideally, to produce high quality layers, the indium should be baked at a much higher temperature, but this would have involved melting it, which would have created experimental problems later. However, at this stage in the development of RDLPE, such high quality was not essential).

vi) The InP for the melt, was next cleaned as follows:

- 1) The pieces of InP were thoroughly washed in acetone, to remove any wax left from polishing in manufacture, and also to remove any dirt or grease that might have accumulated on them.
- 2) Next, the pieces were immersed in concentrated sulphuric acid for five minutes to remove any remaining organic

matter on the surface.

- 3) They were then rinsed in de-ionised water to remove the sulphuric acid.
- 4) Following this, they were immersed in a 10% HCl solution for two minutes, to remove any oxide film remaining, and to make the surface hydrophobic.
- 5) Finally, they were allowed to dry.

vii) The melt dropping assembly was dismantled, so that the cleaned InP pieces, and the dopant, could be added to the indium, already in the melt dropper tube.

viii) The melt dropping section was reassembled and held in such a way, that the melt components could be tapped to the top end of the melt dropper tube. The melt stopper rod was then pulled up, so that it was no longer making a seal with the melt dropper tube, this allowed the sealing surface to be examined. Having ensured that all was correct, the melt stopper rod was then pushed back to make the seal with the melt dropper tube.

The melt dropping assembly was then loaded back into the furnace, which was then, subsequently evacuated and back filled with nitrogen. This was then left, whilst the rest of the preparation was completed.

ix) The substrate was next cleaned ready for growth, as follows:

Steps 1), 2) and 3) are as above for the InP melt Pieces.

- 4) The substrate was next thoroughly rinsed with methanol to remove all traces of the water.
- 5) It was immersed in 1% Bromine in methanol for two minutes. This non-selective etch removed a layer over the entire surface and left no etch pits. N.B. Incomplete rinsing at stage 4), was found to result in milky patches

occurring on the substrate when etched in the bromine methanol solution.

6) Firstly 4) then 3) were repeated.

7) It was then immersed in 10% HCl solution (as for the InP pieces, used in the melt).

8) The substrate was allowed to dry.

x) The InP substrate was weighed.

xi) The rotating assembly, was then put together as shown in fig. 31 and fig. 32, with the substrate being placed on the turntable prior to the glass melt catcher tube being lowered into place. This assembly was then loaded into the furnace.

xii) The turntable was centralised in the furnace, by adjusting the relative tightness of the bolts fixing the baseplate to the inner furnace tube. Then, the melt dropper tube was centralised. This was done by varying the tightness of the bolts fixing the top plate to the inner furnace tube, and by also observing the bottom of the melt dropper tube, relative to the alignment markings made on the turntable surface.

xiii) The furnace was pressurised with nitrogen, after first sealing the outlet; then a thorough examination of all the joints was made to ensure that there were no leaks.

xiv) The outlet was once more unsealed, and the furnace was flushed through with nitrogen for one hour (flow rate of approximately 8 litres/hour). Fig. 40, is a representation of the temperature of the furnace vs. time, with line A-B representing the above stage.

xv) The furnace was next flushed through with palladium diffused hydrogen for an hour (flow rate of approximately 8 litres/hour). This is represented by line B-C on fig. 40.

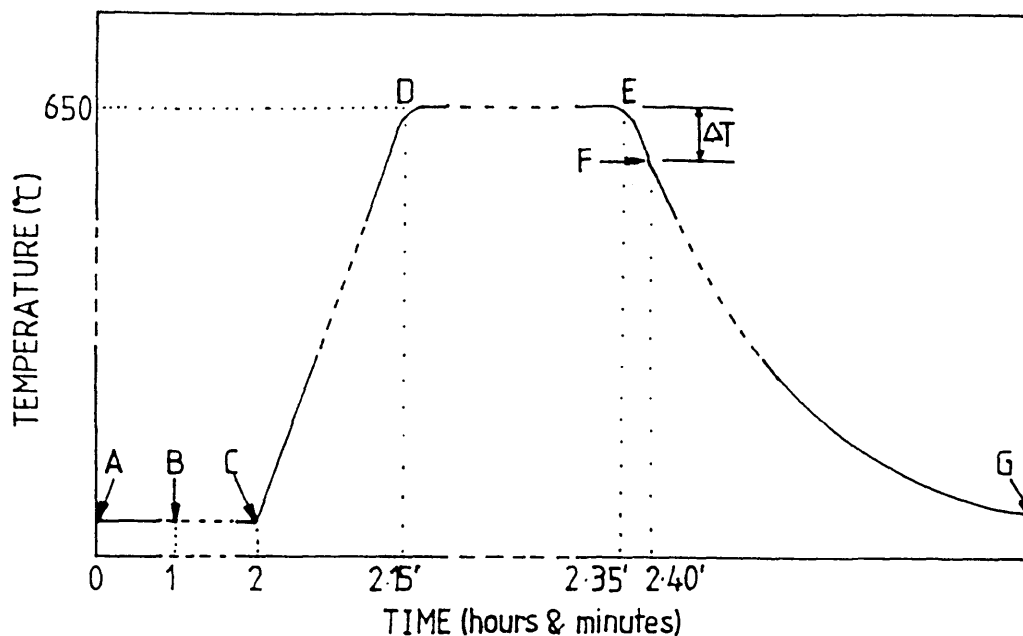


Fig. 40 Variation in the temperature of the furnace during a growth experiment.

xvi) The temperature was then set to 650°C, and the hydrogen flow was reduced to 2.5 litres/hour. This is represented by line C-D in fig. 40. There were two reasons why this slower flow rate of the hydrogen was necessary. One was that, as was experimentally observed by Chu et al. [56], the faster the hydrogen flow, the greater was the decomposition (however, it was still necessary to maintain a flow, to keep the reducing atmosphere over the substrate, and to carry the phosphorous vapour resulting from the bubbling action, over the substrate thus suppressing decomposition). The second reason was that with the reduced flow rate, the bubbling action never became too violent.

xvii) The melt was next held at 650°C for 20 minutes. During this time, the InP in the melt dissolved until equilibrium was reached. It

should be noted, that the bubbling action of the hydrogen through the melt, thoroughly mixed it and equilibrium was thus rapidly reached.

xviii) To supersaturate the melt, the temperature was then dropped by the required amount, in a step-cooling manner, shown as E-F in fig. 40. The melt supersaturation in all the growth experiments was produced by step-cooling, as opposed to the equilibrium-cooling or supercooling techniques (these techniques are described in section 2.4). This method was chosen because the others would require a more complex temperature control, and also, step-cooling was known to produce good layers of controllable thickness.

xix) When the temperature had dropped by the desired amount, growth was started. The procedure for this was as follows:

- 1) The gas outlet of the furnace was sealed, so that when the vacuum was connected to the furnace, no air was admitted.
- 2) The vacuum pump was switched on to evacuate the vacuum line.
- 3) The hydrogen supply valve was closed.
- 4) The vacuum needle valve was slowly opened.
- 5) The motor speed was next increased, to rotate the turntable at the desired rate.
- 6) The melt stopper rod was raised slightly to allow the melt to drop out.
- 7) An observation was kept on the substrate as the melt fell onto it. Immediately this finished, the rate of rotation was rapidly increased, to remove any residual indium (although often a small drop would remain, caught against one of the quartz glass pillars).

xx) Immediately following the growth, the furnace was "shut down",

shown as the curve F-G in fig. 40, the procedure was as follows:

- 1) The motor was stopped.
- 2) The furnace was switched off. This was done as soon as possible, so that the substrate was exposed to high temperatures for as short a period of time as possible, to minimize any decomposition.
- 3) The vacuum needle valve was closed, and the hydrogen valve opened to repressurize the furnace. This was, again done as quickly as possible, to minimize decomposition.
- 4) Once the pressure was above atmospheric, the outlet to the furnace was opened.
- 5) The furnace was left to cool.

xxi) Once cool, the hydrogen valve was closed and the furnace was flushed through with nitrogen, so that the furnace could be dismantled and the substrate retrieved.

xxii) The used melt, which was at this stage solidified in the melt catcher, was tapped gently out and labelled for possible reuse.

xxiii) The melt dropper tube, melt stopper rod and the melt catcher tube, were next cleaned with a HCl/HNO₃ mixture, to dissolve any indium sticking to the glass.

xxiv) The graphite bearing, the graphite melt catcher and the turntable were then loaded into the furnace once more, and baked at 750 °C for approximately eight hours, ready for the next growth experiment.

xxv) The InP slice, which had previously been removed from the turntable, was next given an initial examination under the light microscope. Following this, it was cleaned in a solution of mercuric chloride in dimethyl formamide, whilst being agitated, in an ultrasonic

bath. This solution dissolved away any residual indium on the InP.

xxvi) The InP slice was then weighed again, to form a preliminary idea of the amount of growth on the slice.

xxvii) The slice was then examined to discover the degree, and the nature of the growth, that had occurred. The techniques used for this, will be described next.

6.4 ANALYSIS TECHNIQUES USED

To analyse the layers which were grown, a number of techniques were used. These were as follows:

i) **Light microscopy:** The resulting substrate surfaces were examined under a light microscope, and occasionally, some pieces were cleaved to enable the edges thus formed to be examined. Photographs were then taken, of any interesting features. When a very clear image of any surface relief was required, a Nomarski interferometer was used with the microscope and again photographs were taken where appropriate.

ii) **Staining:** Some of the earlier specimens were tested using this technique, to show up by staining, the presence of a p-n junction; the type which it was hoped to grow in these experiments.

The method employed was to cleave the substrates and submerge them in a warm potassium ferricyanide/potassium hydroxide solution. Unfortunately, this was not a very reliable method of analysis and did not show any real results on the occasions when it was used, and because, during later experiments more reliable and informative methods of testing became available, it was decided to preserve all future substrates for use with these.

iii) **Scanning electron microscopy (SEM):** All the samples obtained from the growth experiments were examined using the SEM, and

photographs were taken where applicable.

This method allows the surface to be examined in far greater detail, than when the light microscope is used (although the light microscope still gives a better view of certain features).

SEM was also used, in conjunction with two other analytical techniques which will be described next.

iv) **Electron Probe (x-ray emission) Micro-Analysis (EPMA):** This is a piece of apparatus attached to the SEM, which analyses the characteristic X-rays which are emitted from a specimen, where the electron beam strikes it.

The technique thus provides identification of the elements present in samples (1% sensitivity).

v) **Electron Beam Induced Current (EBIC):** This piece of apparatus is also, attached to the SEM.

By using the induced current produced by the scanning electron beam, the EBIC in conjunction with the SEM, builds up a picture of the sample.

Using this technique, specimens, (mainly the edges of pieces which had been cleaved for that purpose) were viewed to determine the layer thickness across the sample.

To obtain a clear indication of the junction region between the substrate and the epilayer, it is an advantage when using this method to have a p-n type junction, as the marked change in the induced current across it would show on the image as a noticeable change in contrast.

vi) **Electrochemical profile plotter:** The profile plotter determines how the net carrier concentration varies through a sample. This is achieved by placing the specimen in contact with an electrolyte. The

capacitance of the Schottky barrier formed between them is thus used to determine the net carrier concentration near the surface. By using the electrochemical cell, to etch the sample by a known amount, and by repeating the capacitance measurements, it is possible to get a profile through it.

The profile plotter, in addition, can use illumination to determine whether the surface is n-type or p-type.

Thus, from the profile obtained the epilayer thickness can be determined.

6.5 RDLPE GROWTH EXPERIMENTS - RESULTS AND DISCUSSION

As was explained in section 5.1 and 5.2, the value of the majority of the earlier growth experiments, was that they provided information on places where the equipment needed to be improved, they also yielded useful information on using RDLPE as a technique.

6.5.1 Substrate coverage and wetting

After several earlier experiments, where equipment faults caused problems, the first trouble-free growth experiment took place, using a turntable rotation rate of 1000 rpm.

Other relevant conditions, were a furnace temperature of 650°C prior to a step-cool of 10°C and the melt 1°C hotter than the substrate.

From observation, it was noted that the melt did not completely cover the central piece of substrate before the flow broke up into streams and individual droplets, which flowed off the turntable.

This was considered a poor coverage, and an investigation into the reasons was necessary. Initially, it was thought that this was caused by either, contamination of either the melt, or the substrate surface. The reasoning behind this, was that on several previous occasions the melt had become oxidised which resulted in the substrate being

completely coated. However, even after the cause of the oxidation had been traced and the problem solved, (section 5.2.4), it was still found, that only the central substrate had an almost complete covering, when the above experiment was repeated.

It was next decided to determine if different rotation rates would effect the coverage, while keeping the other growth conditions constant. When a higher rotation rate was used in the experiment, it was found, that the area which was continuously covered by the melt, was reduced in size to a circular area, noticeably less than the dimensions of the central substrate. However, when a slower rotation rate was used, the central piece was covered, but radially beyond this, the melt broke up into streams or drops, as it had done in the earlier experiments. An additional factor, that was noted however, was that at the slower rotation rate, the height of the melt on the substrate was greater.

During these investigations on the different rotation rates, it had been observed that the periphery of the melt, appeared to form a much higher contact angle than one would have expected, that is, when taking into account, that the contact angle for an In-P melt on an indium phosphide substrate had been measured by Konig et al. [53] to be approximately 48 degrees (i.e. with this contact angle the melt would wet the substrate fairly well).

From these results and observations, it was possible to suggest a theory, to explain them. Firstly however, some additional knowledge of the behaviour of a liquid on a surface was necessary.

This follows below:

The contact angle measured by Konig et al. was that of a stationary drop on a solid substrate, and in these circumstances, the shape taken

by the liquid and consequently, the contact angle, would be that of minimal free energy. In fig. 4lb, just such a liquid drop is shown, where β is the contact angle, γ is a surface or interfacial tension, A is an area and the subscripts lg, sg, and sl, refer to liquid-vapour, solid-vapour, and solid-liquid interfaces respectively.

For free energy to be at its lowest value, the following equation must be minimized

$$\gamma_{lg}A_{lg} + \gamma_{sg}A_{sg} + \gamma_{sl}A_{sl}. \quad (6.1)$$

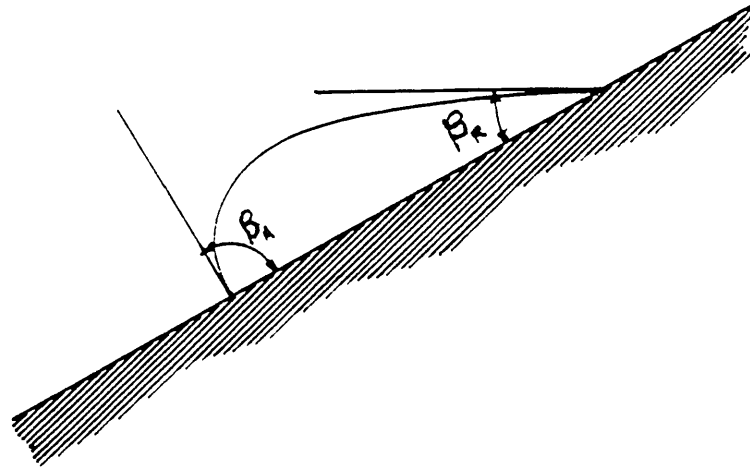
From fig. 4lb, for a plane homogeneous nondeformable surface, this minimization can be seen to yield the equation

$$\gamma_{lg}\cos\beta = \gamma_{sg} - \gamma_{sl}. \quad (6.2)$$

This is known as "Young's Law".

However, so far, we have considered an idealized situation in which there is only one equilibrium contact angle. In practice, this is rarely the case, as a number of stable angles can be measured for a given liquid-solid system, but the most important of these, in terms of the experiments undertaken, are the largest and the smallest. These are called the advancing angle, β_A , and the receding angle, β_R , respectively. The advancing angle, is that measured by advancing the periphery of a drop over a surface, and the receding angle is measured by pulling it back. The existence of these two angles, is demonstrated by having a drop on a plate and tilting it, as shown in fig. 4la. As the tilting is increased, it can be seen from the diagram, that the drop has become distorted, gradually changing its shape to balance the force exerted upon it by gravity. Eventually, a point will be reached beyond which the drop can no longer compensate for the force, i.e. it will roll down the plate. Thus, the angles which the liquid makes on

(a)



(b)

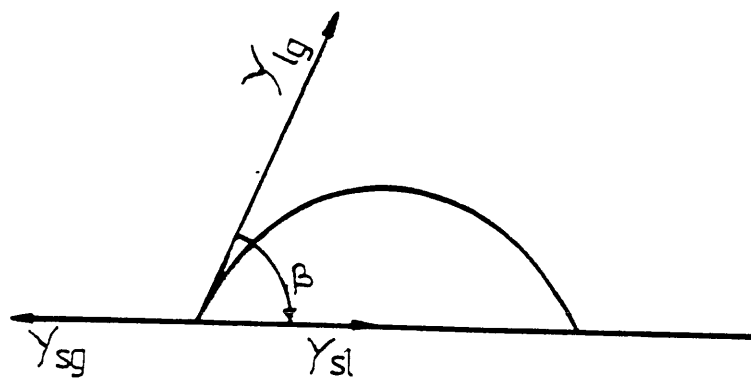


Fig. 41 The contact angles formed by a liquid drop on, (a) a sloping surface, and (b) a flat surface.

the solid at that point, are the advancing and receding angles for that solid-liquid system.

Clearly, in the case of RDLPE, where the liquid is dropped onto a rotating substrate and is spread across it, it will not form the contact angle found by Konig et al. [53], but instead, it will be the advancing contact angle which is much higher, as was in fact observed. Consequently, the melt will not wet the substrate as readily and this will have an unfavourable influence over the coverage, as will be explained later in this section.

It should be noted, that another possible factor, which might have affected the wetting of the substrate adversely, was contamination of the melt components and the substrate surface. However, after taking into account the stringent cleaning processes used, which had been changed several times to improve them with no noticeable effect, and also the high purity chemicals which had been used, particularly in later experiments, it seemed unlikely to be a major factor. However, it could not be completely ruled out, as features, observed on some of the layers which were grown in later experiments, also suggested the possibility of some contamination.

To understand the influence of the rotation rate on the coverage of the substrate, it is necessary to start with a consideration of the effect of the supply rate of the melt. As explained in section 6.2, the rate of supply of the melt for all the growth experiments, was set at 4 g/second. In section 4.2.1 an equation was derived (4.27) which gives the rate at which fluid is flung from a rotating disk at a given radius, when submerged in the fluid. This equation predicts that as the radius increases, so does the rate at which the fluid is pumped from it. The increased flow of liquid being supplied by the disk

drawing in more from directly above.

Clearly from this, when considering the case of RDLPE where the substrate is not submerged, but is supplied centrally by the liquid dropping onto it, one would expect that as the melt is flung outwards, when it reaches a particular radius, the rate of supply will exactly match the rate of removal. However, at greater radii, because all the melt is supplied centrally, the rate of supply of melt is not sufficient to match that ideally required. Consequently, the melt will be forced to try to spread more thinly. There will clearly be a limit to the extent to which this can occur before the need to minimize the free energy of the system makes the flow break up. This enables it to form an energetically more favourable shape and contact angle. Thus the coverage will be directly related to how well the melt wets the substrate.

Thus it follows from this theory that if the rotation rate is increased, then the balance in the flow rates (as described above), will occur at a smaller radius, and hence, the break up in the flow of the melt will also occur at a smaller radius. This was experimentally observed. Conversely, a slower rotation should lead to a greater area of coverage. As mentioned earlier in section 5.2.2, this was not observed with the early turntable designs because as the melt reached the edge of the central InP substrate, it encountered the graphite area of the turntable, resulting in its break up. It should be noted also that the substrates were of different thicknesses and thus they often stood either slightly proud, or slightly below the turntable surface. This hindered further melt coverage.

To overcome this problem, the turntable shown in fig. 32 and described in section 5.2.2 was designed. It was found, when using this

turntable at slower rotation rates and with the single large substrate, that the size of the surface coverage was indeed increased.

As will be discussed in the next section, the size of the coverage during the growth experiment could be fairly accurately determined afterwards since the melt periphery left characteristic growth features on the substrate.

Fig. 42 shows a plot of the radius of the coverage area as a function of the rotation rate (the open circles).

Using equation (4.27) a direct comparison can be made with these results. Thus by rearrangement, equation (4.27) becomes

$$R = \sqrt{\frac{Q}{0.886 \pi \sqrt{\nu \omega}}} \quad (6.3)$$

and by substituting in this equation, a flow rate of 4 g/second and the kinematic viscosity of the melt at 650 °C the following equation is obtained

$$R = 0.0665 \omega^{-1/4}. \quad (6.4)$$

This equation can be used, to calculate the radius at which the supply of melt matches the rate at which the melt is pumped outwards (if the substrate were submerged).

Fig. 42 also shows a plot of this radius, as a function of the rotation rate (the solid line). The important fact being that the radius is proportional to $\omega^{-1/4}$. Clearly from fig. 42 the actual radius at which the coverage ceases, is much less than the calculated radius, using equation (6.4), however, the plotted points fit the following equation very well (dotted line in fig. 42)

$$R = 0.0171 \omega^{-1/4} \quad (6.5)$$

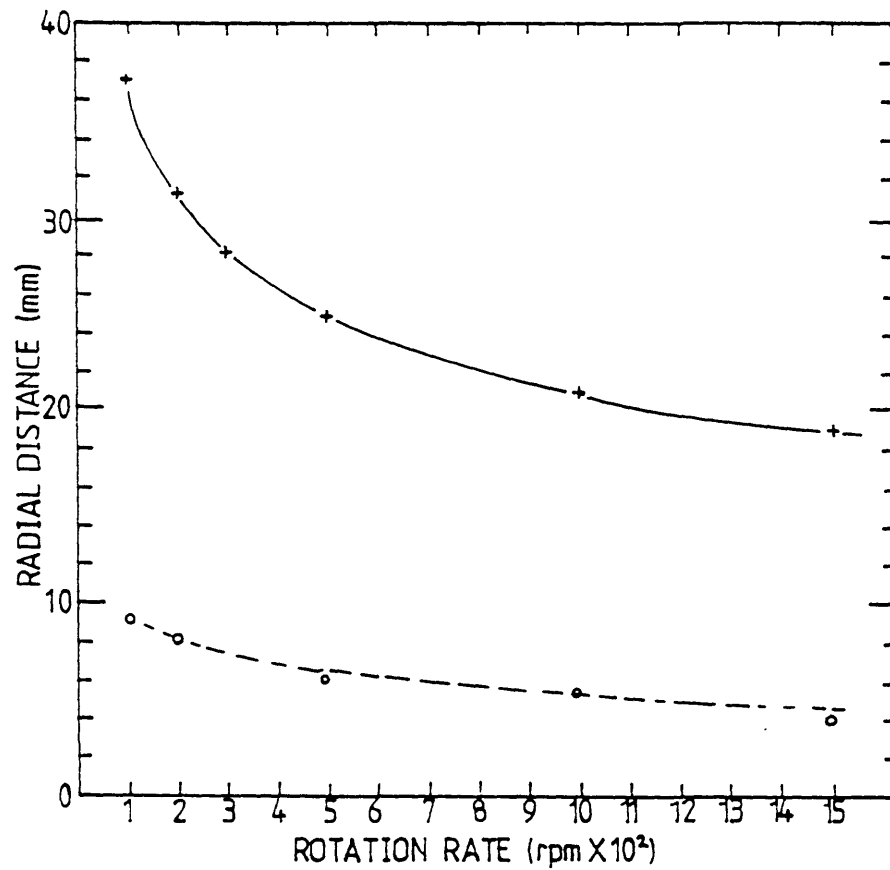


Fig. 42 Radius of the area covered by the melt throughout a growth run, as a function of rotation rate. The (o) points represent experimentally observed results, and the (+) points are from a simple analysis.

Clearly the radius has the same relationship with the rotation rate, as that predicted by equation (6.4). It is thus suggested, that the degree of coverage of the substrate was indeed restricted, by the rate of supply of the melt as previously postulated. In practice the actual radius at which the coverage ceased, was less than that predicted by equation (6.4). This was because the substrate was not submerged in the melt and thus the melt had additional forces acting on it (surface and interfacial tensions). These were trying to make it assume a shape

which would minimize its free energy, this being evident, from the fairly high contact angles observed. Another influencing factor, which had to be born in mind as a possible reason, was that in RDLPE, although the flow simulates that on a submerged rotating disk, it would not be identical.

It is thus clear from the results obtained, that with the equipment design used, the area of coverage was limited by the rotation rate, with only a small area of growth possible at high speed rotations.

From a consideration of this problem, the melt confiner described in section 5.2.9 was designed and made. As explained in that section, the melt confiner formed a plate parallel to the substrate surface. The gap between the two was small enough to forcibly reduce the height of the melt over the substrate, and therefore, caused the melt to cover a larger area. However, as explained in section 5.2.9 because of the difficulties encountered in using the melt confiner, it had to be put aside as a future method of improving coverage. It was decided the best way to proceed, was to investigate the growth within the limited area of coverage.

6.5.2 Investigation of actual growth on the substrates

Initially, the experiments were designed to investigate the performance of the equipment. This led to its gradual improvement, and eventually to a state where experimentation to investigate RDLPE as a growth technique could be conducted. The first of these experiments (described in section 6.5.1) involved varying the rotation rate, in an attempt to increase the area of the substrate which was covered by the melt. The experiment produced substrates whose surfaces, following growth, showed a number of noticeable features which were subsequently investigated.

These were as follows:

i) **"Growth islands"**: These features are shown in fig. 43.

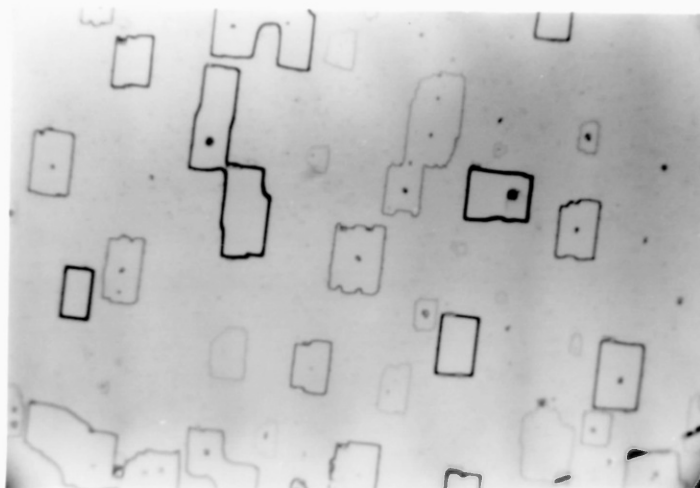
In the first few samples to be investigated, it was only in the central area that they occurred. They were obviously the result of preferential growth at particular sites on the substrate surface. The photographs in fig. 43 show that some of these islands resulted from growth at decomposition pits. A full discussion and explanation of these will be given later.

It was thought at this stage that the islands might possibly be surrounded by a grown layer, the conditions being thought sufficient for layer growth (furnace temperature of 650°C prior to a 10°C step-cool, a 10 second growth time and, with the substrate being 1°C cooler than the melt). Other growth features were also present which indicated the possibility of a surrounding layer.

Rezek et al. [12] grew layers at similar temperatures and cooling steps in a fraction of this growth time, using the sliding boat method.

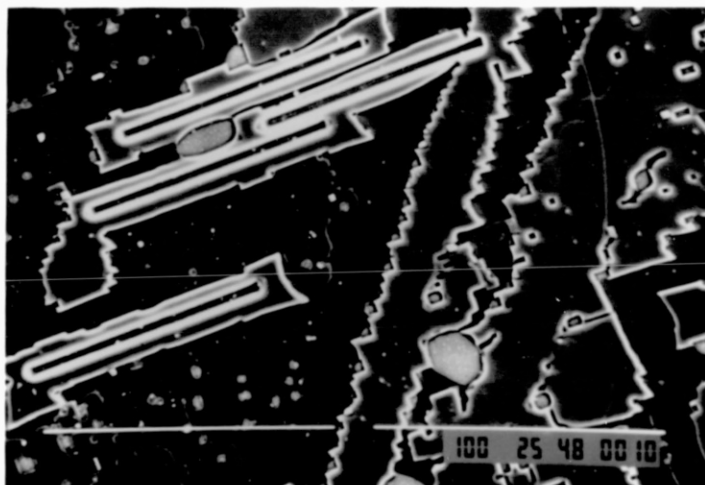
ii) **Decomposition pits**: The surface of the substrates showed signs of decomposition, taking the form of numerous small pits interspersed with a lesser number of larger ones, see figs. 44a and 44b. It was thought that this feature was possibly an indication of the presence of a layer; the larger pits developing on the initial substrate surface, after being exposed to 650 °C for over half an hour, and then propagating through any layer which had grown on the top. Although subsequent to growth, the furnace was switched off and the temperature fell quickly, there would however, in the absence of any protection, still be time for a small amount of decomposition to occur all over the layer, and hence might explain the fine decomposition pits.

As will be explained later, it was found, that there was in fact no



40 μm

(a) Growth islands.

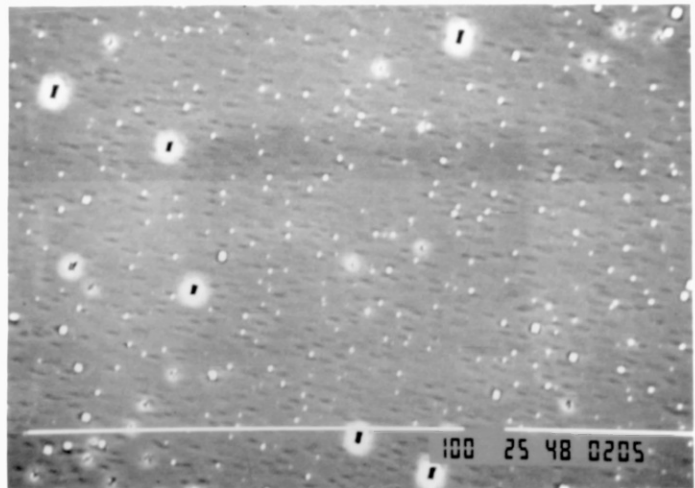


(b) Showing a clear case where growth islands have formed at decomposition pits. The white bars at the bottom of the photo represent 100 μm .

Fig. 43 Photographs of "island growth" features. Where (a) is a light micrograph and (b) is an SEM micrograph.

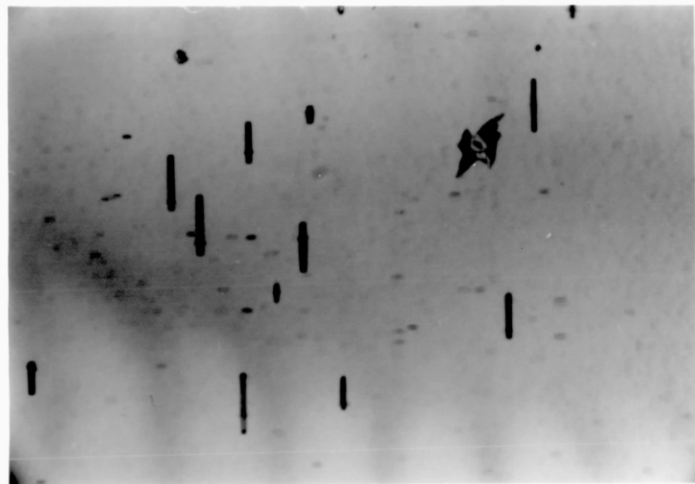
(a) SEM micrograph,
showing an area of
a sample with an
unusually high
density of fine
decomposition pits.

20 μm



(b) Light micrograph,
showing large
decomposition pits.

80 μm



(c) SEM micrograph,
showing high
density of large
decomposition pits
near the substrate
edge.

100 μm

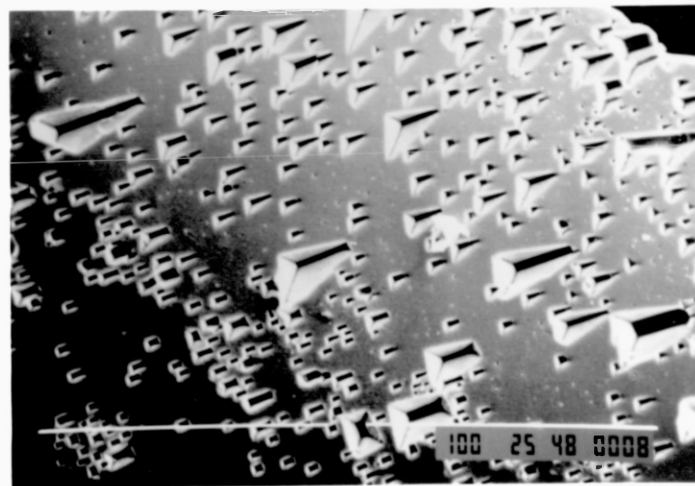


Fig. 44 Photomicrographs of decomposition pits.

layer. Thus, another reason had to be found to explain why there were two distinctly different sizes of decomposition pit present. Sartorius et al. [54] found that the decomposition of an InP surface was enhanced by the emergence of crystal defects at the surface. This would therefore seem to be a likely explanation to the problem. A dislocation emerging on the surface, would enhance decomposition, leading to a much larger pit than would be found on an area of the surface which was free of defects. Here there would not be the same driving force for decomposition, and only smaller pits would be observable. Additional evidence which supported this, was that near the edges of a substrate, particularly where they were curved, there were often areas where there was a high density of larger decomposition pits, (see fig. 44c). These had resulted from accelerated decomposition from defects, which were introduced into the substrate during its manufacture.

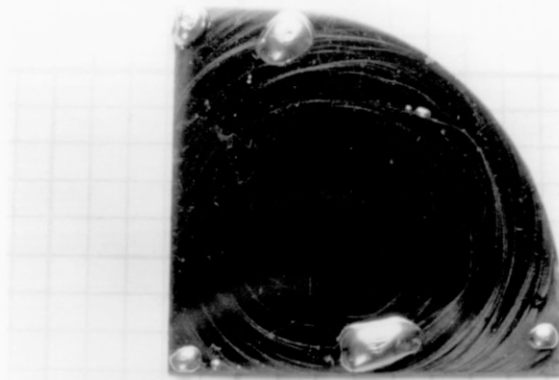
iii) **Growth at the melt periphery:** A characteristic feature of all the growth experiments, was the formation of numerous, long growth hillocks. These corresponded to the position of the periphery of the melt, during the growth experiment. Generally, these hillocks formed roughly parallel sets of lines. On the macroscopic level, the markings outlined the area of the substrate which was continuously covered by the melt during the growth experiment, i.e. they usually formed circular marks on the substrate.

(N.B. For ease of reference in the future, the term "circular markings", will be used for this feature).

Fig. 45 shows a number of photographs of the circular markings. Clearly, these features must result from preferential growth at the edge of the melt. Their formation can be explained by similar features obtained with the sliding boat LPE technique. As explained in section

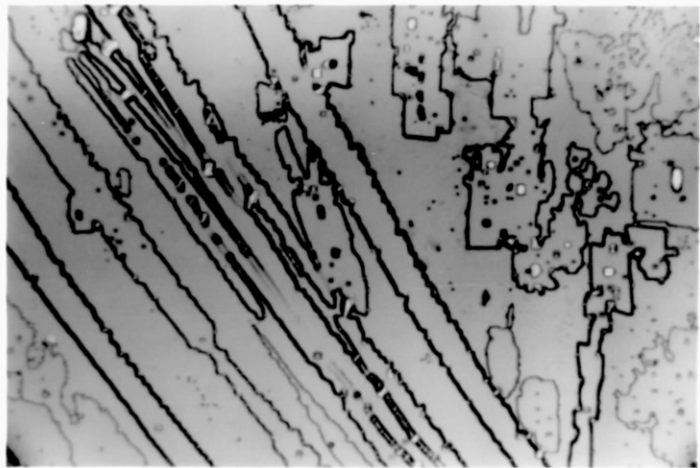
(a) Photo of a sample which shows the circular markings particularly clearly.

10 mm



(b) Light micrograph of typical circular markings.

40 μ m



(c) SEM micrograph showing a circular marking at a cleaved edge. White bars on the photo represent 10 μ m.

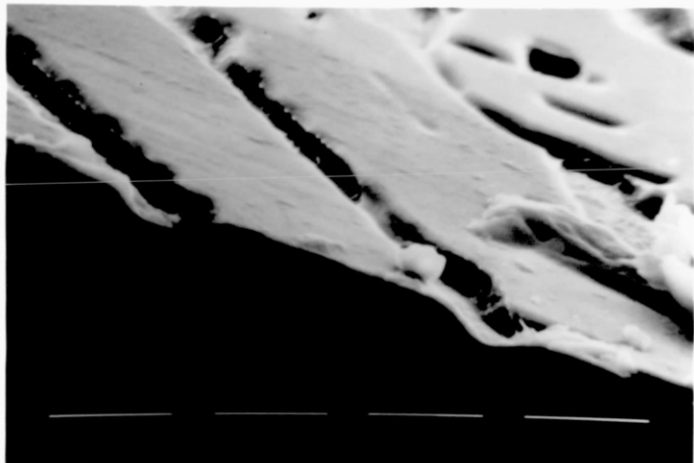


Fig. 45 Photographs of "Circular markings".

2.7.5, the three phase boundary at the melt periphery, moves in a "slip-stick" manner.

Using the sliding boat LPE technique, when the melt is moved from, or onto the substrate, the slip-stick motion results in parallel sets of meniscus lines, which are similar to the circular markings of RDLPE. In cross section the meniscus lines have a characteristic "S" shape. However, fig. 45c shows a cross section through one of the circular markings, and this clearly does not have such a shape.

As well as meniscus lines, an additional growth feature can result from the melt periphery, when the sliding boat technique is used. This feature is known as "edge growth" (see section 2.7.3), and results from the edge of the melt being stationary, for a longer period of time than is required for the formation of meniscus lines. Thus as explained by Small et al. [33], in the case of edge growth, volume diffusion for the transport of material to the growing layer, becomes the dominant process, whereas, for the shorter times involved in the formation of meniscus lines, surface diffusion dominates, and this gives them their characteristic S shape. The cross section through an edge growth feature, is in fact, similar to the circular markings obtained in these experiments.

It is thus suggested, that as the substrate was rotated, the position of the melt periphery moved slightly in a slip-stick manner, leading to the formation of the parallel sets of growth hillocks that was a characteristic of the circular markings. However, unlike the formation of meniscus lines, the periphery was pinned in the "stick" phase of the slip-stick motion for a sufficiently long period of time, for an edge-growth-like features to result.

These same samples were viewed and studied under both the

light microscope and the SEM. Some were also cleaved and tested by the staining method described in section 6.4. This however, did not show up the presence of any layer. Therefore, at this stage there was no firm indication as to whether the island growth features were isolated, or whether they were surrounded by a layer.

It had been intended to follow these tests by having an analysis done on an Electrochemical profile plotter, which was situated at the British Telecommunications Research Laboratories (BTRL). This apparatus, as mentioned in section 6.4, had the capability of revealing not only whether a layer had been grown, but also its thickness, the sharpness of any junction, and the net carrier concentration. It was hoped to use this technique as the principal analysis method. It was decided, out of consideration for BTRL, to wait until an accumulation of results had been obtained and thus, this particular analysis did not take place immediately. It will therefore, be discussed later.

During the intervening period before the visit to BTRL, another series of experiments took place to test the possibility that the islands were not isolated. It was postulated, that if the islands were indeed isolated, then the problem was obviously one of poor nucleation. From basic nucleation theory, it is known that the nucleation density will be increased when the solution supersaturation is increased. This is an effect which has often been observed, e.g. by Astles and Rowland [79] and Small and Crossley [80]. Thus implementing this theory, experiments were conducted at step-coolings of 10°C, 12°C, and 15 °C (the furnace temperature prior to the step-cool being 650°C, with the substrate 1°C cooler than the melt and the substrates being rotated at 200 rpm for each growth experiment).

Subsequent to growth, the surfaces of the InP substrates, showed no

great difference in the concentration of the islands, and if anything, the sample which had the lowest step-cooling, appeared to have a slightly higher density of islands. At the time, this strengthened the view that there might be a layer between the islands. If there were a complete layer, any change in nucleation density would not be seen. It also reinforced the idea, that the islands originated from preferential growth at defects, such as dislocations and decomposition pits. Therefore, the number of these islands that were present, would not be dependent on the amount of supercooling.

This series of experiments did, however, reveal one different growth feature which was particularly apparent at the higher step-cooling of 15°C. This feature is shown in fig. 46. It took the form of angular crystals which appeared to sit on the surface of the substrate. This had already been observed on other InP slices subsequent to growth. However, the sample shown in fig. 46 for the 15°C cooling, had a markedly higher concentration of crystals showing on it, than on those others, and analysis with the EPMA, revealed that the crystals were composed of indium and phosphorous and were thus, almost certainly InP. These features originated from two sources; the first one being that when the InP pieces were loaded into the melt dropper tube, they inevitably, had pieces broken off them. This could also occur during the bubbling of the hydrogen through the melt, causing InP pieces to strike together. The minute fragments that resulted, were able to find their way down onto the substrate when growth was commenced, and here they either grew onto the surface, or they were left on top of it after the melt had all been flung off. It must be remembered that, as the melt was supersaturated, growth would occur on these fragments. This is confirmed by their resultant shape. Also, being of InP, they would



12 μm

Fig. 46 Crystals left on the surface of an InP substrate.

float on the top of the melt and would therefore be the last to drop onto the substrate.

This explanation probably accounts for the crystals found on the previous samples.

The second source of the crystals and the one which had the greatest effect, was from spontaneous nucleation of precipitates in the melt, which only occurred in the melt which had the highest degree of supersaturation, i.e. the 15 °C step-cool experiment. Like those previously described, these crystals had an angular shape and were either incorporated onto the surface or were just left on the top of it.

The generation and incorporation of such precipitates was observed by Hsieh [14] using large step-coolings for the growth of GaAs.

Following this, a number of growth experiments were undertaken to study the effect of rotation on the growth, with a view to finding a relationship of layer thickness to the rotation rate, when the resultant layers came to be examined on the electrochemical profile plotter. These were conducted at 200, 350, 500 and 750 rpm, keeping all the other growth conditions constant throughout i.e. a furnace temperature of 650°C prior to a 10°C step-cool and the substrate being 1 °C cooler than the melt. Also, to give an indication of the reproducibility of the growth, some of these experiments were subsequently repeated.

The surfaces of the resulting InP slices showed the island growth as before, but the density of the islands varied from experiment to experiment, with no noticeable trend. This was consistent with previous theory, (i.e. that they resulted from preferential growth from defects).

These samples were taken to BTRL and analysed using the electrochemical profile plotter. The results from the analysis revealed that none of these growth experiments had in fact resulted in an epilayer. Initially, during analysis, the samples did display to varying degrees, some slight diode behaviour. This however, rapidly disappeared as the sample was etched. The obvious conclusion was that the island growth was indeed only isolated growth, and that these areas slightly affected the forward and reverse characteristics of the sample, and hence, gave the observed results.

This disappointing result, posed the question; Why did such a supersaturated solution, (solutions up to 15°C below the liquidus temperature were used), give such small and patchy growth ?

The following two theories were suggested as possible explanations:

i) Poor substrate surface, leading to growth on only selective areas. This was also thought, to possibly explain the poor wetting observed. See section 6.5.1.

ii) Prior to contacting the substrate, the supersaturation of the melt may have been considerably reduced by growth on the excess, undissolved, InP in the melt. As mentioned previously in section 6.2, an excess of InP had been used to ensure supersaturation and to simplify procedure. The formation of island growth as a result of this, is explained as follows:

When growing a layer from a supersaturated solution, there has to form initially on the substrate nuclei from which future growth can occur. From an analysis of the energy change in the system, when such nuclei are formed, it becomes obvious that there will be a critical size. Any nuclei less than this size will be unstable and will dissolve back into the solution. However, if the atoms come together,

to form a nucleus whose size is greater than the critical size, then it will be stable and growth will continue from this. The critical size, is dependent on the degree of supersaturation, such that, the larger the degree of supersaturation, the smaller the nuclei have to be to be stable. Thus, there will be a greater chance of such nuclei forming, and consequently the density of nuclei will be increased.

Applying this theory to the experiments so far described, the loss in the degree of supersaturation, prior to growth, would increase the critical size of the nuclei. This would explain the low density of the islands observed. Also, because the supersaturation had been reduced, the growth rate would be small, and thus after only 10 seconds of growth, there would be only a few, small isolated islands. However, the melt edges, dislocations and decomposition pits, would provide energetically favourable sites from which growth could be initiated. Hence, the observed association of the growth islands with decomposition pits (see fig. 43b) and the formation of circular markings.

This theory for the growth of islands as a result of poor, low, supersaturation, would agree with the work by Crossley and Small [81], who found that when growing from solutions which were only just saturated, island growth resulted.

N.B. The growth of LPE layers, occurs by the Volmer-Weber mechanism. With this, a stable nucleus first has to form, and thereafter, growth occurs by lateral spreading from the nucleus, which has created a step on the surface. Once two such islands touch, equilibrium is disturbed and merger into one large island will occur. This produces a more favourable shape, and ultimately from this a layer will form.

To test out the first of these theories, higher purity solvents and

acids were used to clean the substrate. Following the cleaning, the InP slice was examined under the light microscope for any obvious contamination, but none could be seen. It was then loaded into the furnace, to repeat the previous growth experiment, having the conditions of, a furnace temperature of 650°C prior to a 10 °C step-cool, a 200 rpm substrate rotation rate and with a 1 °C temperature difference between the substrate and the melt.

The resultant surface on the substrate, displayed the, now, typical island growth structure, which showed that no improvement had occurred by using the purer chemicals. This did not however completely eliminate the possibility of there being contamination. In conventional LPE methods, the best technique for removing surface contamination of a substrate, is the meltback method as explained in section 2.7.6. However, this was not practical for RDLPE, where a complete redesign of the dropping assembly would have been required. Also, it was not known, what effect meltback might have had on the surface morphology of the substrate, and it could well have confused the results. Later, when experiments were used to test the second theory expounded, it became apparent, that contamination was not the predominant factor hindering the formation of the layer, and at worst it would have had, only a minor effect.

The second theory put forward to explain the formation of isolated islands, was considered to be the most likely. However, if this was the case, there were a number of practical problems to be overcome before matters were remedied. Therefore, before testing the theory, it was decided to conduct one more experiment, which it was thought, might possibly yield an improvement. In this, the growth time was extended to 20 seconds, (80g of In for the melt), the idea being, that the islands

having twice as long to develop, might grow to form a layer. Unfortunately, the results of this experiment showed very little change from the others. This, on due consideration of the second theory above, was not too surprising because the degree of supersaturation would have varied from growth to growth, as would the number of nucleation sites. Also, once an island had formed, it would have become a favourable site for growth, thus depleting the growth solution around it, and making further nucleation of islands in surrounding areas less likely. Consequently, the time factor would not have had as great an influence on the number of islands, as one might have supposed.

Clearly the next step was to examine the second theory. At first this proved to be difficult, since as stated previously, it was thought that excess InP was the problem. To correct this it would be necessary to work out the correct quantity to use. That is, just sufficient being added to the melt to ensure that prior to the lowering of the temperature for growth, all had been dissolved and no pieces had been left to reduce the supersaturation before the growth commenced.

The following inaccuracies made this calculation, very difficult:

- i) Equation (3.4) which would be used to determine the amount of InP to add to the melt, was only accurate to $\pm 1^{\circ}\text{C}$.
- ii) The accuracy of the thermocouple was to within $\pm 2.5^{\circ}\text{C}$ at around 650°C
- iii) Another slight inaccuracy was introduced by the Eurotherm which was used to display the temperature.
- iv) The bubbling of the hydrogen through the melt to protect the substrate was designed to pick up phosphorous from the melt. This tended to deplete the melt of the phosphorous to an unknown degree during the growth experiment.

The need to know precisely, the amount of InP present in the melt had an additional drawback. It meant that it would not be possible to reuse the melts, as their phosphorous content would be unknown. This limited the extent of experiments that could be conducted.

It was decided that because of the inaccuracies mentioned above, it would be impossible to work out the exact amount of InP to use. However, by using the equation (3.4) to calculate the quantity as accurately as possible, one could then proceed, by increasing the temperature and keeping a visual check (this being possible with the equipment in use) until all was dissolved. In this way the problem would be overcome.

This was therefore implemented in the next growth experiment. The melt used for this having 40.0000g of In, 0.3788g of n-type InP and 8.0mg of Zn (sufficient to dope an epilayer to 1×10^{19} atoms/cm³). It should be noted, that when this experiment was reached, there was only n-type InP left, which had to be used for both the melt and the substrate material. Thus, to enable growth of a p-n junction, it was necessary to increase the zinc concentration, to 1×10^{19} atoms/cm³ to compensate for the n-type dopant in the InP used for the melt.

Other conditions were, a furnace temperature of 650°C prior to a 11°C step-cool, with the slave temperature controller set at -0.42mV (i.e. an approximate 1 °C temperature difference between the melt and substrate), and 200 rpm rotation of the substrate.

On heating the melt to 650°C, it was apparent that not all of the InP had dissolved. Thus, the temperature was increased and periodically the hydrogen was stopped, so that a clear visual check of the melt surface could be made to ascertain whether there were any InP crystals floating on the top. Eventually, at a temperature of 655°C no InP was visible.

As an added precaution the temperature was once more increased by 1 °C to ensure that all InP had dissolved. The experiment then continued following the procedure described in section 6.3.

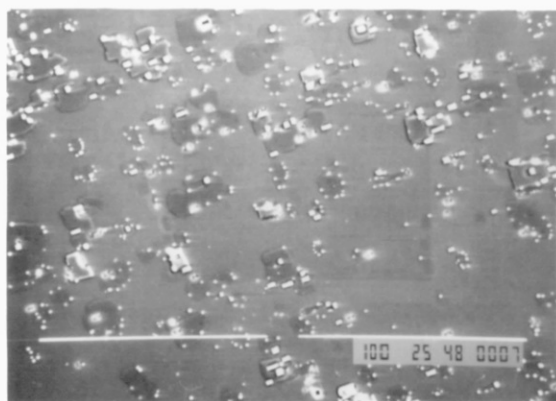
The InP slice, when examined under the microscope, showed, what appeared to be a large increase in the amount of growth, with an almost complete layer in the central zone. Fig. 47a - f shows a series of photographs of the surface of this slice, taken progressively from the near edge to the centre.

Fig. 47a shows an area which was outside the central coverage zone, and as such, was only covered briefly by the melt. Therefore, as can be seen, only a small amount of island growth had occurred. This was a startling change. In the previous experiments this feature was the best result that could be achieved, and only at the centre. Now, it was to be found in an area where the growth time was extremely short.

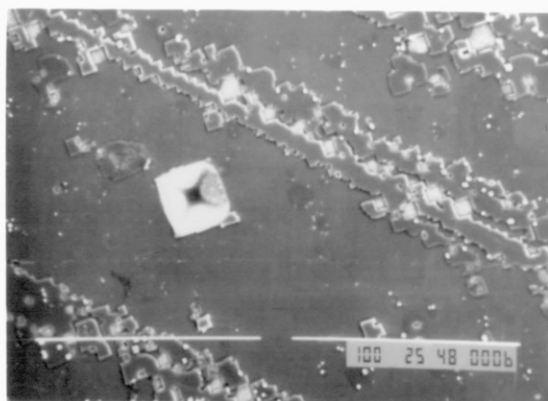
Fig. 47b, taken slightly nearer the centre, shows that in this area, circular markings had been deposited.

The next two photographs fig. 47c and 47d, were taken progressively moving towards the centre, from areas between the circular markings. The outer one showing the growth of much larger islands than those in the photographs from previous regions, and the inner one showing the islands actually merging together. Fig. 47e shows the final area of pronounced circular markings, which were at the edge of the central zone (the area covered throughout the growth experiment by the melt) and lastly fig. 47f shows the central zone itself, where the islands had merged with one another, to form a complete layer. Leaving only isolated pits in the surface.

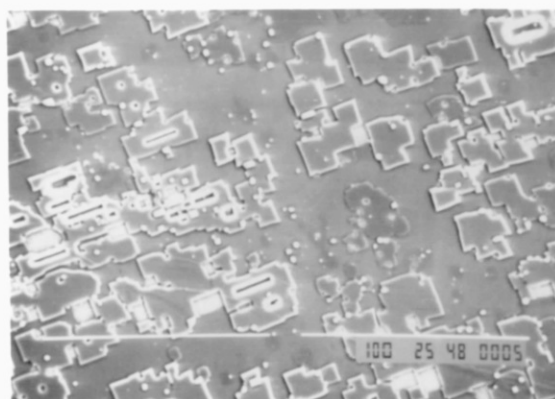
Clearly, the result of this experiment shows, that the excess InP used in previous experiments in the melts, was indeed, considerably



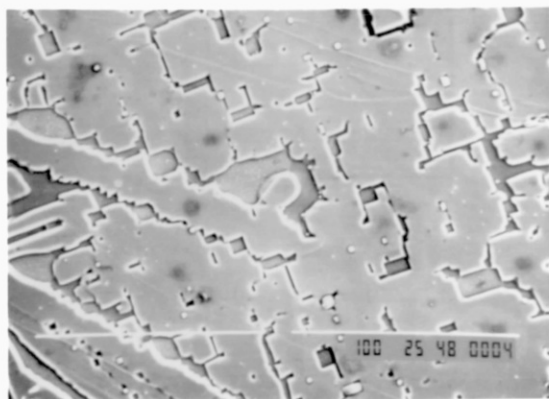
(a)



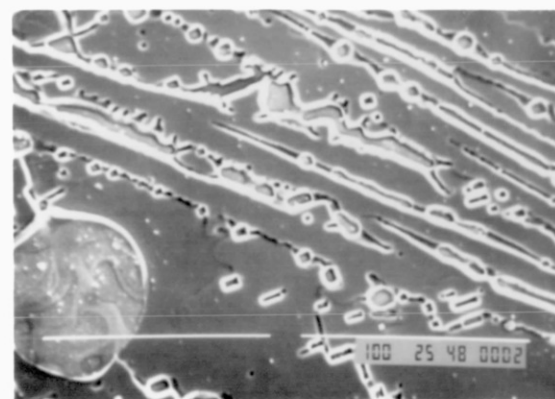
(b)



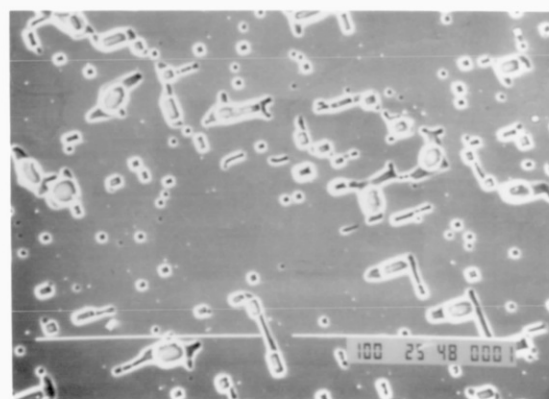
(c)



(d)



(e)



(f)

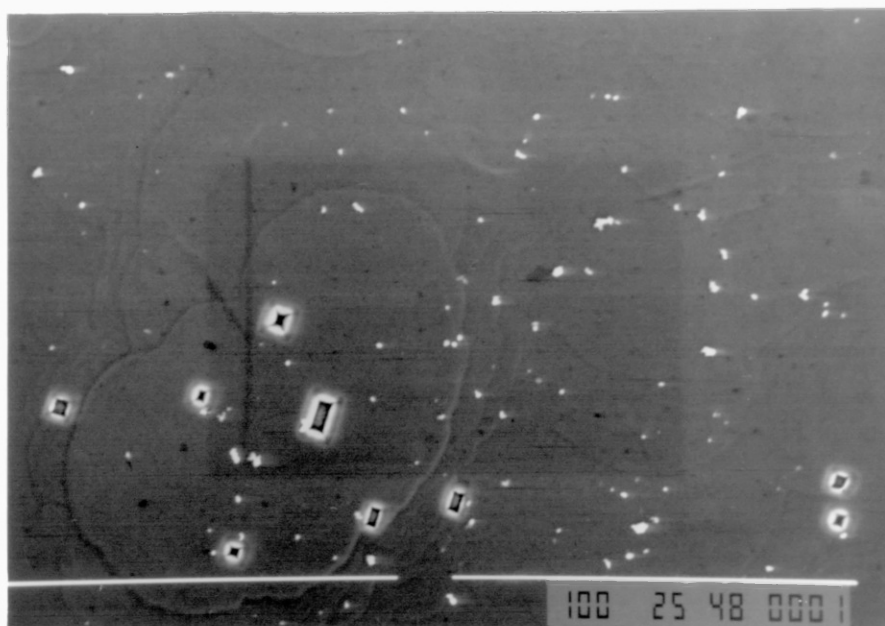
Fig. 47 SEM micrographs of the InP sample resulting from the growth run in which excess InP had been eliminated from the melt. The photographs (a) - (f) show areas of the sample from the edge to the centre respectively. The white bars at the bottom of the photos representing 100 μm .

reducing the supersaturation of the melt, prior to growth. The reason for this was explained earlier in this section.

It was decided, to analyse this sample using the SEM/EBIC combination, (which had recently become available for use) in preference to the electrochemical profile plotter which had been used before, as the EBIC equipment was at hand in the department, and was known to give reliable results. Although with this, the net carrier concentration profile could not be obtained, it had however, the added advantage of producing an image which gave a detailed view of the epilayer and junction area. Also it provided information on the formation of surface features.

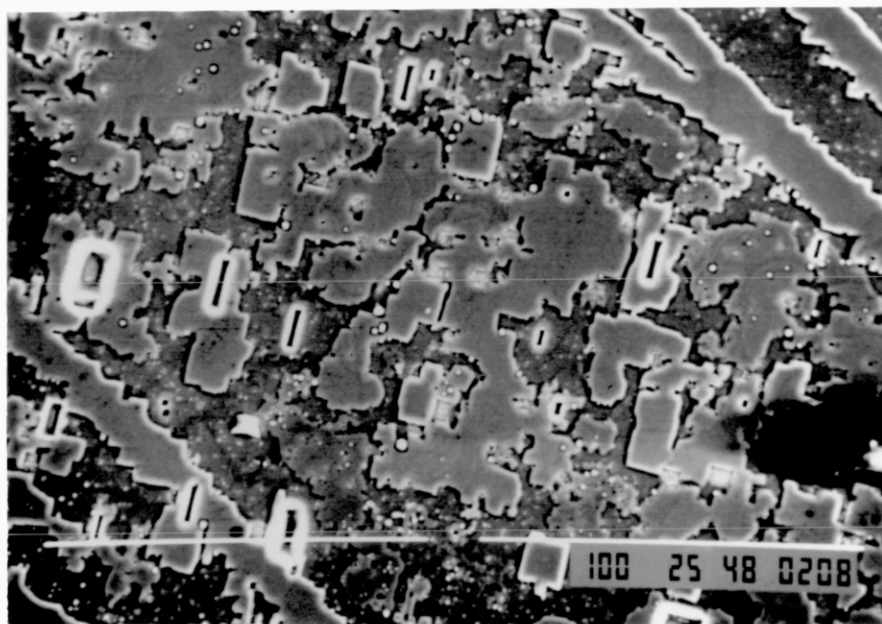
The EBIC was only available at certain times, which restricted its use, and because of this, it was thought profitable to conduct another experiment in the intervening period. This experiment repeated the previous run, as a check, to establish that the result was not just an isolated case. One minor change was made, a 13°C step-cool being used for this experiment, as it was considered that the increased supersaturation would increase the nucleation density, and thus, the driving force for growth, giving a layer with less pits.

Generally, the resultant growth features on the sample, were the same as previously obtained, with the progression from the outer island growth to circular markings, and finally at the centre, the complete layer. However, fig. 48a shows that the central area had a markedly lower concentration of pits. A certain amount of terracing can be seen on the surface, with some of this originating from around the decomposition pits, and therefore, probably being a result of the initial preferential growth around the pits, which had raised these areas slightly above the surrounding layer. From these results, it



100 μm

(a) Layer at the centre of the sample.



100 μm

(b) Area outside the central zone, between "circular markings".

Fig. 48 Photographs of the sample obtained using identical conditions to those which produced the growth shown in fig. 47, except that this time, a 13°C step-cool was used.

would appear that the higher step-cool, had indeed improved growth by increasing the nucleation density. A fact supported by fig. 48b, which is a photograph showing the island growth taken at a very similar position on the sample, as fig. 47c from the previous experiment. It can be seen that there had been a noticeable increase in the number of islands. The effect that the degree of step-cool had on growth, will be discussed again later.

The samples were then prepared for the investigation by EBIC. They were cleaved, to form pieces small enough to fit on gold plated TO5 transistor bases. This was done to each sample in such a way, that one of the cleaved edges passed through the centre of the growth area. The samples were then bonded to the transistor bases, using heat cured silver paste to form an electrical contact. On each sample, from its top surface, a gold wire was bonded to one of the leads from the transistor base, using the silver paste which thus formed the other contact.

When the samples from the two last experiments were viewed, using the EBIC/SEM, there was no contrast visible on either of the samples, across what should have been a p-n junction. So that, although it was confidently believed that there was a layer, it was concluded that the compensation for having to use n-type InP for the melt, could not have been high enough. Consequently, it was n-type layers which had been grown, whose junctions with the n-type substrates, would not have been revealed by EBIC.

Thus, it was decided that higher dopant concentrations would have to be used in future experiments. Therefore, the melt for the following growth experiment, had sufficient Zn added to it, so that an epilayer grown from it, would be doped to 4×10^{19} atoms/cm³. It must be

remembered, that the actual concentration of zinc in the melt at the point of growth, would be less than at the start, because of evaporation, which would also be accelerated by the hydrogen bubbling through the melt. So that the final concentration of dopant in the epilayer could not be precisely predicted.

For this experiment, all the growth conditions were the same as for the previous one, except that the rotation rate was 600 rpm.

Photographs, were taken showing different areas of the resultant sample. Fig. 49a shows the growth found on an area at the centre. Fig. 49b shows the growth within the "central zone" moving outwards from the area of growth that is shown in fig. 49a.

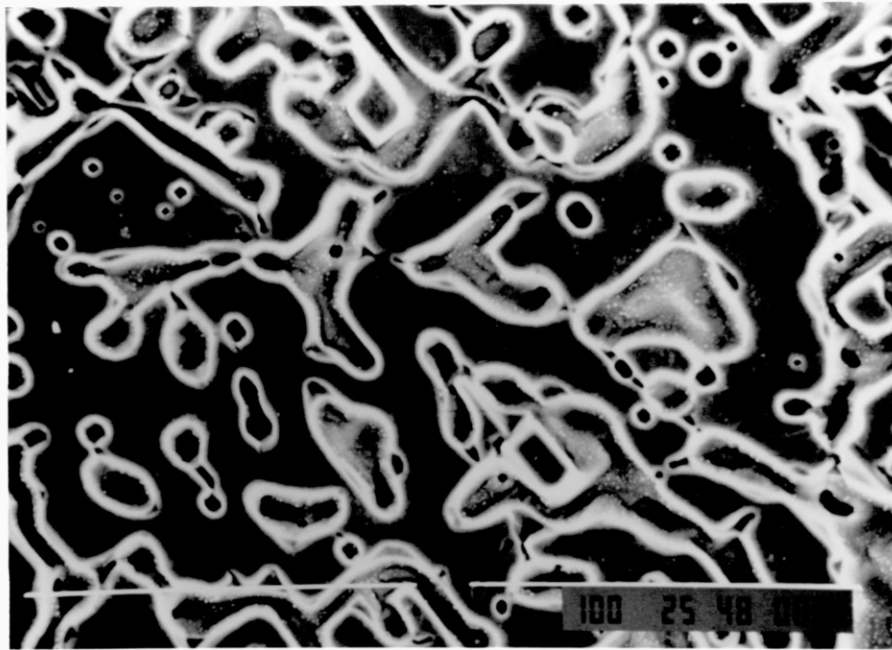
This time, when the sample was viewed using EBIC, a contrast did show up, denoting the presence of a p-n junction.

A series of photographs of the central zone is shown in fig. 50. For each region photographed, the SEM image, the EBIC image and the superposition of the two are shown. It can be seen from these, that in fact, the junction is also visible, on the SEM photographs.

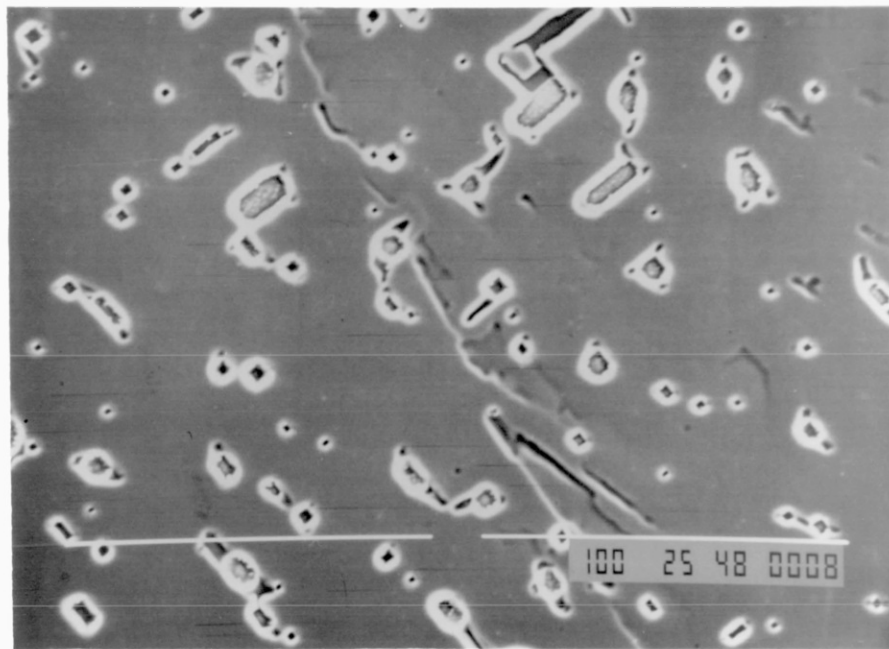
Another factor that becomes obvious from the photographs, is that by increasing the rotation rate, the growth had deteriorated significantly, and it was only near the edges of the central zone, that there were any areas approaching that of the growth experiment at 200 rpm.

From these photographs, it can be seen that there are various noticeable features on the sample, they are as follows:

i) Deep rounded pits in the layer, going down to the substrate surface, which show the surface of the substrate effectively untouched. The pits have a number of small crystals attached to their side walls. Figs. 49a, 50a and 50c.



(a) Layer at the centre of the sample.



(b) Showing growth within the "central zone", but outside the growth area shown in (a).

Fig. 49 Photographs of the sample obtained using identical conditions to those which produced the growth shown in fig. 48, except that this time, the substrate was rotated at 600 rpm. The white bars at the bottom of the photos representing 100 μm .

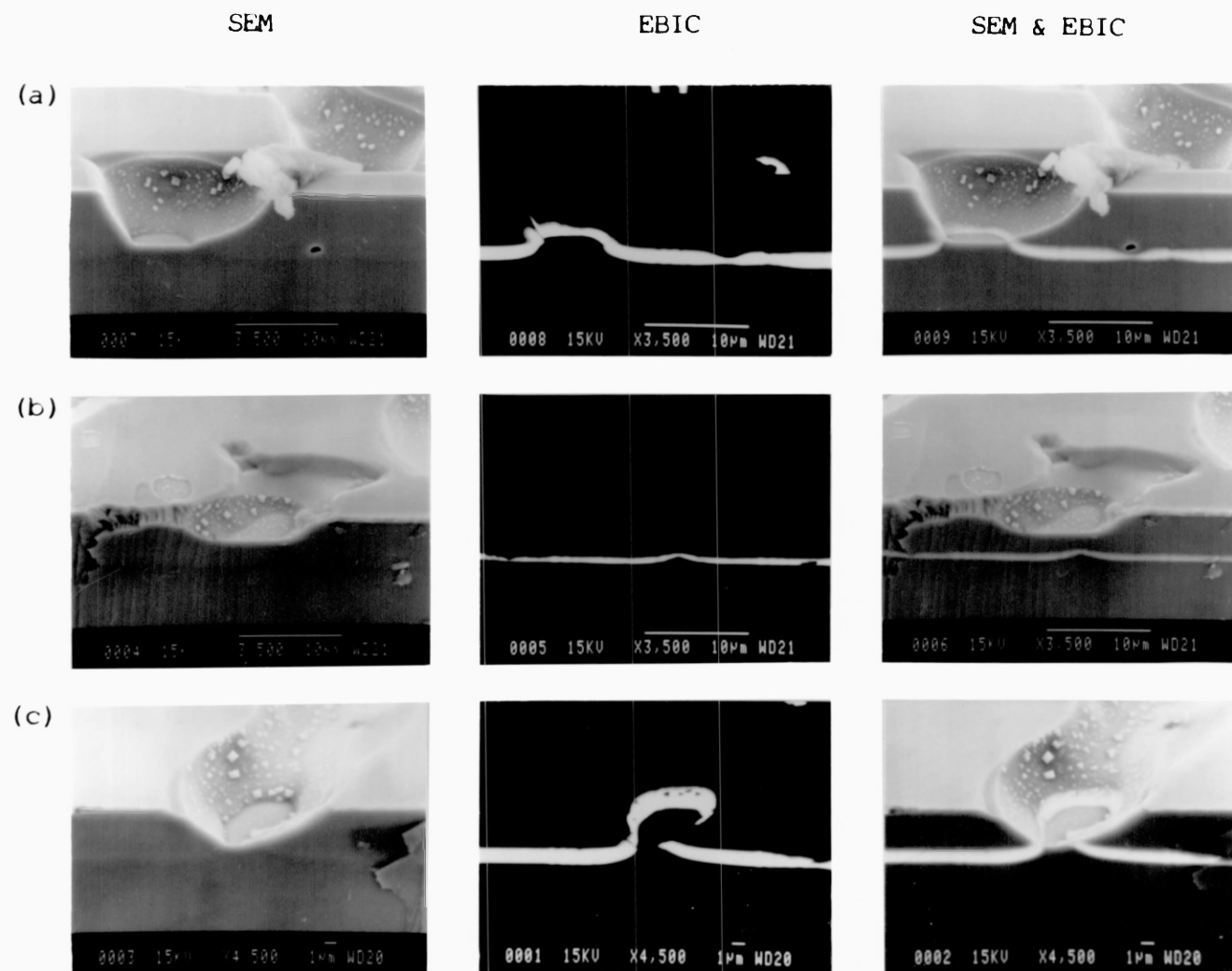


Fig. 50 SEM, EBIC and combined SEM & EBIC images of a cleaved section showing the layer at (a) the middle of the "central zone", (b) midway to the edge of the "central zone" and (c) near the edge of the "central zone". This sample is the same as that shown in fig. 49.

ii) The p-n junction appears to be lower than would be suggested by the position of the substrate surface at the bottom of the deep pits. Figs. 50a and 50c.

iii) Shallow rounded pits. These pits do not penetrate as far as the substrate surface, and they can be seen to have a scattering of crystals attached to their surfaces. Figs. 49a and 50b.

iv) Internal holes in the layer, occurring at the original substrate surface (that is, the position of the original surface, as marked by the base of the deep pits). Shown in fig. 50a.

v) The layer thickness is not uniform, being thinner nearer to the edge of the central growth zone. Fig. 50.

A detailed explanation of the results and the features in this experiment will be discussed later in this section.

Having achieved the growth of a layer by RDLPE which could be successfully viewed, using the EBIC, it was decided to conduct a series of experiments on the remaining substrate pieces. These, it was hoped, when taken with the results from other recent experiments not using excess InP, would give useful information on the effects of the rotation rate, the size of the step-cooling and the temperature gradient from the substrate to the melt, on the growth of layers by RDLPE.

The results of this series of experiments are as follows:

i) The effect of rotation rate:

Three experiments were conducted at the different rotation rates of 0, 200 and 400 rpm. All other growth conditions were constant. Growth experiments having a furnace temperature of 656°C prior to a 13°C step-cool and a slave temperature controller setting of -0.48mV (i.e. a temperature gradient where the substrate was 2°C cooler than the melt).

N.B. In other experiments from the series, which are still to be described, but which had however, been conducted earlier to test for the effects of other conditions, it had been found that the temperature gradient as given, and step-cool of 13°C would provide the best conditions for growth.

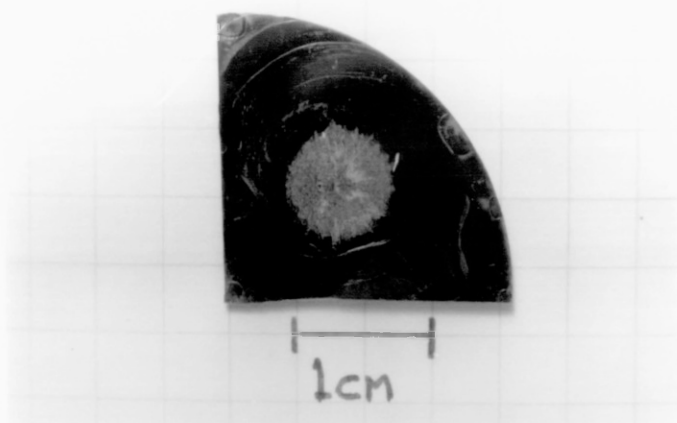
The three InP slices resulting from these experiments, are shown in fig. 51. From these photographs, it is clear that the growth at 200 rpm has by far the best surface. On the other two slices, at their centres, there can be distinctly seen large, circular shaped regions with rough surfaces. However, the slice from the 200 rpm growth experiment, exhibits a surface which is generally, "mirror like", with only a very small rough area right at its centre. This result is in agreement with the previous experiments.

Fig. 52a and b show the growth achieved at the centre of, firstly, the sample grown without rotation, and secondly, the one at 400 rpm. These areas are seen to be very similar to that obtained with the previous sample which was rotated at 600 rpm, shown in fig. 49a. Also, like this sample, the rough area at the centre, was surrounded by an area still within the "central zone", which was of much better growth and had very few pits. In fact, the growth in this area was comparable to that shown in fig. 48a.

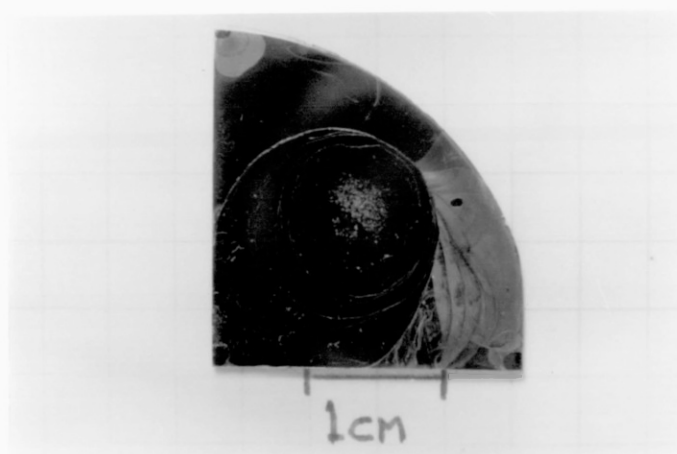
Fig. 53 shows SEM and combined SEM and EBIC images, of the cleaved edge of the 400 rpm sample. It should be noted however, that the EBIC signal was very low and consequently the junction is not clearly defined. Fig. 53a and b are regions within the rough central area and fig. 53c is in the central zone but outside the rough area.

Fig. 54a, b and c show the cleaved edge of the 200 rpm growth experiment and fig. 54d, e and f are of the cleaved edge of the slice

(a)



(b)



(c)

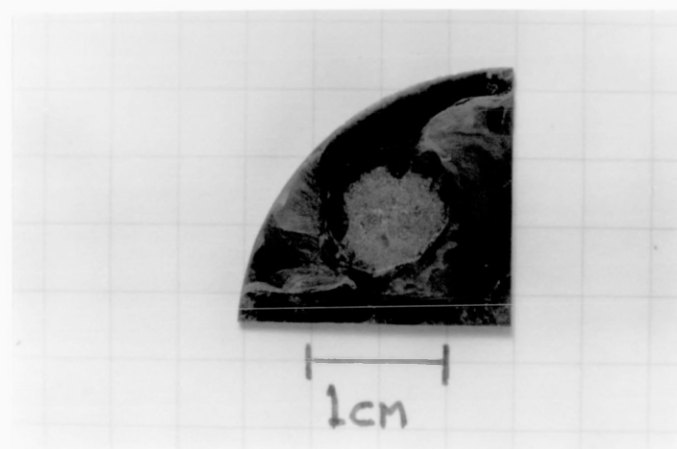
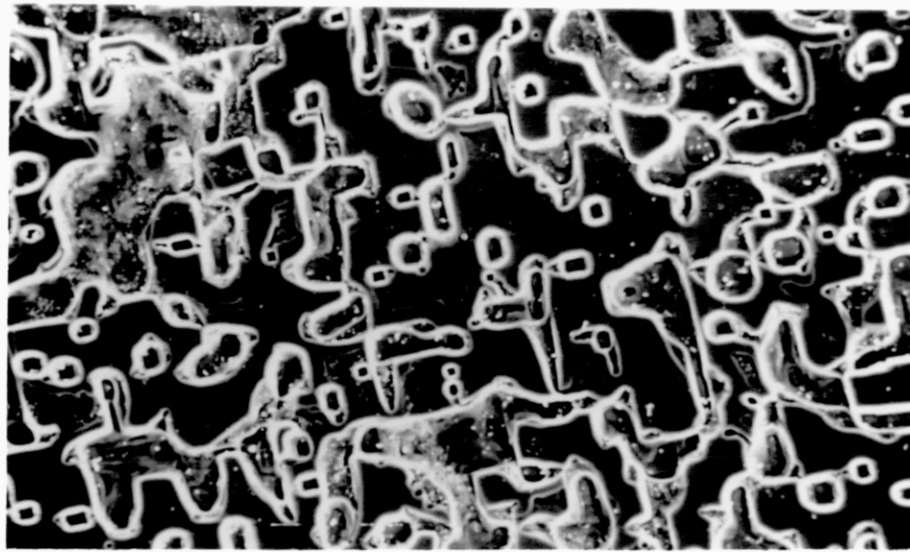


Fig. 51 Photographs of the samples obtained at the different substrate rotation rates of (a) 0 rpm, (b) 200 rpm and (c) 400 rpm. The other growth conditions were, a furnace temperature of 656°C prior to a 13°C step-cool and a slave temperature controller setting of -0.48 mV .



100 μm

(a)



100 μm

(b)

Fig. 52 SEM micrographs of the middle of the "central zone", of the samples which were rotated at (a) 0 rpm and (b) 400 rpm during growth, and shown in fig. 51.

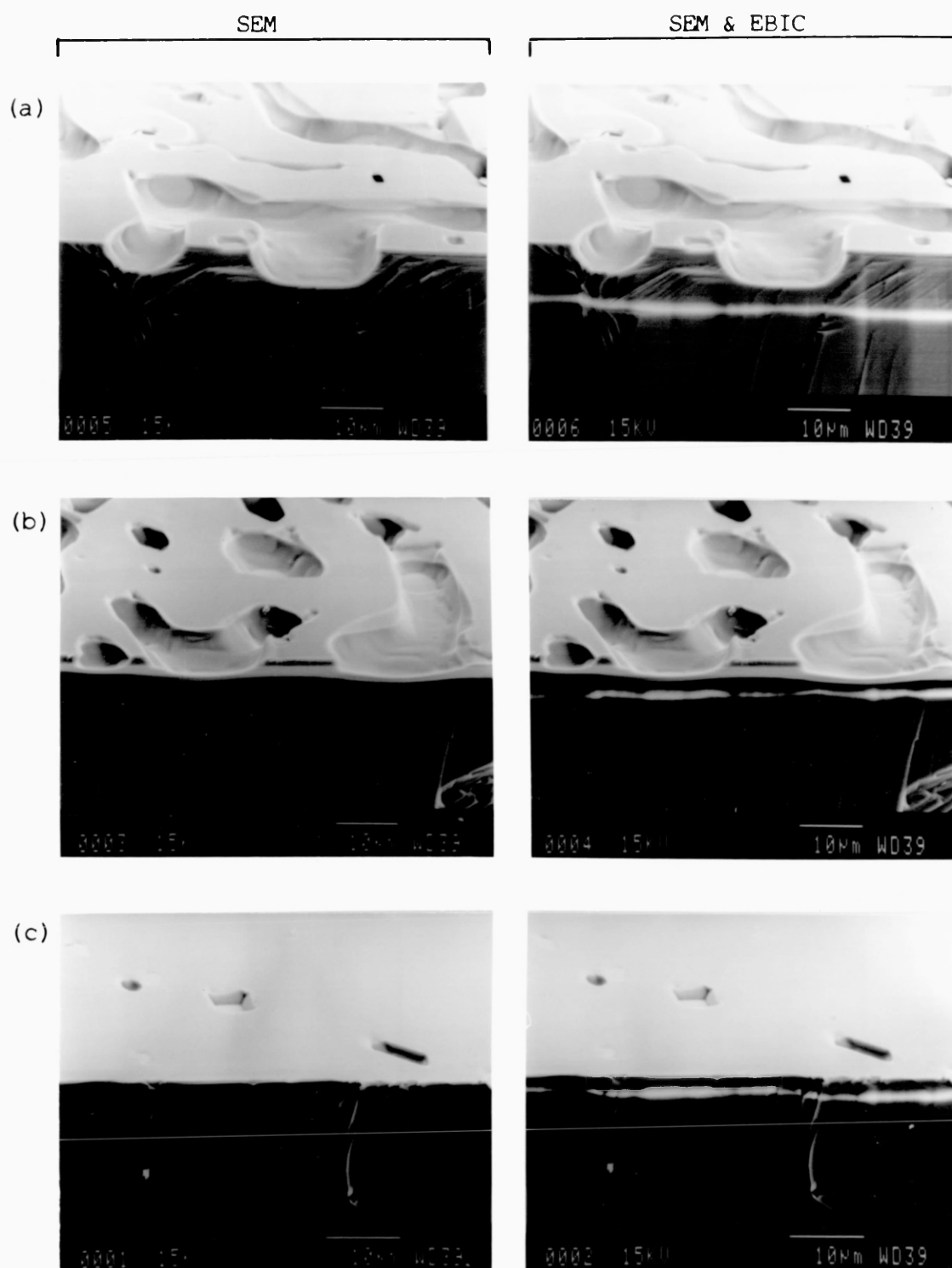


Fig. 53 SEM and combined SEM & EBIC images of a cleaved section of the 400 rpm sample shown in fig. 51, at (a) the middle of the "central zone", (b) midway to the edge of the "central zone" and (c) near the edge of the "central zone".

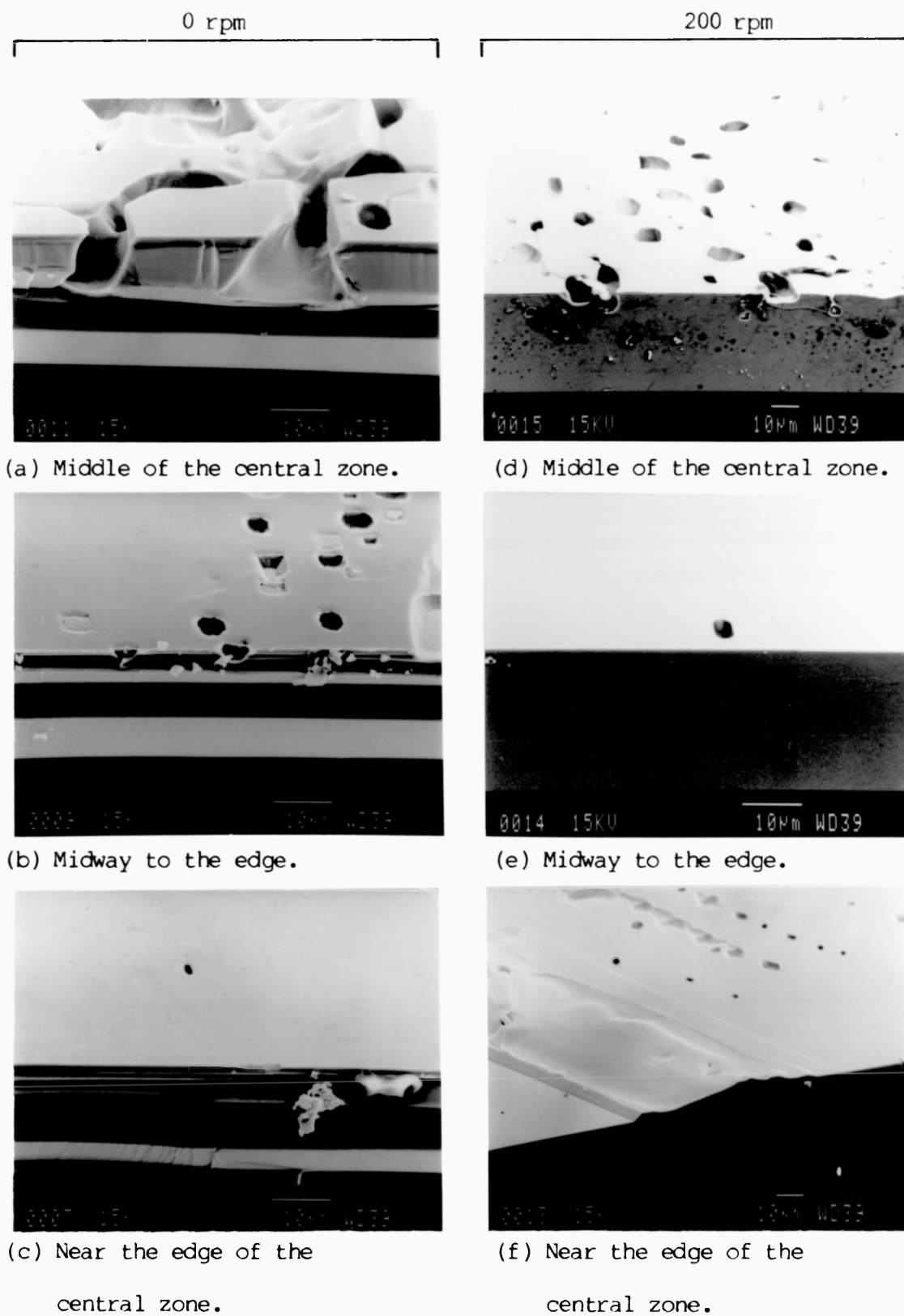


Fig. 54 SEM micrographs of cleaved sections of the 0 rpm and 200 rpm samples shown in fig. 51.

which was stationary during growth. Again, although all the features observed were indicative of the presence of a layer, unfortunately neither of these two samples showed a signal with the EBIC. The explanation for this, is that the zinc, which was added in these experiments, did not compensate for the n-type dopant in the InP added to the melt. Although the n-type dopant would be much more dilute in the melt than the zinc, the distribution coefficient of sulphur, which was the dopant used in the majority, but not all of the InP pieces for the melt, is such that the concentration of the sulphur in the growing layer, would be up to 10 times that which was in the melt. Whereas, the concentration of the zinc would be slightly less than it was in the melt. Secondly, the carrier concentration of zinc saturates at a concentration of approximately 3×10^{18} atoms/cm³ (concentration found by Kuphal [52]), with any excess Zn being built in as neutral Zn. Consequently, the limited carrier concentration of the zinc was, for the majority of growth experiments, insufficient to compensate for the n-type dopant. Hence, for these experiments no p-n junction was produced. Instead an n-type layer was grown. It should be noted that this explains the lack of an EBIC signal for samples from certain other experiments which will be described later.

The inability to obtain an EBIC signal does not, however, prevent the position of the interface being determined. Fig. 54, shows edge on views of the 0 and 200 rpm samples. From the features and the contrast shown one can tell, with reasonable certainty, the position of the junction. However, this was not possible near the edge of the central growth zone of the 0 rpm sample, as can be seen from the photograph. Also for the midway area of the sample at 200 rpm, it is difficult to find, from the photographic print shown, the location of the junction.

A difference in contrast between the layer and substrate could clearly be seen on the negative, and it was from this that the measurement was taken.

	EDGE	MIDWAY	CENTRE
0 rpm	- - -	4 μm	13 μm
200 rpm	4 μm	6 μm	11 μm
400 rpm	3 μm	7 μm	12 μm

TABLE 1. Layer thicknesses, at the edge, midway and centre of the central growth zone, derived from figs. 53 & 54.

From table 1. it would appear, that the growth rate was not rotation rate dependent as one might expect from the theory (outlined in chapter 4). However, this effect can be explained by the conditions, which were far from perfect, particularly near the centre, where the nature of the growth observed, had resulted from the occurrence of constitutional supercooling.

The explanation of constitutional supercooling was given in detail in section 2.6.1, where it was stated that, for a given temperature gradient, there would be a critical growth rate above which the growing interface becomes unstable. Crossley and Small [81] and others, noted that the resultant substrate surface is rough with many inclusions. In fact their results are very similar to the surfaces found in the centre of the 0 rpm, 400 rpm and 600rpm samples from RDLPE. Significantly, the experiments conducted at 200 rpm, showed only very small amounts of such growth.

It is thus postulated, that the flow of fluid to the substrate and the flow on the substrate itself, for the 200 rpm growth experiments, was a close match to the ideal conditions of a rotating disk submerged in a fluid and gave a relatively smooth flow. This resulted in the growth of a fairly smooth layer. However, when the substrate was stationary, the flow of fluid was extremely turbulent, resulting in fluctuating growth conditions, which, as is described in section 2.6.2, would have produced non-uniform growth in the form of protruberances. Non-uniform growth, in the presence of conditions suitable for constitutional supercooling, would have led to the unstable growth of the layer and thus, the observed rough central growth region. These conditions would have arisen from turbulence on the substrate, particularly near the centre where the jet of melt hit it. This fluid motion would have resulted in the growth rate exceeding the critical rate for the onset of constitutional supercooling, and thereby causing the rough growth. Further from the centre, where the turbulence had died down, the growth rate would not be sufficient for constitutional supercooling to take place. This gives rise to the smooth layer observed in this area.

It is thus suggested that such growth would also be expected for substrate rotation rates less than 200 rpm. Here the flow of fluid due to the rotation, would not be sufficient to prevent turbulence occurring when the jet of melt fell onto the substrate's centre. Consequently, constitutional supercooling would occur. A previous experiment, conducted at 100 rpm was in agreement with this theory and, showed very similar features to the 0 rpm specimen.

At rotation rates higher than the ideal 200 rpm, once again the surface showed the effects of constitutional supercooling. Two factors

might be considered possible causes of this. Firstly, the theory (given in chapter 4) predicted that as the rotation rate was increased, so the boundary layer thickness would decrease and as a result of this the growth rate would increase. It is thus possible, that the critical growth rate for the onset of constitutional supercooling would have been exceeded. However, if this were the main factor, then features due to constitutional supercooling, e.g. rough growth, would have occurred all over the "central zone". The second factor, which seemed to be more likely, was that at rotation rates above 200 rpm, the flow to the rotating substrate (this being the rate of supply of the melt and the shape of its jet), did not match that which would have resulted naturally if the substrate were rotating when submerged in a fluid. Consequently, turbulence was generated on the substrate and this resulted in constitutional supercooling.

The fact that unstable growth was occurring near the centre on all the samples, even the most ideal of 200 rpm, explains why the layers were thickest in this area. The growth rates being approximately $1.2 \mu\text{m}/\text{second}$.

It is now possible to suggest an explanation for the features observed at the centre of the substrates, where the growth had occurred as a result of constitutional supercooling. These are clearly shown in fig. 50 and can also be seen in figs. 53 and 54.

Growth would have been initiated by the formation of nuclei. As these grew and began to coalesce, the melt in contact with the substrate would have become increasingly depleted, but because their growth was so rapid in these areas, constitutional supercooling would have occurred. Therefore, the islands which were essentially protruberances on the surface, would have grown preferentially out into the melt. Once

the protruberances, either from this source, or as a result of turbulence, started to grow, the melt caught in the pits between them would have become rapidly depleted, preventing further growth. Therefore an inclusion such as can be seen in fig. 50b, could have resulted from what was initially, just a slight dip in the layer. Alternatively, if a patch of the surface was not wetted by the melt, either because of contamination, or, because gas was trapped by the melt at the base of the pit, then the kind of inclusion shown in fig. 50a, would have resulted. Here, it can be seen that a pit passed right through the layer to the substrate surface, which had an untouched appearance. Finally, where particulate contamination was present on the surface, growth would have been prevented. However, with the growth occurring all around it, it would have been eventually enveloped, leaving what appeared to be a hole in the layer at the substrate surface, as shown in fig. 50a.

The photographs of these pits provide further information as to the way in which they were formed. The following sequence is postulated to explain their shape. At the end of a growth experiment, the furnace was immediately switched off, and thus the temperature fell extremely rapidly. The heat capacity of the turntable resulted in a temperature gradient across it, with the surface being coolest. Consequently, any melt trapped in the pits would have had a temperature gradient across it. It is suggested, that with the rapid cooling in the furnace, spontaneous precipitation occurred near the top of the trapped melt, forming InP crystals, which floated to the surface. This situation, then resembled the steady-state growth technique outlined in section 2.4.1. Here any InP crystals on the melt surface would have acted as substrates, and the InP sample, would have acted as a source crystal,

i.e. the temperature gradient from the sample to the melt surface, would have created a solute concentration gradient, which would have provided the necessary driving force to transport solute from the sample to the melt surface. The effect of this was that the walls of a pit, which were initially of well defined crystallographic orientation, were dissolved back, often undercutting the surface. This left the characteristic rounded pits in the surface of the layer. This effect can clearly be seen in fig. 50a, where above the level of the remaining melt, the initial pit walls can be seen intact. Below this, the clear outline of the melt can be seen. The walls of the pits below this level, have been dissolved and the back wall has been undercut.

The pits, such as are shown in fig. 50a can also be seen to have crystals growing out from the walls. These crystals all appear to have the same orientation, and could well have resulted from the furnace temperature dropping at a fast enough rate to cause the melt in the pits to become supersaturated throughout. The solute still left in the solution at this stage, would have started to grow on the walls.

The shape of the pits shown in figs. 50a and c, and also their fairly featureless bases, indicate that the melt never touched the substrate here. This, as explained previously, may have been a contamination problem, or, perhaps have been caused by trapped gas at the base of the pit.

Another feature observed was that on either side of the pits where they had penetrated to the surface of the original substrate, the p-n junction appeared to bend downwards. Also, from the position of the holes seen between the layer and the original substrate surface, it appeared that the junction was below this, both these features can be seen on fig. 50a. The reason for this was that the zinc dopant, had

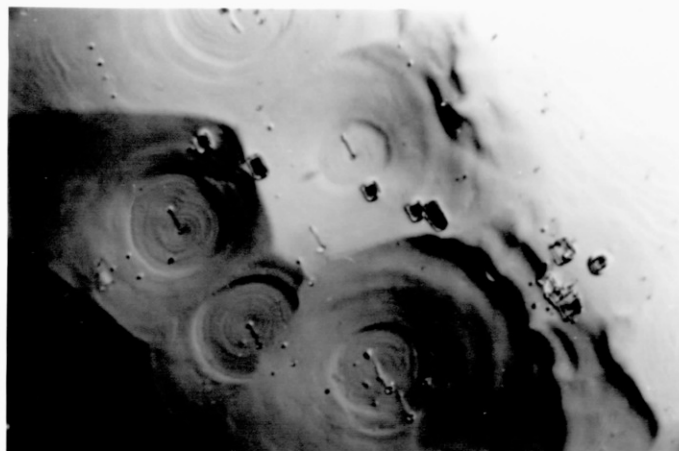
a comparatively high diffusion coefficient, of between $2 - 5 \times 10^{-10}$ cm^2/s in the InP, and thus, in the time that it took the furnace to cool down, the zinc diffused into the n-type substrate, displacing the junction (previously reported by Kuphal [52]). It therefore follows, that at the base of the pits, where there had been no growth, no junction would be seen. However, at the pit edges, where the growth was very small, the diffusion would have occurred to a lesser extent and hence, the junction appeared to bend upwards to the pit bottoms.

Growth hillocks associated with stacking faults, were often observed in the smoother growth region which surrounded the rough central area. Figs. 55a and b, show typical Nomarski images of these hillocks. Fig. 55c, shows a particularly "hilly" area, next to the rough central area of a sample, which had resulted from preferential growth at the stacking faults. It can be clearly seen that each hillock had an associated slash near its centre. It also appears, that the growth occurred at the ends of the slash. Moon and Antypas [23], found identical features to these, when growing layers of InGaAsP on InP substrates. They attributed the features to spiral growth, occurring at two closely spaced screw dislocations. Because the slash is to be found at the top of the mound, and because they observed that the spiral growth was of opposite sense at either end, they concluded that the growth was associated with a stacking fault. This type of growth has also been observed in the LPE growth of layers on GaAs substrates, by Horikoshi and Furukawa [82], who also attributed them to stacking faults.

In the samples from the RDLPE experiments, these features were usually seen as slight undulations near the edge of the central growth zone, becoming more prominent, the nearer they occurred to the centre.

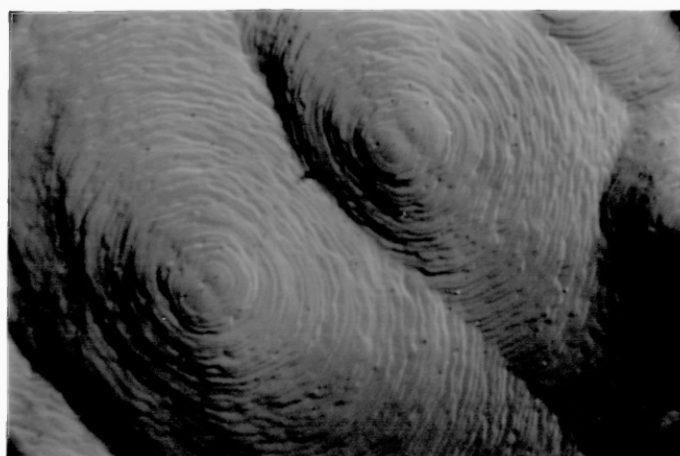
(a)

40 μm



(b)

80 μm



(c)

150 μm

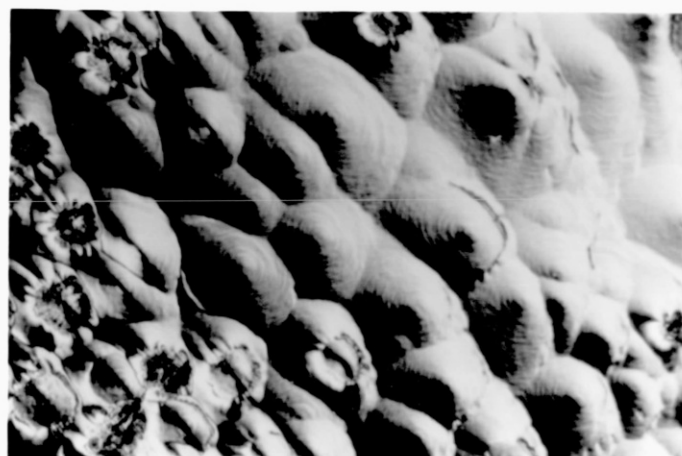


Fig. 55 Light micrographs of growth hillocks resulting from preferential growth at stacking faults.

Here the growth conditions would have been near, or actually those, required for constitutional supercooling to occur. This encouraged the outward growth of such hillocks. These features were only clearly seen, when using the Nomarski interferometer.

The cause of such defects is not clear, but Moon and Antypas [23] and Horikoshi and Furukawa [82] attributed it to surface contamination, such as oxide patches. Takahashi and Nagai [58] suggested they were a result of fine decomposition pits. Such fine pits are known to have existed on the substrates used in the RDLPE experiments, (see fig. 44a).

ii) **The effect of the step-cool:**

A set of three experiments, were conducted at a furnace temperature of 656°C, with a slave temperature controller setting of -0.42mV, and a 200 rpm rotation of the substrate. The step-cool conditions, prior to growth, for each of these experiments, were 11°C, 13°C and 15 °C, respectively.

A rotation rate of 200 rpm was chosen, in order to give the best possible layers.

Fig. 56 shows the resulting InP slices from these experiments, plus an SEM photograph of the middle of the "central growth zone" (it should be noted, that at 200 rpm, none of these slices showed the distinct features due to constitutional supercooling, which had been found on the samples from the different rotation rate series. In fact, they showed that the growth was best nearest the centre).

Two points are to be noted before discussing the results of these experiments:

Firstly, in fig. 56a, only half of the original slice is shown, the other half had previously been used for analysis.

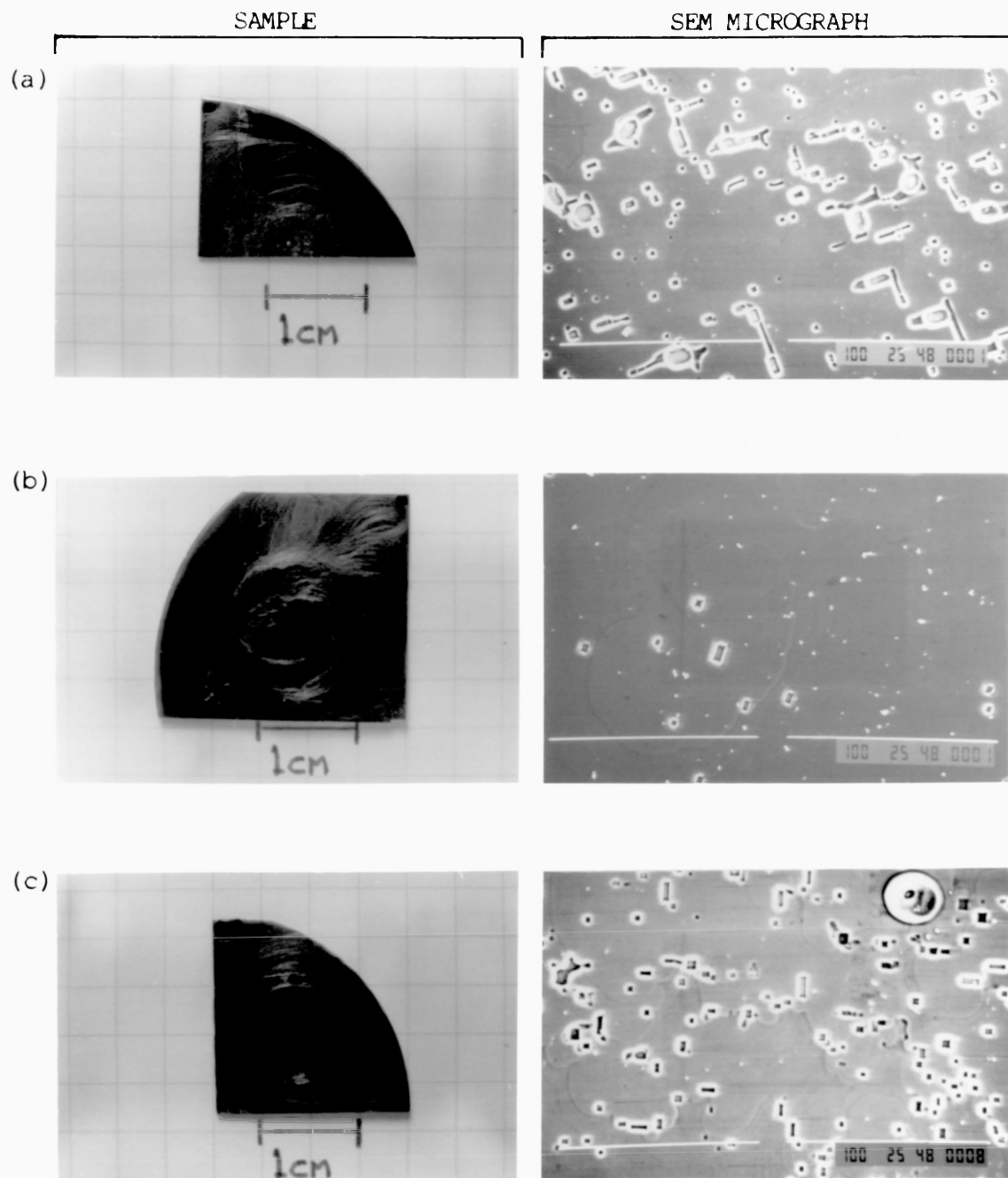


Fig. 56 Photographs of the samples obtained using a (a) 11°C, (b) 13°C and (c) 15 °C step-cool prior to growth. Other growth conditions were kept the same for each of the experiments. A photograph of the sample and an SEM micrograph of the middle of the central zone is given for each. The white bars at the bottom of the SEM micrographs represent 100 μm .

Secondly, in fig. 56b, only the lower half of the "central zone" was used for analysis, the top half being unsuitable as a result of the flow of melt at the termination of the growth experiment. This caused the melt periphery to wander across half of its central zone, leaving a series of circular markings there.

The 11°C and 13°C samples from this set of experiments have already been discussed earlier in this section, these being the first two samples analysed using EBIC. To recap however, fig. 56a shows that on the 11°C step-cool sample, the original growth islands had developed sufficiently to form a layer. However, there still remained a number of pits where growth islands had not completely merged. By increasing the step-cool to 13 °C, the supersaturation in the melt was increased. Consequently, the nucleation density and driving force for growth was increased. In fig. 56b, this resultant growth can be seen. It is apparent, that there had been a marked decrease in the number of pits in the surface.

On increasing the step-cool to 15°C, it can be seen from fig. 56c, that here the growth had in fact deteriorated, with an increase in the density of the pits. The reason for this was thought to be that spontaneous nucleation of precipitates within the melt was occurring, and was therefore reducing the supersaturation of the melt. This consequently resulted in growth similar to that obtained at the lowest step-cool. This was in agreement with the findings of Kishi et al. [83], who measured the critical supersaturation for the growth of InP from an In melt to be 14°C at a growth temperature of 650°C. At higher step-cools than this, they found that spontaneous precipitation occurred.

iii) **The effect of the temperature gradient:**

A series of three experiments were conducted with the substrates rotating at 200 rpm, a furnace temperature of 656°C prior to a 13 °C step-cool and slave temperature controller settings of -0.42mV, -0.48mV and -0.675mV making the substrate 1°C, 2°C and 3°C cooler than the melt respectively.

Fig. 57, shows photographs of the resulting InP slices from this series. It can be seen that as the temperature gradient was increased, the growth in the centre of the different substrates graduated from, being near to a complete layer, to showing the effects of growth due to constitutional supercooling. In fact the sample with the smallest temperature gradient, had its best growth at its centre. Whereas, for the samples shown in figs. 57b and c it can be seen that the best growth was away from the centre (where constitutional supercooling did not dominate).

It is clear from these samples shown in fig. 57, that increasing the temperature gradient had in fact improved the growth in the stable growth areas, with the layer becoming virtually free of inclusions. The reason for this improvement was that with the higher temperature gradient, the melt fell onto a cooler substrate. Thus, the melt in direct contact with the substrate, had a greater degree of cooling, and thus a higher degree of supersaturation. Consequently, the nucleation density and the growth rate were higher and gave a better layer. However, although the temperature gradient had been increased, clearly the increased supersaturation resulted in the growth rate exceeding that needed for constitutional supercooling, particularly in the centre, where the flow was not quite ideal. Hence, there was a deterioration in the quality of the growth in this region, as described

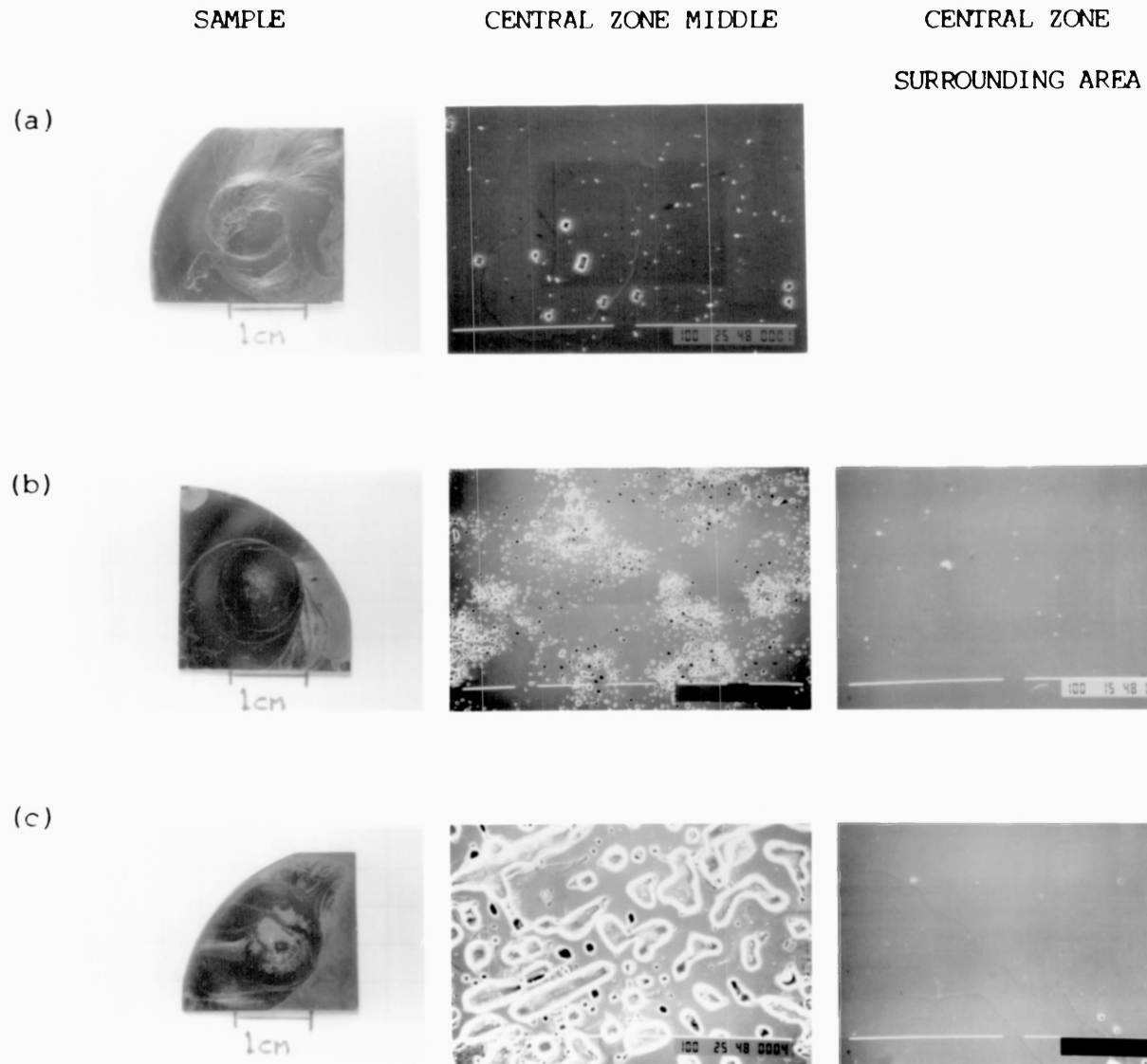


Fig. 57 Photographs of the samples and SEM micrographs of the growth obtained using slave temperature controller settings of (a) -0.42mV , (b) -0.48mV and (c) -0.675mV . Other growth conditions were the same for all of the experiments. The white bars at the bottom of the SEM micrographs represent $100\text{ }\mu\text{m}$.

in the section on the effect of the rotation rate.

6.5.3 Comparison of observed growth rates in RDLPE with those expected from conventional LPE.

It is useful to form some sort of comparison between the growth rates of the rotating disk technique and those of the sliding boat LPE method.

To do this it is necessary to compare the growth rate obtained from the rotating action to that which one could predict, under identical conditions with the sliding boat technique. The equations in section 2.5 allow calculation of the epilayer thickness in the sliding boat technique. Equation (2.2) relates to the growth from a step-cooled solution. Using this equation and assuming a 13°C step-cool, a growth temperature of 643°C, a 10 second growth time, a diffusion coefficient for InP in In of $1.9 \times 10^{-5} \text{ cm}^2/\text{s}$ (Bachmann [48]), and the slope of the liquidus curve being calculated from equation (3.4), one would expect a layer thickness of approximately 0.45 μm . This is considerably less than that obtained for RDLPE, where there was a minimum thickness of 3 μm , and in the areas where growth due to constitutional supercooling had occurred, a maximum of 13 μm . This much higher growth rate for RDLPE, was a direct result of the fluid motion, which reduced the boundary layer thickness, and thus increased the rate at which the solute reached the growing interface.

Therefore, it can be seen that with RDLPE, a higher growth rate and a thicker layer for a given time results. However, it must be remembered, that constitutional supercooling will occur if a critical growth rate is exceeded. From the results of the experiments undertaken in this work, it can be seen that with conditions favourable for growth of an epilayer, the rotation used, creates a fluid motion resulting in

a growth rate which comes near to this critical value. Just a very small alteration to the growth conditions, results in unstable growth. Fig. 57b, shows the substrate with the best layer and fig. 57c shows the substrate that had just a 1°C increase in the temperature gradient. The result of unstable growth is apparent.

6.6 SUMMARY

Growth in the early experiments was restricted to a central area of the substrate and resulted in island growth only. This area was surrounded by edge growth features, which produced circular markings on a macroscopic scale. This gave a useful indication of the area of the substrate which was covered totally during the growth period.

It was postulated that the size of the central growth zone (the area of the substrate completely covered throughout the growth), was controlled by the rate of supply of the melt and the rotation rate. Thus, it was suggested, that the break up in the flow, with all other conditions being constant, was determined by the point at which the radial flow due to the rotating action matched the rate at which the melt was dropped (remembering that the radial flow increases at greater radii). This theory was experimentally supported by the fact that the radius of coverage was found to be proportional to the (rotation rate)^{-1/4}. This agreed with an approximate analysis of the flow rates.

The island growth, in the central growth zone, was eventually determined to result from the solution having a low degree of supersaturation. This resulted from growth taking place on the excess InP in the melt, prior to the melt being dropped onto the substrate. Moreover, the possibility of growth being hindered by contamination, could not be completely discounted.

Once the excess InP was eliminated, layer growth was obtained in the central growth zone. A series of experiments, were then performed to determine the effects that rotation rate, step-cooling and temperature gradient, had on growth.

It was found, that for the island growth features to completely merge to form a layer with no pits, the step-cool had to be increased from 11°C to 13°C. However, increasing this by only 2°C, resulted in an apparent reduction in the amount of growth. This was believed to result from spontaneous precipitation.

When altering the temperature gradient, it was found that a 2 °C temperature difference between the melt and the substrate was the optimum. Less than this and the island growth did not completely merge and pits (inclusions) were left in the layer. A greater temperature gradient, led to constitutional supercooling in the middle of the central growth zone.

Similarly, when investigating effects of the rotation rate, the optimum speed was found to be 200 rpm. Speeds above and below this resulted in growth effects, due to constitutional supercooling in the central growth zone.

The constitutional supercooling was a result of the growth rate exceeding a critical value. The forced convection which resulted from the rotating action, created a small boundary layer. Thus, a high growth rate resulted. It would appear, that for the 200 rpm case, the flow of fluid was near to ideal and gave a smooth layer. However, the growth rate at 200 rpm, was still close to the critical value. This was seen, when a higher temperature gradient was used, thus, increasing the growth rate and consequently the quality of the growth was seen to deteriorate.

For rotation rates other than 200 rpm, the high growth rates which were necessary, for constitutional supercooling to take place, were mainly believed to result from turbulence due to non-ideal flow.

The features resulting from the area of unstable growth were discussed, and a theory was postulated to explain their formation and shape.

On the samples where poor growth occurred due to constitutional supercooling, there was a region within the central growth zone and surrounding the area of rough growth, which was of much better quality. In many cases, this was found to contain growth hillocks associated with stacking faults. They were attributed to either, growth at fine decomposition pits, or to the results of surface contamination.

The growth rate with RDLPE, was found to be much greater than that with the sliding boat LPE method. This was attributed to, (a) the boundary layer thickness being reduced by the fluid motion, (b) the stacking faults resulting in hillocks in some areas, and (c) to the effects of constitutional supercooling, causing growth rates of up to $1.2 \mu\text{m/s}$, in the centre of many of the substrates.

CHAPTER 7. CONCLUSIONS AND FUTURE WORK

7.1 CONCLUSIONS

The technique of RDLPE was developed in an attempt to overcome many of the problems which are associated with conventional LPE methods, in particular those connected with the sliding boat technique, which is the one most commonly used.

The technique of RDLPE requires a supersaturated solution to be dropped onto a rotating substrate. It was predicted that this would produce uniform layers, forming abrupt junctions with the substrate over large areas and that the rotation rate would provide an additional control on the growth. Such advantages were derived from the theory of an analogous hydrodynamic situation of a disk rotating whilst submerged in a fluid, and also, by taking into account similar methods such as spun-on film techniques.

With this in mind, equipment was successfully designed and developed over a number of experiments, making it possible to grow epilayers by this technique.

The resulting design allowed substrates of any shape or size to be used. These were held in position on the turntable by suction, which permitted substrate rotation rates of 3000 rpm. The speed of rotation was accurately and remotely controlled up to 3000 rpm and was measured optically to be displayed on a Digital Panel Meter (DPM).

The melt prior to growth was held in a silica container. This, unlike the method used for conventional sliding boat LPE, was designed to prevent the melt contacting graphite surfaces before growth. Consequently, melt contamination by the apparatus was minimized.

The initiation of growth was achieved by permitting the melt, which

had first been step-cooled, to exit its container by the lifting of the piece of apparatus called the melt stopper rod. This rod was designed to be multifunctional, allowing the passage of a thermocouple down its length to the melt area. It also successfully provided a novel means of suppressing the decomposition of the InP substrates used.

The use of a gold reflecting furnace, allowed visual monitoring of all the growth experiments. The inclusion of a purpose built vessel to the design, made it possible to collect the melt which was flung from the turntable. Any remaining at the end of a run, was effectively removed by a rapid increase in the rotation rate. The melt was then simply tapped out and stored for possible future use, and cleaning was minimized.

Early growth experiments using this equipment resulted in island growth only, and it was not until excess InP in the melt was eliminated that layers were obtained. However, these early experiments did produce growth features characteristic to RDLPE. These were in the form of circular markings left on the substrate surface at the position where the melt periphery had been. It was suggested that these resulted from preferential edge growth together with a "slip-stick" motion of the melt periphery.

The existence of the circular markings, gave a useful indication of the area of the substrate which was totally covered during the growth period. This allowed important conclusions to be drawn about the RDLPE technique. Thus, it was found that the area of complete coverage by the melt was limited by the substrate rotation rate used. It was suggested that this was a result of (a) poor wetting of the InP substrate by the melt as a result of melt motion and possible substrate contamination, and (b) because of the limited flow rate of the melt and the

behaviour of a liquid drop to minimize its energy. In fact, the radius of coverage was found experimentally to be proportional to (rotation rate)^{-1/4}, a relationship to be expected from a simple analysis.

Following the initial experiments, the problem of excess InP in the melt was solved and the growth of a layer was achieved. Subsequently, three separate series of experiments were conducted. From the results obtained from these, it was found that the best growth was obtained at a 656 °C furnace temperature prior to a 13 °C step-cool, with a temperature difference of 2°C between the melt and the substrate, and a 200 rpm substrate rotation rate.

The first of these series of experiments to be undertaken, investigated the effects of different substrate rotation rates. Here it was found, that at rotation rates other than 200 rpm, the growth deteriorated markedly due to constitutional supercooling. It was suggested, that with a 200 rpm rotation, the flow of fluid on the substrate was closest to that of the case of the submerged rotating disk. This resulted in a smooth fluid flow, and consequently a good layer. It was suggested, that at other rotation rates, turbulent flow resulted on the substrate, and thus the growth rate exceeded the critical rate needed for constitutional supercooling.

The SEM and EBIC analysis carried out on the samples obtained from these growth experiments revealed a number of characteristic features in the central growth area. A detailed explanation of the formation of these features was postulated from a close examination of the results of the analysis.

From this first series of experiments, it was originally hoped to obtain a relationship between the growth rate and the substrate

rotation rate. However, because of the dominating influence of constitutional supercooling on the growth, no dependency at all was seen. This is therefore an area for future investigation.

The second series was an investigation of the effects of using different step-cools. From these it was found that a 13 °C step-cool gave the best layer. If either a lower, or a higher step-cool was used, incomplete layer growth was obtained. The first as a result of a lower nucleation density and growth rate, and the second due to spontaneous precipitation within the melt reducing the supersaturation. Thus, producing the same effect.

In the third and last series of experiments the effects of different temperature gradients from the substrate to the melt were investigated. It was found that a temperature gradient which made the substrate 2°C cooler than the melt, gave the best layer. When a lower temperature gradient was used, then an incomplete layer resulting from a lower nucleation density and growth rate was obtained. At higher temperature gradients, an increase in the supersaturation of the melt in contact with the substrate led to the growth rate exceeding that needed for constitutional supercooling, and consequently the growth deteriorated.

The growth rates obtained throughout these experiments, were found to be higher than those expected for the conventional sliding boat technique under comparable conditions. It was suggested that this was a result of the melt motion associated with RDLPE producing a smaller boundary layer thickness, and hence, higher growth rate. Additionally, in the central growth region of many of the samples, the growth rate was enhanced by conditions of constitutional supercooling and turbulence.

The information and results obtained from this work, while achieving

the original aims outlined in the introduction, have also opened up many avenues for future research in the field, and it is clear that there is still much to be investigated. It is equally clear that the potential exists for RDLPE to develop as a new and useful technique for epitaxy.

It is thought, that it would be appropriate here to suggest some lines for future investigation. They are listed below.

7.2 SUGGESTIONS FOR FUTURE WORK

i) The deposition of layers at slower growth rates. This would suppress the occurrence of constitutional supercooling and its deleterious effect on growth, and would allow further investigation of the effects of rotation rate on the growth rate.

This could be achieved by using a much lower step-cool. However, results of this work have shown that in such a case a longer growth time would be needed for epilayer growth. This could be achieved if a larger melt were used.

ii) Increasing the coverage of the substrate by the melt.

This could be achieved simply, by increasing the flow rate of melt onto the substrate. This would again require the use of a larger quantity of melt, possibly proving uneconomic.

Alternatively, a more thorough investigation into the use of the melt confiner described in section 5.2.9, might be undertaken. This does have the potential to overcome the limited substrate coverage, and it is felt that it could lead to a decrease in the actual quantity of melt required.

It is also possible to envisage that a melt confiner with a porous base might be devised, which would allow the melt to be drawn onto the substrate as if this were submerged in the melt, and thus produce the

ideal flow.

iii) Investigation of possible kinetic limitations on growth.

The dependence of the growth rate on the speed of rotation could result in kinetics limiting the growth at higher rotation rates.

iv) In situ cleaning of the substrate surface, to remove any contamination which might possibly have been affecting the surface coverage and the observed growth rates.

A possible way of achieving this would be to drop an unsaturated melt onto the substrate prior to the growth solution. But as mentioned earlier in this work, a thorough investigation of the effects of this on the substrate surface, would have to be conducted first.

v) Use of phosphine gas to prevent substrate decomposition.

Although the technique employed during the experiments was very effective in suppressing the decomposition, it did not prevent it completely, and the resultant fine decomposition pits may have been the cause of the formation of stacking faults during the growth. Therefore, it would be advantageous to incorporate a source of phosphine into the equipment, as this would remove the problem of surface decomposition.

This had not been previously possible, for safety reasons.

vi) Finding by investigation a way to overcome the limitations of having only one substrate rotation rate that is free of turbulence.

A way to do this might be by using different melt flow rates to achieve matches with different rotation rates.

This problem would be completely overcome however, if a melt confiner, as described above, with a porous base could be designed.

vii) To attempt the growth of ternary and quaternary compounds, as well as the binary compounds, this being considered essential for RDLPE to be technologically useful.

The growth of these more complex compounds would allow analysis of the sharpness and the compositional uniformity of the layers grown.

viii) The growth of devices by RDLPE.

Initially, these might simply be single epilayer devices such as a diodes. Ultimately, however, the apparatus would be designed to deposit multilayered devices.

APPENDIX A

NAVIER-STOKES EQUATIONS: EQUATIONS OF MOTION FOR A VISCOUS FLUID

The Navier-Stokes equations have been derived from a consideration of forces that can act on a viscous fluid to define the fluid's motion. This section will give a brief summary of their origin, (for a complete derivation the reader is referred to Kay and Nedderman [84]).

The stresses that can act on a fluid element $dx\ dy\ dz$ are shown in fig. 58. The rectangular cartesian co-ordinate system has been used, with axis x , y and z .

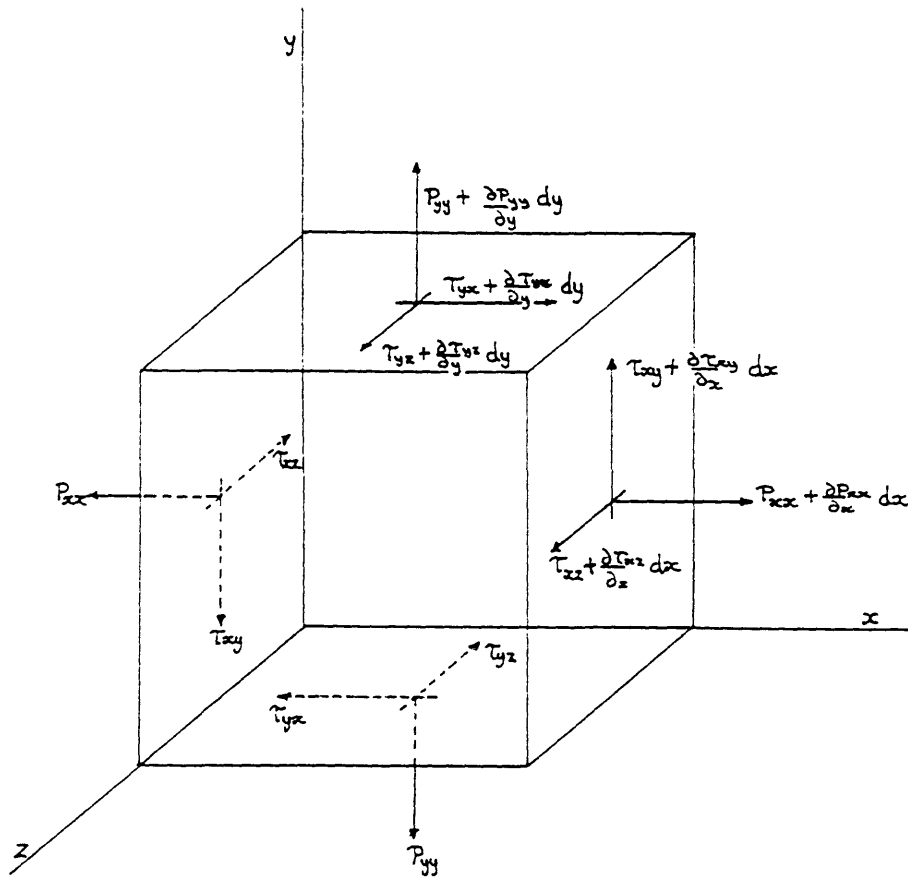


Fig. 58 The stresses acting on a fluid element $dx\ dy\ dz$. To avoid confusion, stresses have been omitted from the two faces perpendicular to the z -axis.

In fig. 58 the p terms are components of the pressure and the τ terms are components of the shear stresses set up in a fluid as a result of viscosity. This state of stress is similar to that occurring in an elastic solid. The nine stress components are therefore:

	x plane	y plane	z plane
x direction	p_{xx}	τ_{yx}	τ_{zx}
y direction	τ_{xy}	p_{yy}	τ_{zy}
z direction	τ_{xz}	τ_{yz}	p_{zz}

The normal stresses p_{xx} , p_{yy} , p_{zz} are taken as being positive in tension.

To obtain an equation of motion for a viscous fluid, the possibility of a body force, $\mathbf{F}$ per unit mass of fluid (e.g. gravity) in addition to the surface stresses shown in fig. 58 must be considered. This force will have the vectorial components F_x , F_y , F_z .

From a consideration of these stresses on the fluid element it is possible to write equations for the forces acting on it, in the x , y and z directions. By subsequently writing the fluid pressure and shearing stress components in terms of the "rate of strain" the **Navier-Stokes equations** result.

Hence for the x direction the Navier-Stokes equation is:

$$\rho \frac{Du}{Dt} = \rho F_x - \frac{\partial p}{\partial x} + \mu \nabla^2 u + \frac{1}{3} \mu \frac{\partial}{\partial x} (\text{div } \mathbf{u}), \quad (\text{A.1})$$

$$\text{where } \nabla^2 u = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2},$$

$$\text{and } \text{div } \mathbf{u} = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}.$$

In these equations ρ is the density, μ is the coefficient of viscosity, t is time and u, v, w are the velocity components in the x, y, z directions respectively. The Navier-Stokes equations for the y and z directions are similarly defined. Hence the three component equations may be combined into one vectorial equation (letters shown in bold typeface indicate vector quantities).

$$\rho \frac{D\mathbf{u}}{Dt} = \rho \mathbf{F} - \text{grad } p + \mu \nabla^2 \mathbf{u} + \mu/3 \text{grad div } \mathbf{u}. \quad (\text{A.2})$$

APPENDIX B

FURNACE TEMPERATURE PROFILES

The temperature was measured above the substrate in the furnace under almost identical conditions to those occurring during a growth experiment, the only difference being that the melt could not be present. However, later experimentation revealed the melt temperature to be the average of the temperatures across it. During growth experiments, the bottom and top of the melt were 70mm and 100mm above the substrate respectively.

The profiles were determined for two positions of the lower furnace zone thermocouple, as shown in fig. 26, and at different slave temperature controller settings. The master temperature controller was set to give a substrate temperature of 650°C.

The results of this calibration are shown in tables 2. and 3.

Distance above substrate (mm)	Slave Temperature Controller Setting (mV)					
	0.0	-0.2	-0.4	-0.6	-0.8	-1.0
0	650	650	650	650	650	650
20	650	651	651	653	653	654
40	648	650	651	654	655	657
60	645	648	650	654	656	658
80	642	645	648	652	654	657
100	637	641	644	649	651	656
120	632	637	640	645	648	653

TABLE 2. The furnace temperature (°C) at various heights above the substrate and for different slave temperature controller settings, where the thermocouple for the lower furnace zone was 65mm above the base of the furnace.

Distance above substrate (mm)	Slave Temperature Controller Setting (mV)					
	0.0	-0.2	-0.4	-0.6	-0.8	-1.0
0	650	650	650	650	650	650
20	650	652	652	653	654	654
40	649	651	653	654	657	658
60	646	650	652	654	657	659
80	643	648	651	653	657	659
100	639	643	648	650	654	657
120	634	639	643	646	651	654

TABLE 3. The furnace temperature ($^{\circ}\text{C}$) at various heights above the substrate and for different slave temperature controller settings, where the thermocouple for the lower furnace zone was 75mm above the base of the furnace.

APPENDIX C

CALCULATIONS OF THE TIME TAKEN TO EMPTY A TANK CONTAINING FLUID

Equations relating to the time taken to empty a fluid filled tank are easily derived. Fig. 59 gives the height above the base of the tank as h_1 , where $h_1 = h_2 = 0$ and the height of the liquid surface is at $h_1 = h_2$. The area of the top liquid surface is given as A_2 and the area of the outlet in the base of the container as A_1 . At the outlet of the container the stream of fluid enters the atmosphere, and thus, the pressure here, P_1 , is effectively equal to the pressure on the top of the liquid, P_2 , and both are equal to the atmospheric pressure.

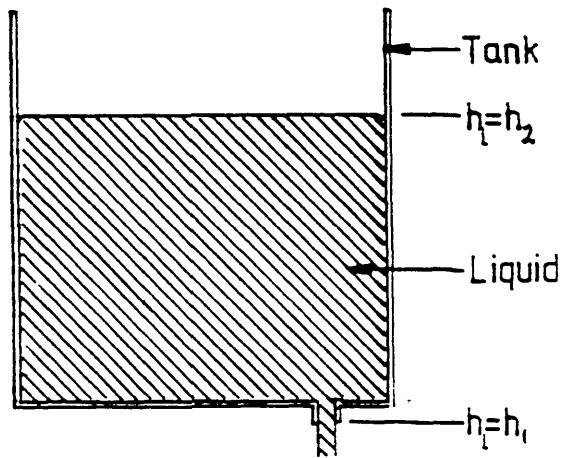


Fig. 59 Schematic diagram of an emptying tank.

If one assumes the viscous forces to be negligible, then one can use the Bernoulli equation, (a simplified form of the Steady Flow Energy Equation)

$$\frac{P_1}{\rho} + \frac{U_1^2}{2} + gh_1 = \frac{P_2}{\rho} + \frac{U_2^2}{2} + gh_2, \quad (C.1)$$

where U_1 and U_2 are the fluid velocities at the outlet, and at the top

fluid surface respectively, ρ is the density of the liquid and g is the acceleration due to gravity.

Equation (C.1) for this situation therefore becomes

$$\frac{U_1^2}{2} = \frac{U_2^2}{2} + gh_2. \quad (C.2)$$

However, for continuity, the volume flow rate of the dropping liquid inside the tank, must equal the flow rate out of the tank i.e.

$$\rho U_2 A_2 = \rho U_1 A_1, \quad (C.3)$$

thus

$$U_2 = \frac{U_1 A_1}{A_2}. \quad (C.4)$$

Thus, substituting (C.4) into (C.2) and rearranging the resulting equation, the following is obtained

$$U_1 = \left[\frac{2gh_2}{(1 - (A_1/A_2)^2)} \right]^{1/2}. \quad (C.5)$$

Thus assuming $A_1 \ll A_2$ then equation (C.5) simplifies to

$$U_1 = (2gh_2)^{1/2}. \quad (C.6)$$

Therefore the volume flow rate, Q , is given by

$$Q = U_1 A_1 = A_1 (2gh_2)^{1/2}. \quad (C.7)$$

It can thus be seen, from equation (C.7) that as the tank empties and h_2 decreases, the flow rate will decrease.

In the case of RDLPE, the melt dropper tube can be considered to be

such a tank and a consideration of the results of this analysis was used in its design.

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