

*Crystal Growth  
from  
High-Temperature  
Solutions*

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Online-Edition of the original book  
with additional Chapter II and Appendices A and B



Academic Press London New York San Francisco

A Subsidiary of Harcourt Brace Jovanovich, Publishers

## Part 011

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## 8. Liquid Phase Epitaxy

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### 8.1. Introduction to Liquid Phase Epitaxy (LPE)

The development of electronic technology has been increasingly in the direction of devices utilizing a thin layer of material. Such planar devices offer advantages not only of ease of access for the input and retrieval of information in some form but also in terms of the material requirements. Many materials of interest are difficult to prepare as bulk crystals without serious inhomogeneities, strain, inclusions or other defects. The preparation of thin crystalline films therefore makes possible a range of devices which would not be possible (or economically feasible) if only bulk crystals were considered. Epitaxial chemical vapour deposition has already reached the stage where computer-controlled plants are used for commercial device production, and the realization of a similar stage in liquid phase epitaxy (LPE) appears to be close at hand.

In this chapter the methods and mechanisms of LPE will be reviewed, with particular reference to the two types of device which appear to offer the greatest current promise for commercial production. Although several devices have been proposed and investigated, the great majority of the effort to date has been concentrated on two types of material—the III–V semiconductors for applications as light-emitting diodes, including lasers, and magnetically anisotropic garnet materials which exhibit cylindrical “bubble” domain structures.

LPE normally involves the deposition of epitaxial films, typically several  $\mu\text{m}$  in thickness, on carefully prepared substrates of similar structure. The substrate material should approximately match the material to be deposited both in lattice parameter and in linear thermal expansion

coefficient, otherwise strains are introduced into the film and dislocations or cracks occur if the mismatch is excessive. A distinction is made between *homoepitaxy*, in which case the film is of the same composition as the substrate except possibly for the nature or concentration of some dopant (as in *p-n* junction fabrication) and *heteroepitaxy* where the film and substrate differ markedly in composition.

The widespread use of LPE, especially for devices based on relatively thick layers ( $>1\ \mu\text{m}$ ), depends upon its convenience and on the high quality of the deposited film compared with that which can be obtained from the melt or from the vapour phase. An important advantage of LPE films over those grown from the melt is in the low concentration of point defects, which may be particularly troublesome in semiconductor devices which require a low residual impurity concentration. In addition, as shown by Vilms and Garrett (1972) for the growth of GaAs, certain impurities in the source material are removed from the gallium solution by evaporation into the stream of hydrogen gas flowing over the solution. It is possible that similar purification processes are operative in other solutions in addition to the normal impurity rejection by the growing crystal.

The LPE process involves the introduction of a carefully prepared substrate into a supersaturated solution, or into a nearly saturated solution in which supersaturation is created after a short period during which etching may occur. After growth of the layer has occurred, the substrate is removed and it is necessary to ensure that the surface is free from any drops of excess solution.

There are essentially two ways of promoting growth on the substrate crystal: either the substrate may be immersed in the solution, or the solution may be transported into the region of the crucible in which the substrate is located. There are, however, many variations on these basic processes and we shall examine the experimental methods in some detail. A comparison will be given in this chapter between the various techniques used by different workers and an attempt will be made to establish the important factors which determine the quality of the films, and to suggest the direction of future trends in this rapidly changing field.

A complementary approach has been adopted in a review of liquid phase epitaxy by Dawson (1972), who considers the application to specific III-V semiconductors and solid solutions. A recent review of LPE of magnetic bubble materials has been given by Ghez and Giess (1974).

## 8.2. Light-Emitting Diodes

The methods used for film growth by LPE have been evolved in many cases to meet a particular device requirement and it is desirable to consider the principal applications of LPE films prior to a detailed discussion of the

experimental techniques. Of the major applications of devices which utilize LPE films, that with largest potential market is probably for semi-conducting diodes which emit visible light. These light-emitting diodes (LED's) have the advantages of cheapness, low power consumption, reliability and ease of fabrication into complex arrays, and are particularly attractive for numerical display and similar applications. Consideration has been given to their use for TV displays and for general illumination although these are some way from realization. Reviews of the preparation and properties of LED's have been given by Casey and Trumbore (1970), Thomas (1971), and, along with a comparison of chemical vapour deposition and LPE, by Minden (1973).

The excitation of electromagnetic radiation relies on the injection under forward bias of minority carriers, predominantly of electrons into the *p*-type region. The fraction of minority carriers that recombine with emission of radiation to the total that recombine is termed the *internal quantum efficiency* of the diode. A more meaningful quantity, however, is the *external quantum efficiency* which is lower because of the loss of photons by absorption within the material.

The wavelength  $\lambda$  of the emitted radiation depends upon the energy band gap  $W_G$  of the semiconductor according to the relation  $\lambda \simeq hc/W_G$ , where  $h$  is Planck's constant and  $c$  the velocity of light. For the emission of visible light, the band gap must exceed 1.8 eV, which corresponds to a wavelength of about 7000 Å. This requirement excludes germanium and silicon and, although the II-VI semiconductors have band gaps in the required region, they will also be excluded from this chapter since attempts to make a stable *p-n* junction have so far been unsuccessful. The III-V compounds which remain may be divided into two categories according to their band structure—in *direct gap* materials such as GaAs a photon is absorbed by the crystal with the creation of an electron and a hole, while in *indirect gap* materials like GaP the excitation of carriers involves a lattice phonon for momentum conservation.

Emission of radiation from direct gap materials is a relatively simple process in which the injected electrons recombine directly with holes, with the emission of a photon. The energy of the photon will be the same as the band gap except for a decrease with increase in the doping level due to the formation of a "tail" on the valence band by the merging of impurity levels with the band edge. The major problem with direct gap semiconductors is self-absorption by the material of the radiation emitted, since the characteristic wavelength for absorption is the same as that for emission. As an illustration, Archer and Kerps (1967) reported an internal quantum efficiency for GaAs of nearly 50% but the external quantum efficiency was only 1%. Rupprecht *et al.* (1966) produced GaAs diodes of

external efficiency 4% with silicon as the dominant impurity, and attributed this high value to the close compensation of the dopant. This value may be considerably improved by the use of a domed structure, and Ashley and Strack (1969) achieved values as high as 20% for a domed GaAs diode. Since the band gap of GaAs is only 1.4 eV, the radiation emitted is in the infra-red.

Because of the high efficiency of GaAs devices, LED structures have been made in which a diode is covered by a layer of phosphor which transforms some of the radiation into the visible region. An alternative approach is to alloy the GaAs with an element which results in an increase in the bandgap. Table 8.1 lists some of the materials which are currently

TABLE 8.1. Materials for Light-Emitting Diodes (after Thomas 1971)

Direct gap		Indirect gap		GaAs + phosphor	
Alloy	$W_{\max}(\text{eV})$	Compound	$W_G(\text{eV})$	Phosphor	$W_{ph}(\text{eV})$
$\text{GaAs}_{1-x}\text{P}_x$	2.0	GaP	2.3	YOCl(Yb, Er)	1.9
$\text{Ga}_{1-x}\text{Al}_x\text{As}$	1.9	SiC	3.0	YF <sub>3</sub> (Yb, Er)	2.3
$\text{Ga}_{1-x}\text{In}_x\text{P}$	2.2			YF <sub>3</sub> (Yb, Tm)	2.6

of interest for LED's.  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  layers are readily grown by LPE on GaAs substrates since the lattice parameters of GaAs and AlAs differ by only 0.009 Å. One problem which is encountered in the production of such layers is the large distribution coefficient of Al which normally leads to a decreasing aluminium concentration during growth.

The maximum direct gap of 2.2 eV in the  $\text{Ga}_{1-x}\text{In}_x\text{P}$  system makes possible the emission of a range of wavelengths from red to green. The red-emitting  $\text{GaAs}_{1-x}\text{P}_x$  alloys are widely used commercially but the diodes are normally prepared from the vapour phase.

In GaP and other indirect gap materials the emission of radiation is a much more complex process which involves an interaction with *exciton* centres. The emission of red light depends upon the presence on adjacent lattice sites of zinc (or Cd) and oxygen atoms which form a neutral Zn—O complex. An electron trapped by the complex can decay by pair emission with a hole bound to the Zn acceptor or by radiative (exciton) decay with the bound hole. The great advantage of indirect gap materials is that absorption at the gap energy is very small so that self-absorption by the material is low. The external quantum efficiency is not so high as in Si-doped GaAs but the value of 7% reported by Saul *et al.* (1969) still appears to be the highest for any electroluminescent device emitting in the visible region.

Nitrogen in GaP also acts as a shallow electron trap due to the difference in atomic number between nitrogen and phosphorus, although both are trivalent. The trapping energy in this case is only about 0.01 eV. When electrons are injected into a nitrogen-doped *p*-type region, they are trapped by the nitrogen and can attract holes to form a bound exciton, which decays with the emission of green light. The efficiency of nitrogen-doped diodes is relatively low, about 0.6%, but the diodes appear roughly as bright as the red-emitting diodes because of the greater sensitivity of the eye to green light. Lorim *et al.* (1973) proposed that higher efficiencies could be achieved by overcompensation as a means of producing the junction; this has the advantage that the wafers need not be removed from the solution during growth.

Silicon carbide is included in Table 8.1 since it could be used for the emission of a wide range of wave lengths, including the ultraviolet region. The bandgap varies according to the polytype and yellow emission has been reported for the hexagonal 6H form. However the difficulty of fabrication of epilayers and of substrate crystals has prevented the widespread development of practical devices.

In Fig. 8.1 a comparison is given of the light output from various LED structures, according to the review of Thomas (1971). The red GaP diodes are seen to require the lowest power for displays and are therefore preferred at present but other materials are capable of development by a greater factor, and rapid changes are likely in the immediate future. InP LED'S have been studied recently by Williams *et al.* (1973), who report a quantum efficiency of 1.5% at 300°K.

*Lasers.* The emission of high intensity electromagnetic radiation from junction diodes led to early attempts to fabricate laser diodes, and Nelson (1963) reported the first semiconductor lasers to be made by LPE. The diodes were made by cleaving the wafers to provide plane-parallel ends perpendicular to a flat *p-n* junction obtained by deposition of *n*-GaAs on a *p*-GaAs substrate. The threshold current for these devices was lower by a factor 4 than for diffused diodes of the same geometry.

Subsequent attempts to reduce the threshold current density  $J_{th}$  in order to achieve continuous laser action at room temperature were reported by Dousmanis *et al.* (1964) and by Rupprecht (1967). The threshold of the GaAs devices made by the former group was about  $4 \times 10^4$  A cm<sup>-2</sup> at 300 K, while Rupprecht achieved a value of  $2.6 \times 10^4$  A cm<sup>-2</sup> at the same temperature, using a modified laser structure. Silicon, which exhibits a temperature-dependent amphoteric doping behaviour, was the principal dopant for both *n*- and *p*-type material.

Still lower threshold currents may be achieved if heterojunctions are used so that there is a sharp discontinuity in band structure and refractive

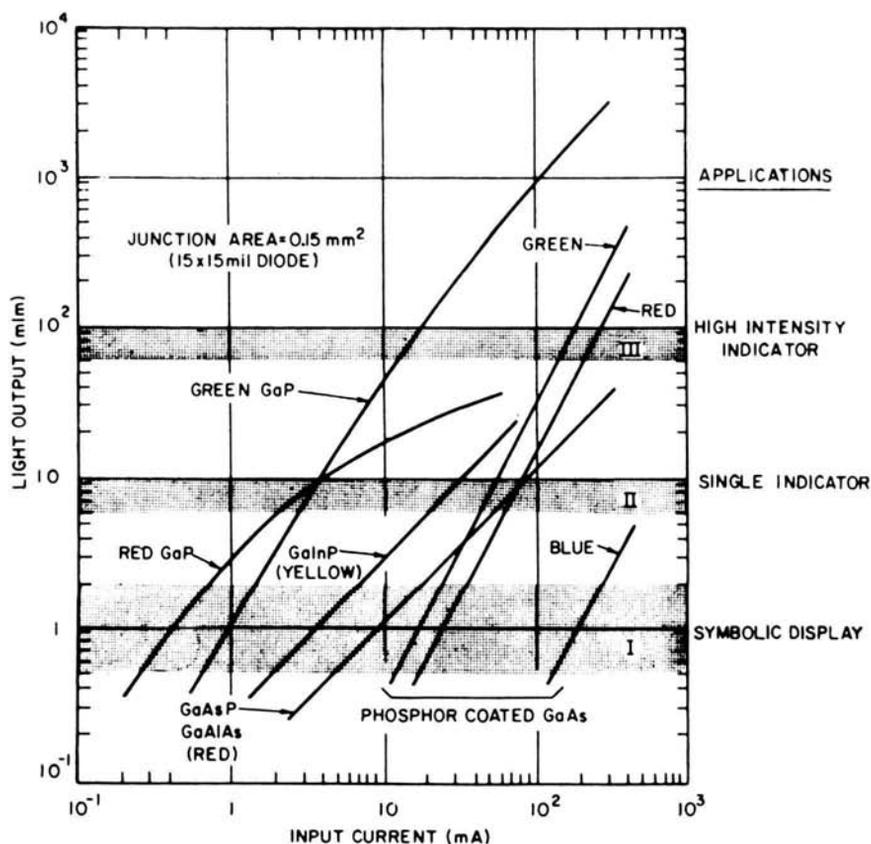


FIG. 8.1. Light output versus current for various types of LED. The values quoted are the highest reported (Thomas, 1971).

index at the  $p$ - $n$  junction. The use of heterojunction diodes was suggested by Krömer (1963), and Rupprecht *et al.* (1967) reported the fabrication of LED'S using  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  deposited on GaAs. Single heterojunction (SH) lasers with thresholds as low as  $1.0 \times 10^4 \text{ A cm}^{-2}$  were made by Hayashi *et al.* (1969).

A comparison of the homo- and single hetero-junction laser diode structures is given in Fig. 8.2. Electrons injected into the  $p$ -GaAs layer of Fig. 8.2(b) are repelled by the step in the conduction band at the boundary with the  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  layer, while hole injection is prevented by the difference in the effective bandgap of highly doped  $n$ -GaAs and the compensated  $p$ -GaAs. Recombination therefore occurs between the  $p$ - $n$  junction and the hetero-layer boundary, and the threshold current depends

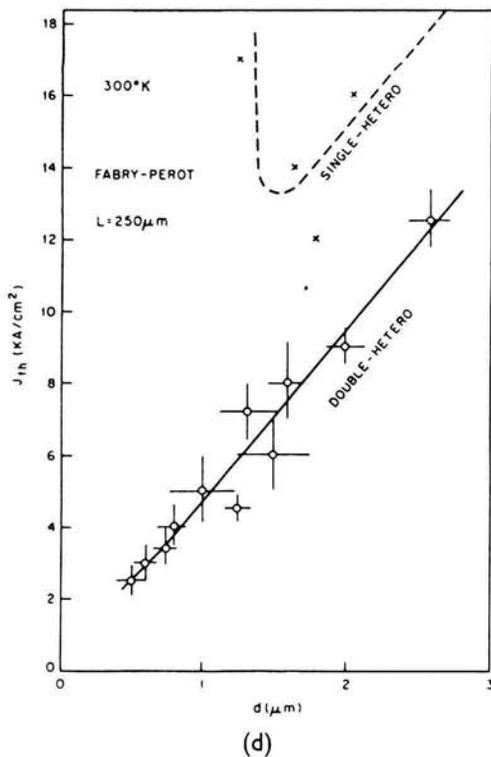
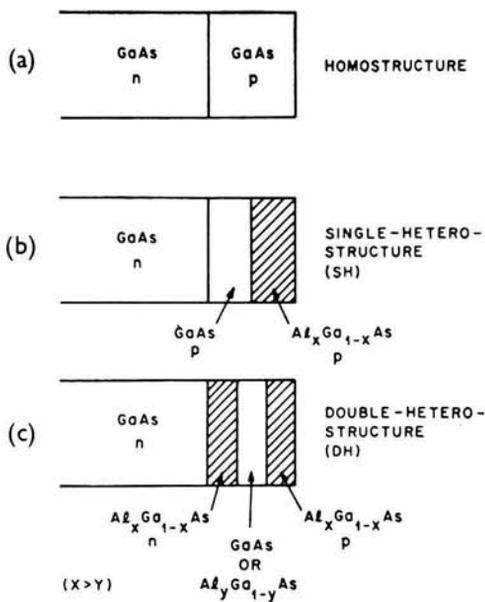


FIG. 8.2. Schematic cross-section of (a) homostructure, (b) single heterostructure and (c) double heterostructure lasers, (d) threshold current density *versus* film thickness  $d$  for SH and DH diodes for a Fabry-Perot device of length  $250 \mu m$  (Hayashi *et al.*, 1971).

very strongly on the width of the  $p$ -GaAs layer. A value of  $2\ \mu\text{m}$  was found to be optimum, with an increase leading to a lower light intensity for a given current and a decrease causing a higher  $\mathcal{J}_{\text{th}}$  because of hole injection.

The threshold current density may be still further reduced by the use of double heterostructure (DH) diodes as shown in Fig. 8.2(c). Alferov *et al.* (1969b, c) reported a room temperature threshold current of  $4.3 \times 10^3\ \text{A cm}^{-2}$  and Casey *et al.* (1974) subsequently achieved values around  $650\ \text{A cm}^{-2}$  for a square totally internally reflecting diode. The discontinuity in the bandgap at a  $p$ - $p$  junction in the  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  system is entirely in the conduction band (Alferov *et al.*, 1969a) so that electrons are blocked by this potential barrier. Hole injection is prevented by the residual potential barrier in the valence band and low values of  $\mathcal{J}_{\text{th}}$  are observed, particularly if the thickness of the GaAs layer is below  $1\ \mu\text{m}$ . A comparison between  $\mathcal{J}_{\text{th}}$  values for SH and DH structures is shown in Fig. 8.2(d). Fabry-Perot lasers on diamond heat sinks have been operated continuously at room temperature, giving about 20 mW maximum power at a current of 1 A, corresponding to a current density of about  $3000\ \text{A cm}^{-2}$ . A review of the development of DH lasers has been given by Hayashi *et al.* (1971). One of the problems in the application of DH lasers for high density data transmission via glass fibres is the lifetime of the devices, which at present does not exceed 100 hours.

It is expected that even lower thresholds will be possible with a one-dimensional superlattice structure in which the composition varies periodically with a spacing of 100–200 Å between layers (Esaki and Tsu, 1970). Such a structure has been achieved by vapour growth and techniques for its realization by LPE will be discussed in Section 8.4. This structure may also lead to novel high frequency devices.

### 8.3. Bubble-Domain Devices

It was established by Bobeck and coworkers (Bobeck, 1967; Bobeck *et al.*, 1969) that magnetically anisotropic materials of low magnetization will support highly mobile cylindrical or "bubble" domains which are of great interest for memory applications. Garnet materials appear to be most suitable for this application since both the bubble diameter and the mobility have acceptable values (Bobeck *et al.*, 1970; van Uitert *et al.*, 1970). The growth of garnet films and the factors affecting the choice of composition have been reviewed by Robertson (1973) and by Stein (1974).

The bubble diameter  $b$  is related to the saturation magnetization  $M_s$ , magnetic exchange energy  $W_{ex}$  and uniaxial magnetocrystalline anisotropy  $K_u$  by an expression due to Thiele (1969)

$$b \simeq W_{ex}^{1/2} K_u^{1/2} M_s^{-2}.$$

$4\pi M_s$  is typically about 150 gauss at room temperature, the reduction in magnetization compared with the undoped iron garnets normally being achieved by replacing some tetrahedral Fe by Ga or Al. The magnetization should be substantially independent of temperature and this requirement is often fulfilled by selecting a composition in which room temperature lies midway between the Curie temperature and the compensation temperature.

The uniaxial magnetic anisotropy arises either from stress-induced anisotropy due to mismatch between the lattice parameters of the film and the substrate or from growth-induced anisotropy. According to Rosencwaig and Tabor (1971) and Callen (1971), the latter effect is due to ordering of the ions occupying the dodecahedral sites in the garnet structure and their models explain most of the observed data at least qualitatively. However, Isherwood (1968) demonstrated that even undoped yttrium iron garnet exhibits a departure from cubic symmetry and Stacy and Tolksdorf (1972) reported a noncubic magnetic anisotropy in YIG. The latter observation was explained by Stacy and Rooymans (1971) in terms of ordering of defects such as impurity ions or vacancies and it is possible that other non-annealable mechanisms may contribute to the anisotropy.

The stress  $\sigma$  in an epitaxial film is given (Besser *et al.*, 1971, 1972; Carruthers, 1972) by

$$\sigma = \frac{E}{(1-\mu)} (1-\eta) \left( \frac{a_s - a_f}{a_f} \right) + \eta(\alpha_s - \alpha_f) \Delta T$$

where  $E$  is Young's modulus and  $\mu$  Poisson's ratio of the film,  $a_s$  and  $a_f$  the room temperature lattice parameter of substrate and film respectively,  $\alpha_s$  and  $\alpha_f$  their expansion coefficients,  $\Delta T$  the temperature difference between the growth temperature and ambient, and  $\eta$  the fractional stress relief. The lattice parameter mismatch between the film and the substrate may be made negligibly small but stress arises from the difference in expansion coefficient between the gallium garnet substrate ( $\sim 9.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) and the iron garnets ( $\sim 10.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ). In the absence of stress relief the resulting tension would be in the region of  $3 \times 10^8 \text{ Nm}^{-2}$  or 45,000 p.s.i. (Blank and Nielsen, 1972). This value is close to the fracture limit of many oxide materials and cracking may be expected if the mismatch in  $a$  or  $\alpha$  has a larger value. For garnet films grown on {111} substrates, the anisotropy resulting from the stress is given by

$$K_u = -\frac{3}{2} \sigma \lambda_{111}$$

so that the anisotropy may be varied by selecting rare earth ions having the appropriate magnetostriction coefficient  $\lambda_{111}$ . The values of this parameter together with other useful data for the choice of a garnet composition are given in the paper of van Uitert *et al.* (1970). Current practice

(Roberson, 1973) is to minimize stress-induced anisotropy and to choose a composition in which a rare earth ion of large ionic radius such as Y, Gd or La is combined with one of small ionic radius such as Tm, Yb or Lu. Ions in a spectroscopic S-state are preferred since the bubble mobilities are found to be higher than in materials in which there is an orbital contribution to the magnetic moment. Bubble mobilities of the order of  $10^3 \text{ cm s}^{-1} \text{ Oe}^{-1}$  are required for devices.

Another factor which might influence the choice of film composition is the requirement of a good mismatch of lattice parameter and expansion coefficient with the substrate. However a variety of non-magnetic garnets are available as high quality crystals for use as substrates and it is often more convenient to change the substrate rather than the film composition to achieve a suitable match.

The variation in stress-induced anisotropy for films grown on substrates of different lattice parameter has been studied by Giess and Cronmeyer (1973), and the change in anisotropy due to the dependence on temperature of the misfit was investigated by Stacy *et al.* (1973).

## 8.4. Experimental Techniques

### 8.4.1. Tipping

The development of liquid phase epitaxy, first reported by Nelson in 1961, was stimulated by the paper of Nelson (1963) which describes the epitaxial growth of germanium and gallium arsenide. The apparatus used is shown diagrammatically in Fig. 8.3(a). The substrate wafer is held tightly against the base of a graphite boat which is located in the centre of a uniform temperature zone of a furnace, inside a quartz glass tube through which hydrogen gas is flowed.

Initially the substrate wafer is well clear of the solution and the furnace is heated to form a solution of, for example, GaAs in Sn. The power is then switched off and the furnace tipped so that the wafer is covered by the solution. Initially the solution is not quite saturated and some dissolution of the substrate material occurs. On continued cooling, the solution becomes saturated and eventually supersaturated so that epitaxial growth occurs on the GaAs substrate. After deposition of a suitable layer, typically  $20 \mu\text{m}$  in thickness, the furnace is tilted back to its original position and the graphite boat immediately removed from the furnace and any remaining solution wiped off the epitaxial layer. The type of temperature programme used by Nelson is shown in Fig. 8.3(b). The cooling rate will depend on the volume of solution used, the linear growth rate being in the region of  $200 \text{ \AA s}^{-1}$  as for bulk crystals. A period of only 20 minutes is required for the growth of a layer of sufficient thickness for device fabrication compared

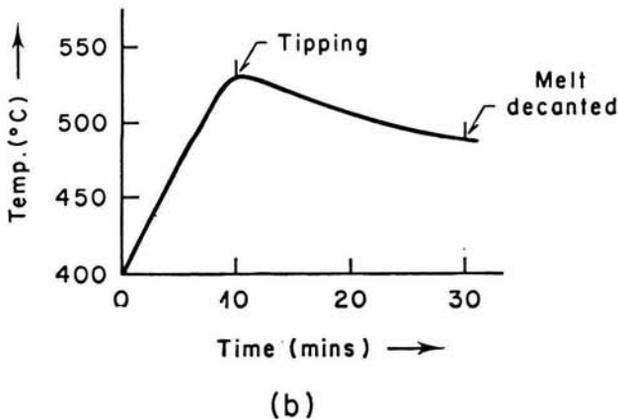
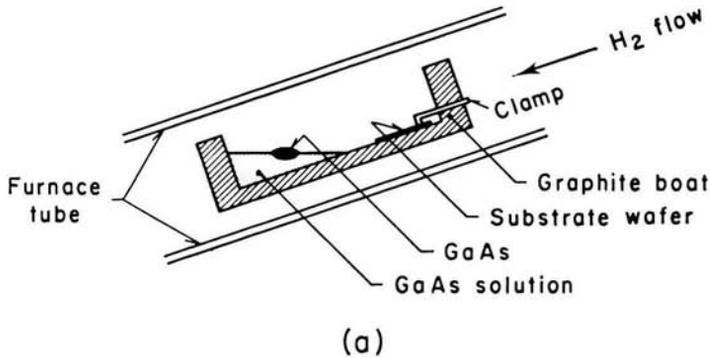


FIG. 8.3. (a) Apparatus for epilayer growth by tipping, (b) temperature programme (Nelson, 1963).

with many days for the growth of a bulk crystal. Nelson prepared GaAs laser diodes from Sn or Ga solution and Ge tunnel diodes using indium as solvent.

Burns (1968) used a similar arrangement to prepare *n*-GaSb from Ga solution but with a different type of temperature programme. In this case the temperature changes were carried out rapidly in steps of 2–7°C, with long holding periods after each change. The advantage of this procedure would appear to be that etch-back of the substrate, equilibration and growth occur under substantially isothermal conditions but a comparison of the resulting films with those grown by the type of programme used by Nelson was not given.

Trumbore *et al.* (1967) drew attention to the importance of the method of doping for the properties of a  $p$ - $n$  junction, considering in particular the preparation of (Zn + O)-doped GaP films. They used an open-tube system with a flow of hydrogen and nitrogen, with a separate Zn source to provide Zn vapour to compensate for evaporation losses from the solution. A two-zone furnace was used in order to regulate the partial pressure of zinc in the region containing the solution. Direct flow of gas over the solution was avoided in order to reduce the loss of Zn and Ga<sub>2</sub>O by evaporation. The principal disadvantage of this system is the poor control of the oxygen content of the solution.

Tipping in a closed tube system was reported by Shih *et al.* (1968) and by Allen and Henderson (1968). Ladany (1969) used a gas flow but with a covered boat in order to reduce dopant evaporation. Saul *et al.* (1969) achieved the very high value of 7.2% for the efficiency of a GaP light emitting diode by performing a 2-step anneal in the closed tube tipping furnace. The importance of doping in relation to the performance of light-emitting diodes will be discussed further in Section 8.6.

The first successful preparation of magnetic garnet films of high quality was described by Linares (1968) using a method very similar to that of Nelson (1963) but with a platinum boat. Gadolinium gallium garnet was found to be the best substrate material, mainly because of the lattice parameter match to the magnetic garnets at the growth temperature. Irregular surfaces developed on (111) substrates if the growth rate exceeded  $100 \text{ \AA s}^{-1}$ .

Orthoferrite films were grown by Shick and Nielsen (1971), who used a platinum screen to prevent undissolved particles of orthoferrite from drifting into the growth region. The substrate, fastened to a platinum sheet, was mounted in a vertical position at the end of the boat since this position was found to give a more uniform temperature distribution across the wafer. Best results were obtained with the substrate held some 5–10°C below the temperature of the solution prior to tipping, in order to prevent partial dissolution of the substrate. The solvent was 50PbO:1B<sub>2</sub>O<sub>3</sub> and the linear growth rate only  $10 \text{ \AA s}^{-1}$ . Growth was not possible on any non-magnetic substrate due to the relatively rapid dissolution of these materials. In all hetero-epitaxial deposition it is important to realize that the solution is not saturated with respect to the substrate material, and kinetic factors determine whether epitaxial layer growth will occur in preference to substrate dissolution.

Shick *et al.* (1971) described the growth of magnetic garnet films on gadolinium gallium garnet using the same technique and discussed the characteristics of the resulting materials in relation to their application in bubble-domain devices.

Recently it appears that tipping has become less popular for the growth of garnet films than the dipping techniques which will be described in the next section. A notable exception is the work of Plaskett (1972) who reported the highly reproducible growth of films of good quality. An important problem in the achievement of uniform, homogeneous films is the avoidance of temperature gradients across the substrate, and Plaskett has mounted the substrates in such a way that the surface is horizontal during growth, rather than inclined to the surface of the liquid at the tipping angle.

In the growth of semiconductors by tipping, Donahue and Minden (1970) introduced rotary crucibles in which the tilting is replaced by a rotation of  $180^\circ$  or  $360^\circ$ . The principle of this technique is analogous to that used for nucleation control in flux growth of bulk crystals by Bennett and Tolksdorf which is described in Chapter 7. The great advantage of this

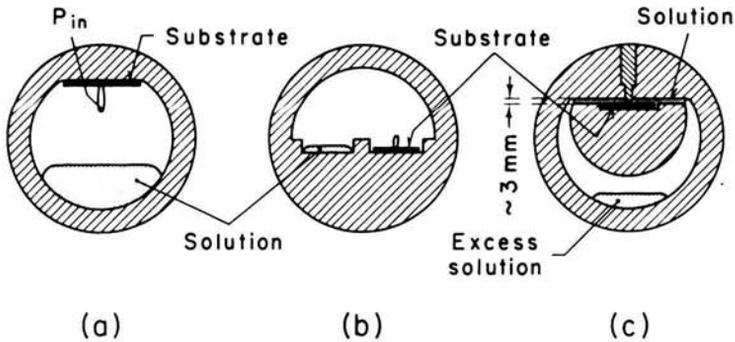


FIG. 8.4. Apparatus for epilayer growth using small volume of solution (Donahue and Minden, 1970).

technique is that only the crucible is moved, rather than the whole furnace. The various boats used by Donahue and Minden are shown in cross-section in Fig. 8.4. In the simplest version, depicted in Fig. 8.4(a), the substrate wafer is held against a flat portion of the inner wall of the cylindrical graphite crucible by an L-shaped pin which is anchored in the base. The solution, which has a relatively small volume, is made to flow over the substrate by inverting the crucible.

The crucible shown in Fig. 8.4(b) is an alternative version in which the substrate is held in one of two wells, the second of which contains the solution. A  $360^\circ$  rotation is necessary in this case to bring the solution into contact with the substrate. Rotation in the opposite direction is used to decant the melt after growth of the film by slow cooling.

In the crucibles described so far, the wafer is normally located further

from the axis of the furnace than the solution, so that the temperature gradient is in the wrong direction for stability according to the supersaturation gradient criterion. This is remedied in the version shown in Fig. 8.4(c) in which the substrate wafer is held in a recess so that it is closer to the furnace axis than the solution. This design has the additional advantage that only a very thin layer of solution is in contact with the wafer. The solution is held in place by surface tension in a 3 mm gap between the substrate and the crucible wall. In all the experiments of Donahue and Minden, 5% of Zn was used in place of the equivalent amount of gallium; this was found to enhance wetting of the substrate without appreciable substitution in the lattice. The design shown in Fig. 8.4(c) was found to give the best quality films, but all the films showed an irregular surface structure.

Rotatable crucibles were also used by Stringfellow and Greene (1971), who required to grow films under isothermal conditions. They encountered particular difficulties in attempting to grow  $\text{InAs}_{1-x}\text{Sb}_x$  solid solutions by polythermal methods, because of the large distribution coefficient of As and the relatively strong dependence of the lattice parameter on the As concentration. As with the growth of bulk crystals of solid solutions, a steady state method is required in which a temperature gradient is maintained across the solution with nutrient material at the hotter and the substrate wafer at the cooler end. Because of the large distribution coefficient of the arsenic, InAs was used as substrate material since the rate of depletion of Sb from the melt was slight.

The apparatus is shown in Fig. 8.5. The constituents of the solution

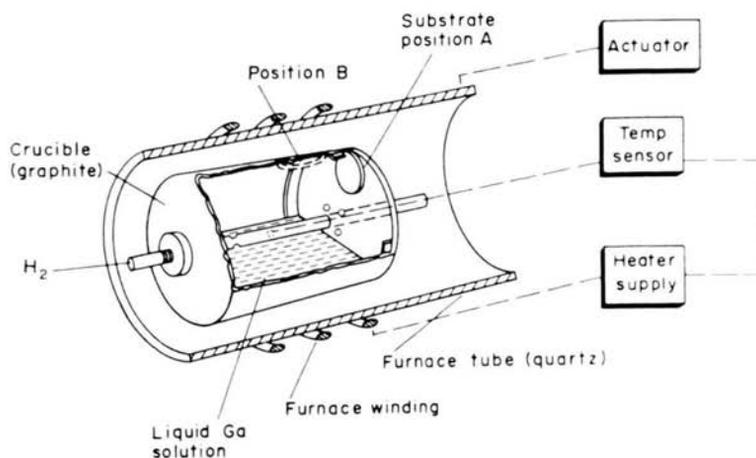


FIG. 8.5. Rotary crucible (Vilms and Garrett, 1972).

are placed in the crucible and held at the growth temperature for several hours in order to achieve equilibration. The substrate and source are then simultaneously introduced into the solution by rotating the crucible through  $180^\circ$  about the axis of the furnace. Rotation to the original position is used to terminate growth after a suitable period. A temperature difference between source and substrate of  $7\text{--}15^\circ\text{C}$  was found to be optimum, with higher values resulting in the incorporation of solvent inclusions. No evidence was found of substrate dissolution prior to growth. With an InAs substrate, the composition of the epitaxial layer varied from that of the substrate to that of the solid solution within the first  $4\ \mu\text{m}$  of growth, and remained constant over the  $80\ \mu\text{m}$  of subsequent growth. The greatest Sb concentration in the epitaxial layer was  $x=0.25$ , beyond which the lattice parameter mismatch with InAs is excessive.

A steady state method of epitaxial growth had been used previously by Panish *et al.* (1966), who utilized a radial temperature gradient to transport GaAs from nutrient material at the perimeter of the solution to a central seed mounted onto a silica heat sink.

Vilms and Garrett (1972) have given a detailed account of the growth of GaAs using the type of rotary crucible shown in Fig. 8.5, describing in particular the impurity concentration of doped and undoped layers. It was found that small air leaks in the gas supply are a major cause of impurities in the epilayers. In a leak-tight system the concentration of  $1\text{--}2 \times 10^{14}\ \text{cm}^{-2}$  was achieved by growth at temperatures below  $700^\circ\text{C}$ . The rate of growth, about  $4 \times 10^{-7}\ \text{cm s}^{-1}$ , was reproducible to within 12%, and the variation in thickness across a film was in the region of  $\pm 20\%$ . The average doping density was reproducible to within  $\pm 6\%$ . A comparison was not given between wafers mounted horizontally and those mounted vertically.

One disadvantage of the methods described so far is that the solution is stationary during growth so that stirring occurs only by thermal and solutal convection. Controlled stirring could be achieved in principle in the crucible of Fig. 8.5 by alternate rotation in opposite directions about its axis by, say,  $10\text{--}15^\circ$ . As discussed extensively in Chapters 6 and 7, growth in an unstirred solution may result in more rapid growth at the edges of the substrate and the maximum stable growth rate will be much less than that in a stirred solution. An apparatus for the simultaneous growth of epilayers on several substrates under stirring has been proposed by Scheel and Schulz-DuBois (1972) and is shown in Fig. 8.6. The wafers are located in recesses in a shallow crucible which can be tilted by about  $15^\circ$ . The solution is allowed to homogenize in an outer reservoir *A* and the crucible is then tilted so that the solution runs into the central chamber where it is retained by a dam which separates this chamber from the reservoir. Growth occurs by programmed cooling with the crucible in its

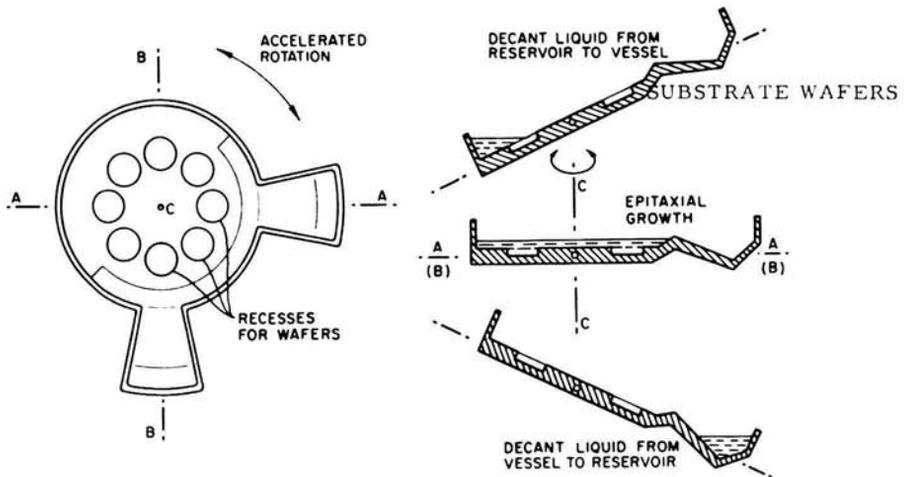


FIG. 8.6. Crucible for epilayer growth of several wafers in stirred solution (Scheel and Schulz-DuBois, 1972).

horizontal position, with stirring by accelerated rotation (see Chapter 7). When the epilayer has been grown, the solution is decanted from the central compartment by tilting the crucible about either the *A*- or *B*-axis. The use of more than one reservoir permits multiple layers to be deposited. A simpler means of stirring, by rotation of a horizontal substrate, was also mentioned by Scheel and Schulz-DuBois (1972), and suitable substrate holders are shown in the next section. In the apparatus of Lien and Bestel (1973) the solution is forced from an inner chamber to an outer one containing eight substrates by centrifugal force as the crucible is rotated at 500–1000 rpm.

#### 8.4.2. Dipping

The dipping method, in which the substrate is immersed into a supersaturated solution, appears to have been first reported by Linares *et al.* (1965), who grew garnet films by gradient transport onto YAG and GdGaG substrates. A similar technique was used by Rupprecht (1967) who required to deposit *n*-GaAs on a *p*-type substrate. The advantage of dipping is that the time of growth is short and well-defined, and no movement of the crucible is necessary.

Deitch (1970) advocated a “quick dip” method for the growth of GaAs from Ga solution, with the substrate temperature some 50° lower than that of the solution. The initial growth is then very rapid, but the large temperature gradient at the substrate-solution interface has a stabilizing effect. In subsequent studies of the same system by Crossley and Small (1972),

smoother layers and better reproducibility were obtained when the substrate was undercooled by only 5–10°C, and most workers have preferred to avoid a large temperature difference between substrate and solution.

Levinstein *et al.* (1971) pointed out that the particular advantage of the dipping technique for LPE growth of magnetic garnet films is that the solution in a 50PbO : 1B<sub>2</sub>O<sub>3</sub> flux may be supercooled by up to 120°C and that the supercooled melt can be stable with respect to garnet nucleation. Growth may occur under isothermal conditions and several films can be grown by dipping of successive substrates with the solution remaining at constant temperature. In these experiments the substrate was held in a vertical position and maintained just above the melt for 5 min. before dipping in order to attain a temperature close to that of the solution. The growth rate for a supercooling of 30°C was 70 Å s<sup>-1</sup>. The wafer was slowly withdrawn and the solution found not to wet the film during withdrawal. The density of etchable defects was less than 10 cm<sup>-2</sup> and a value of zero found in some cases. The uniformity of the film was ±2 to 5% over an area of 0.6 cm<sup>2</sup>.

More detailed investigations of a similar system were carried out by Blank and Nielsen (1972) and Blank *et al.* (1972) and a cross-section of their apparatus is shown in Fig. 8.7. The crucible has a volume of about 80 ml and is located in a constant temperature region about 15 cm in length. The constituents of the solution are initially melted in a larger crucible and the solution poured into the crucible to ensure uniformity and to produce only small garnet crystallites, so that redissolution is rapid on heating to the growth temperature.

In order to deposit garnet films it is necessary to select a region of the phase diagram such that garnet is the only stable phase. The general features of the pseudoternary phase diagram flux—R<sub>2</sub>O<sub>3</sub>—Fe<sub>2</sub>O<sub>3</sub> are shown in Fig. 8.8, and the composition range found by Blank and Nielsen (1972) to be optimum for the growth of their garnet films is summarized in Table 8.2. The distribution coefficient for gallium in yttrium iron garnet grown from an unstirred solution was found to vary from 2.26 at 1077°C to 2.09 at 879°C and was substantially independent of the garnet composition. These values are slightly higher than those of Giess *et al.* (1972) or Janssen *et al.* (1973) but there is general agreement on the tendency of the distribution coefficient to decrease with decreasing temperature. The actual values observed will depend on the growth rate.

The investigations of Blank and Nielsen revealed some very unusual features of the behaviour of the supersaturated solution. In the region where the orthoferrite is the stable phase, the *maximum* supercooling is only about 5°C and the addition of only about 0.2% by weight of the total melt of Fe<sub>2</sub>O<sub>3</sub> will increase this value to 30–60°C if it displaces the com-

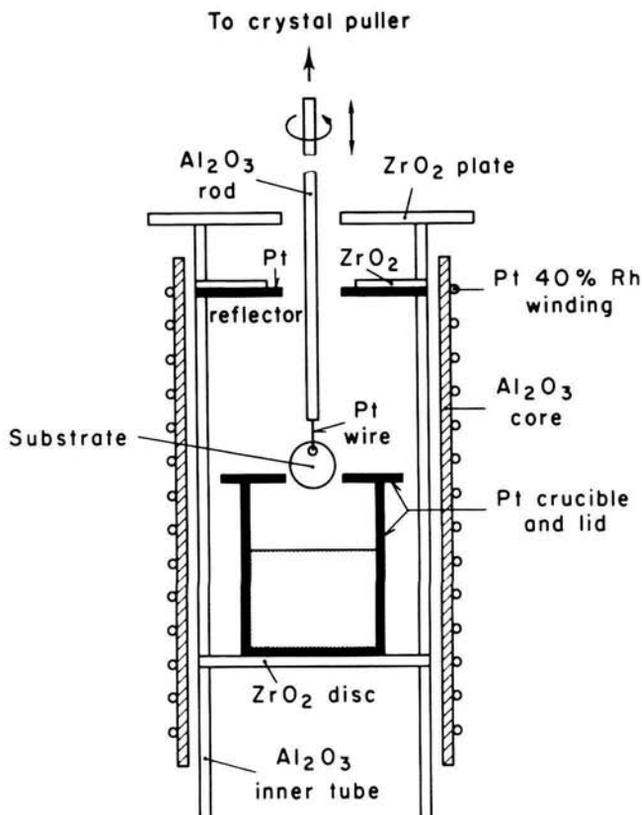


FIG. 8.7. Furnace for garnet film growth on vertical rotating substrate (Blank and Nielsen, 1972).

position into the garnet stable region. By selecting a composition close to the phase boundary, it is possible to produce a solution saturated with respect to orthoferrite but supersaturated with respect to garnet, so that a garnet film may be grown epitaxially in the presence of orthoferrite crystallites, but without the spontaneous nucleation of any garnet. The time over which a supercooled melt is stable increases with the distance from the orthoferrite boundary.

As stressed by Nielsen (1972), high growth temperatures must be avoided in order to prevent appreciable dissolution of the substrate. A lower growth temperature will also reduce the rate of solvent evaporation and hence the attack on the substrate prior to immersion.

Blank and Nielsen also found that there exists a critical mismatch between the lattice parameters of a garnet film and the non-magnetic

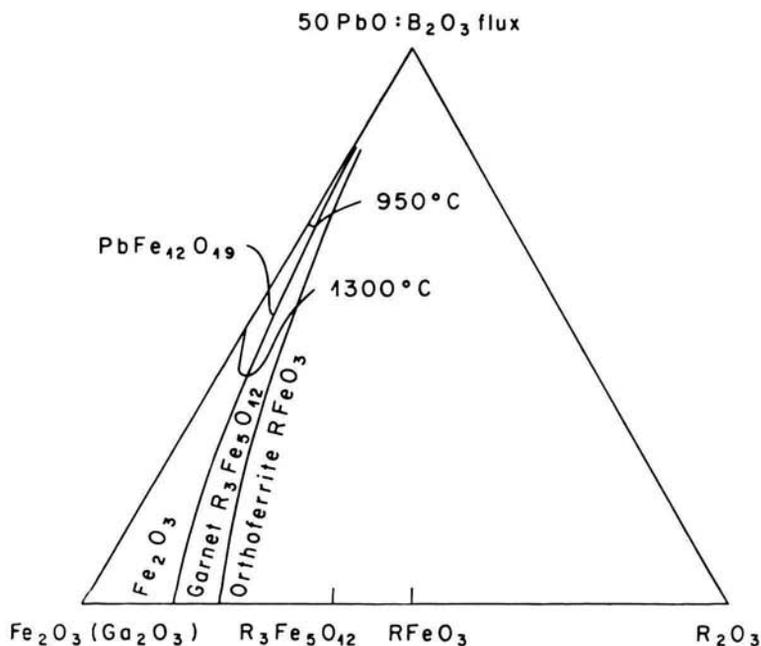


FIG. 8.8. Pseudo-ternary phase diagram showing stability fields of garnet and orthoferrite phase (Blank and Nielsen, 1972).

garnet substrate. Nucleation did not occur even in a strongly supersaturated solution if the mismatch between the substrate and the stable solute phase exceeded 0.19 Å. This value is of course much larger than that for cracking of the films, which Tolksdorf *et al.* (1972) reported to be 0.015 Å.

If devices based on LPE films are to be commercially viable, holders suitable for the simultaneous growth of several films under stirring are necessary, and designs discussed by Scheel and Schulz-DuBois (1972) are shown diagrammatically in Fig. 8.9. In the version shown in Fig. 8.9(a),

TABLE 8.2. Solution Composition for LPE Growth of Magnetic Garnets

Ratio	Recommended values (Blank <i>et al.</i> , 1972)
Fe <sub>2</sub> O <sub>3</sub> : R <sub>2</sub> O <sub>3</sub>	14-25
Fe <sub>2</sub> O <sub>3</sub> : Ga <sub>2</sub> O <sub>3</sub> (or Al <sub>2</sub> O <sub>3</sub> )	6-16
PbO : B <sub>2</sub> O <sub>3</sub>	15-6
Garnet : Total solution	~0.08
Er : Eu in Er <sub>3-x</sub> Eu <sub>x</sub> Fe <sub>4.3</sub> Ga <sub>0.7</sub> O <sub>12</sub>	1.7-3

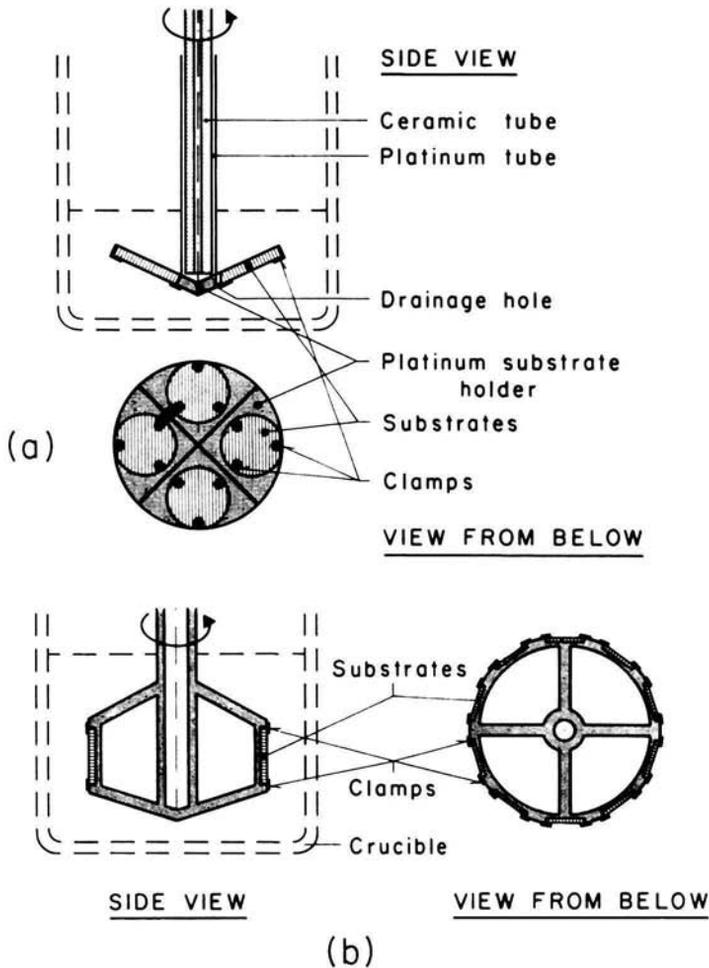


FIG. 8.9. Rotating substrate holder (a) with slightly inclined substrates, (b) with vertical substrates (after Scheel and Schulz-DuBois, 1972).

the wafers are held at a small angle to the horizontal in order to facilitate wetting by preventing air bubble formation during dipping and to make possible complete drainage of the solution. If the clamps are flat, the substrates may be withdrawn from the solution without adhering droplets. The clamps should be of minimum thickness in order to avoid irregular flow patterns. A drainage hole is provided to prevent trapping of the solution in the hollow region above the substrates. The rotatable substrate holder should be made of a platinum alloy containing not more than 5% of rhodium (for increased strength) in the case of oxide layer growth. For

semiconductor growth, the substrate holder would be made from graphite. Stirring has been used in the apparatus of Lorim *et al.* (1973) who used two vertically mounted GaP wafers on a holder moved over  $30^\circ$  in an oscillatory motion.

Figure 8.9(b) shows an alternative version in which the substrates are mounted in a vertical position. The turbulence introduced on rotation will be minimized if several wafers are supported around the periphery of the holder so that its circumference is almost circular. The advantages of the simultaneous preparation of a batch of devices instead of single ones are obvious for applications in research and industry. †

Giess *et al.* (1972) used a single horizontal rotating substrate dipped into a supercooled melt in order to grow bubble garnet films. The wafer is held against a flat platinum base by a number of platinum tabs bent over the edges of the wafer.

Prior to immersion in the solution, the wafer is heated to a temperature close to that of the liquid. During this preheating it is necessary to protect the substrate from attack by the flux vapour. Rotation is maintained during growth but is stopped as the wafer is removed; when the wafer has cleared the melt surface, rapid rotation at about 1000 r.p.m. is used in order to remove any droplets of solution which may be adhering to the surface. The holder may be withdrawn from the furnace extremely rapidly and cooled to room temperature in about 3 min, apparently without cracking or similar damage to the film. The concentration of lead from the flux was in the range 0.2–3.0 wt%, increasing with the growth rate. Film thickness uniformity was within  $2 \times 10^{-5}$  cm, or 2% for a 10  $\mu\text{m}$  film, and the composition was found to be uniform across the film.

Several films can be produced from the same melt, the depletion of solute due to film growth being offset to some extent by solvent evaporation. The process is now controlled by an automated system which permits accurate control of the time during which growth occurs. The operation of apparatus over extended periods and the resulting reproducibility of film parameters have been discussed by Stein (1974).

Hiskes and Burmeister (1972) proposed the use of a  $\text{BaO}/\text{BaF}_2/\text{B}_2\text{O}_3$  flux, which has a much lower volatility than the  $\text{PbO}/\text{B}_2\text{O}_3$  flux. An additional advantage of the barium flux is that the Ba concentration in the garnet films was some two orders of magnitude lower than the Pb concentration found when the lead flux was employed. The magnetic properties and defect densities were comparable to those of films grown from  $\text{PbO}/\text{B}_2\text{O}_3$ , but the lattice parameter and optical absorption exhibited marked differences (Hiskes and Burmeister, 1972). The high surface tension of these fluxes is

† The simultaneous growth of films on several horizontal substrates mounted in a vertical stack has been achieved in various laboratories.

an important disadvantage (Elwell *et al.*, 1974) since the solution is difficult to remove from the film after it has been raised out of the liquid.

#### 8.4.3. Sliders

Sliders are boats, normally of graphite, in which a small volume of solution is transported by the lateral movement of a graphite plate. The initial development of sliders resulted from the requirement to remove all traces of excess solution from a semiconductor film following growth.

The earliest form of slider appears to be that of Rosztoy (1968), mentioned in the review of Casey and Trumbore (1970), the operation of which is illustrated in Fig. 8.10. The initial homogenization of the solution and the epilayer growth is by a conventional tipping procedure, as shown in Fig. 8.10(a) and (b), except that the substrate is held in a recess with its surface level with the base of the boat. When the boat is tilted to terminate growth, as in (c), the movement of the sliding section wipes the solution off the surface of the film and confines the residual solution in a region well removed from the wafer. Panish *et al.* (1969) described a slider used simply to remove any oxide layer from the surface of the solution prior to the introduction of the seed.

Sliders also have the advantage that they are particularly suitable for the deposition of multiple films as required for single or double heterostructure lasers. In the version described by Panish *et al.* (1971), tipping is used to

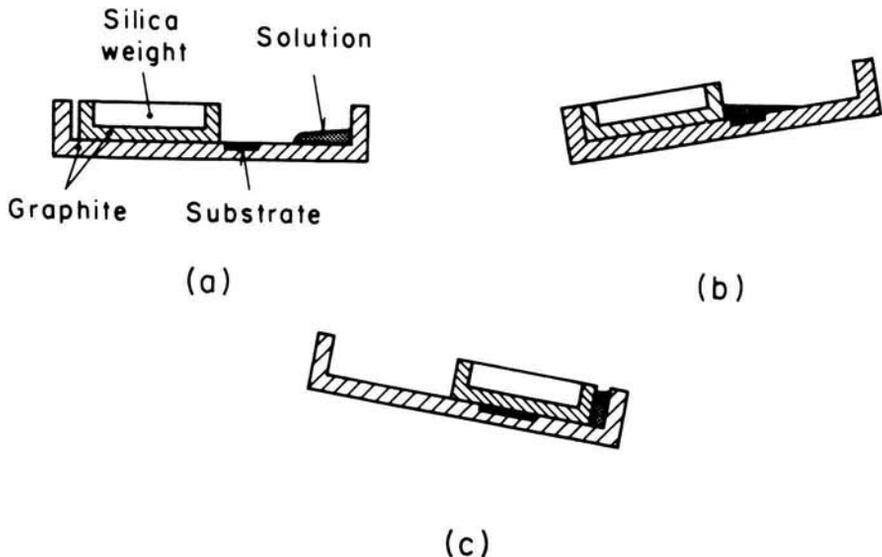


FIG. 8.10. Slider used to move solution in tipping process (Rosztoy, 1968).

move successively three solutions containing  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  with different dopants over a single substrate so that  $p$ -type layers of different composition are deposited on an  $n$ -type substrate. The time of contact can be extremely short so that very thin layers may be deposited. In the alternative design of Hayashi *et al.* (1970) a push rod is used so that the boat remains in a horizontal position during growth. Continuous cooling at  $1\text{--}3^\circ\text{C}/\text{min}$  was used for the deposition of multiple  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  layers and films of thickness  $1\text{--}3\ \mu\text{m}$  (apart from the initial layer) were deposited in a time of only 15 seconds.

A sliding shutter was employed by André *et al.* (1972) in the LPE growth of  $\text{Ga}_{1-x}\text{Al}_x\text{As}$ . The shutter covered the wafer prior to growth of the epilayer and was used only as a means of initiating growth.

Blum and Shih (1972) described an improved form of slider which is illustrated in Fig. 8.11. The solution is contained in a cavity in plate 2, which is held in position by the weight of plate 1. After equilibration with the source material, the solution is moved to a position over the substrate by displacement of plate 2, and an epitaxial layer is grown by cooling the furnace. When a layer of suitable thickness has been grown the solution is returned to its original position and any solution on the surface of the layer is wiped off during the displacement. Suitable dopants for subsequent layers may be introduced into the solution by displacement of plate 1.

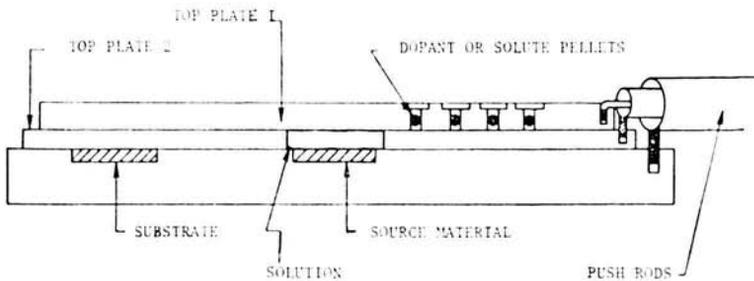


FIG. 8.11. Apparatus with two sliding plates (Blum and Shih, 1972).

The slider is located in a vertical temperature gradient with the substrate cooler than the solution, but the temperature is constant in the horizontal direction. In the growth of  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  films on a GaAs substrate the variation in thickness across the film was  $\pm 6\%$ , and the reproducibility between different runs was within  $\pm 8\%$ . A modified version of this apparatus was used to prepare four wafers each  $2\ \text{cm}^2$  in area on one wafer. High-quality light-emitting diodes were made by depositing a  $p$ -type  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  layer on a  $p$ -type GaAs substrate prior to deposition of the  $n$ -type layer to form the diode.

A further development was described by Lockwood and Ettenberg (1972) in which a very small volume of solution containing the appropriate dopant is used for each layer. The GaAs source material floats in each compartment on a layer of solution about 0.2–1 g in weight and 1 mm in thickness. A quartz glass rod and graphite spacer are used to cover the solution, and so this design should have the advantage of low volatilization as well as the stability expected from the use of a thin layer of solution.

Bergh *et al.* (1973) have proposed design features of a commercial system for LPE growth using slider arrangements and thin solvent "aliquots". The quality of the substrates and the amount of dopant rather than the degree of constitutional supercooling were found to affect the usefulness of the layer.

#### 8.4.4. Other methods

Woodall (1971, 1972) has developed apparatus for the growth of very thin layers of  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  for application in heterojunction lasers and which avoid the use of mechanical wiping on termination of growth. The wiping may result in damage to the epilayer if too high a pressure is applied, or to imperfect wiping of residual solution if the pressure is insufficient.

In the earlier version (Woodall, 1971) growth is terminated by rapid isothermal transfer of the substrate from the solution, or into a solution of different composition, by rotation of a central cylindrical substrate holder. In the outer region of the graphite crucible are located two annular regions containing respectively the solution used for deposition of the epilayer and a second solution which will normally contain a low concentration of solute if a single film is to be grown. Alternatively the second solution may be a saturated solution of different composition, and continued slow cooling with periodic transfer then used to prepare multiple heterojunction films. One disadvantage of this apparatus is that a small amount of solution is transferred with the wafer as it is rotated from one solution to the other.

In the later version (Woodall, 1972), which is shown in Fig. 8.12, the substrate is supported horizontally in a recess in part b, which is situated immediately below part c which contains a cavity of cross section slightly larger than that of the substrate. Part a is an outer crucible which contains b, c and also part d in which are located separate cavities containing the solutions. The location of the GaAs source material is shown at e, while f is a quartz glass tube used for the addition of a dopant during the growth cycle.

In operation, b and c may be rotated from one melt to the other. If the temperature is lowered continuously with the wafer in contact with one or other of the melts, growth occurs as in the conventional tipping process. Alternatively the substrate may be rotated to a position between the

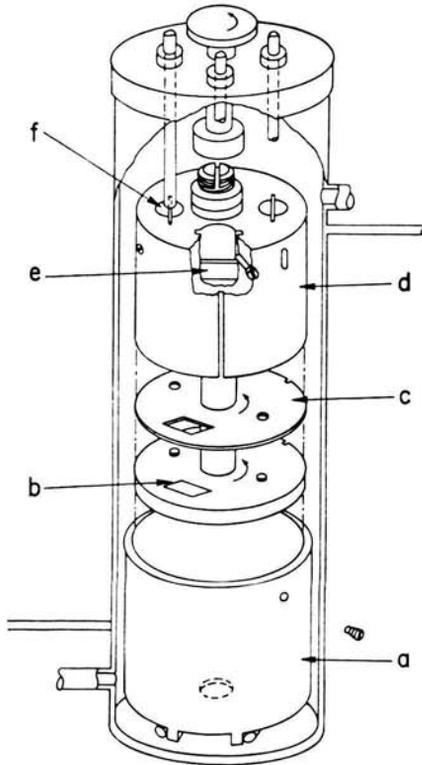


FIG. 8.12. Apparatus for substrate transfer between two solutions by rotating of central holder (Woodall, 1972).

solution chambers and cooling promoted so that deposition occurs from a very small volume of solution. A third possibility is that the substrate is rotated alternately between two melts of different composition. Growth occurs as a small volume of Ga/Al/As solution, which is transferred with the wafer, is mixed with a second solution in equilibrium to produce a new supersaturated solution. This technique is termed *isothermal solution mixing* by Woodall and its principle may be understood with reference to Fig. 8.13. This diagram shows the portion of the Ga/Al/As phase diagram in the Ga-rich corner. Points A and B represent two compositions on the same isotherm at which solid and liquid phases are in equilibrium. If liquids of these compositions are mixed, the composition will lie along the straight line joining A and B and the resulting composition will be in the supersaturated region, below the equilibrium liquidus curve.

In the preparation of very thin layers, the second method appears to offer the greatest advantages and Woodall was able to prepare linear

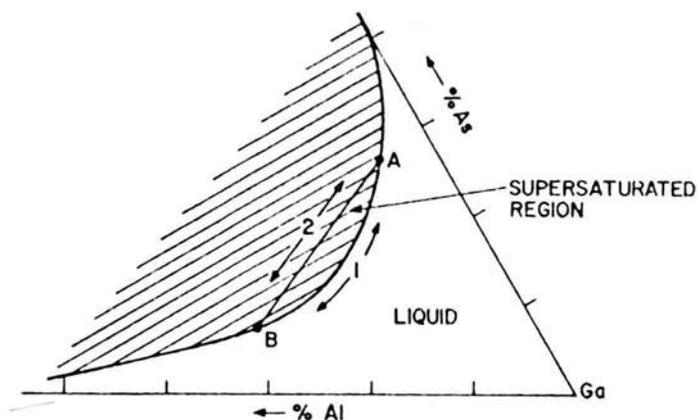


FIG. 8.13. Phase diagram of Ga/Al/As at Ga-rich corner showing creation of supersaturation by isothermal solution mixing.

superlattice structures of periods as low as  $0.1 \mu\text{m}$  by successive deposition from two solutions of different composition. An example of such a superlattice structure is given in Fig. 8.14, which shows a scanning electron micrograph of a section through a  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  layer. The volume of melt in contact with the layer may be conveniently varied by changing the thickness of the spacer  $C$ , which may be used as a means of varying the film thickness.

The deposition of thin layers using a small volume of solution was also

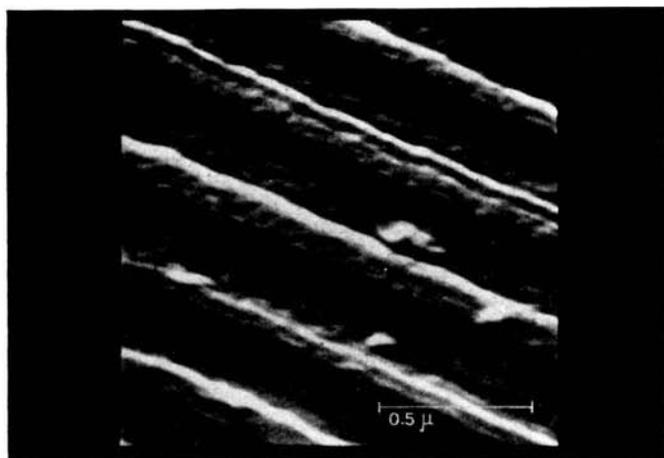


FIG. 8.14. Scanning electron micrograph of superlattice structure of  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  films (Woodall, 1972).

investigated by Panish and Sumski (1971) using the simple method shown diagrammatically in Fig. 8.15. The pair of wafers are separated by etching one wafer to produce small feet or shims of the desired thickness. The wafers are heated by a carbon strip heater having water-cooled electrodes and any oxide on the outer surface is removed by a flow of hydrogen when the temperature is above  $800^{\circ}\text{C}$ . The solution is introduced by capillary flow from a small drop on the end of a micromanipulator. A solution is formed by contact between the drop and the GaAs rod but wetting is

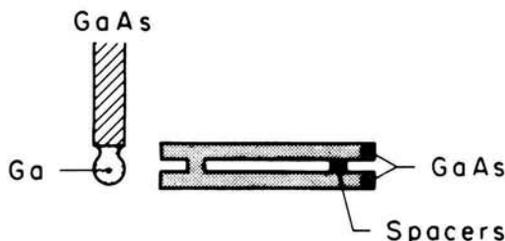


FIG. 8.15. Apparatus for epilayer growth by temperature gradient transport in a thin layer of solution (Panish and Sumski, 1971).

found to occur only if the solution is unsaturated. Growth occurs by transport from the hotter to the cooler wafer in the temperature gradient and abrupt junctions may be obtained.

Popov and Pamplin (1972) described a method for the deposition of thin layers using a VLS method with a thin zone of solvent which is made to move across the substrate by the travelling solvent method.

### 8.5. Growth-Rate Controlling Mechanisms in LPE

In addition to their practical significance, LPE experiments have also provided some of the most interesting measurements of growth rates under carefully controlled conditions. LPE growth of semiconductors to date appears to have been carried out mainly in unstirred crucibles and at rather high supersaturation, so that it is reasonable to assume that the growth rate will be controlled by solute diffusion. Mitsuata (1970) gave expressions for the growth and etch-back in terms of the solubility data and temperature programme assuming a homogeneous solution and his results suggest that volume diffusion is rate-determining. Diffusive transport has been assumed to be the rate-controlling factor by Small and Barnes (1969), by Minden (1970) and by Ghez (1973). Crossley and Small (1971) applied numerical methods to calculate the rate of etch-back and growth and interpreted data for both tipping and dipping experiments from a number of laboratories. Boundary layer diffusion was found to give

the best fit to the experimental data for the vertical dipping geometry, with growth rates of  $50\text{--}300 \text{ \AA s}^{-1}$  and boundary layer thicknesses in the region of 0.5 mm. With the horizontal tipping geometry bulk diffusion gave a better fit, and in both geometries allowance was necessary for nucleation within the solution, particularly at the higher cooling rates. The authors concluded that solutal convection had a major effect on the dipping systems. With the relatively short growth periods, limited melt volumes and rapid cooling rates used in LPE, steady state conditions will not be realized in the majority of experiments. The instantaneous growth rate will therefore depend upon the previous temperature programme, and average growth rates estimated from the total layer thickness and the duration of cooling may differ appreciably from the maximum value. Examples of the expected variation with time of the deposition rate are quoted in the above references and by Tiller and Kang (1968). Moon and Kinoshita (1974) find that the film thickness varies as  $A \, dT/dt \, t^{3/2} + B$ , where  $A$  and  $B$  are constants; the term  $B$  depends on the initial transient. The diffusion coefficient for GaAs in Ga was found to be about  $3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at  $700\text{--}900^\circ\text{C}$ .

Since it is difficult to obtain information on the interface kinetic mechanism by growth rate measurements in LPE growth of semiconductors, the main evidence for the kinetic process is provided by observations of the surface features. Most of the epilayer growth described in the literature is on substrates of high dislocation density and the resulting films frequently exhibit irregularities such as corrugations and cusps, although very flat areas may be present on the same films. It appears likely that the substrate should be considered as a rough surface with nucleation occurring randomly rather than at screw dislocations. Evidence for this conclusion is provided, for example, by Vilms and Garrett (1972), who found that cusps on the surface did not correspond to dislocations in the substrate. The surface features observed under normal conditions of film deposition will, however, depend on the substrate perfection and flat films are to be expected on films free from etchable defects.

Of vital importance to the performance of semiconductor junction devices is the profile of the dopant and problems might be expected from compound formation or complexing between the dopant and the solvent. However, simple theoretical models appear to be appropriate for estimates of the dopant distribution. As an example, André *et al.* (1972) were able to account for the aluminium distribution in  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  layers by the assumption of a regular solution in the gallium solvent and an ideal solid solution between GaAs and AlAs. Complications will arise if a dopant undergoes appreciable diffusion in the solid at the growth temperature, as in the case of Zn in GaP (Peaker *et al.*, 1972). It should also be noted that Jordan *et al.* (1973) reported that Te doping in GaP was found to be

lower than expected from the equilibrium value, and an interface limitation was postulated to explain results for oxygen doping.

Growth-rate measurements on magnetic garnet films by LPE have been reported by Giess *et al.* (1972), Blank and Nielsen (1972), Blank *et al.* (1973) and Knight *et al.* (1974). In each case growth occurred by dipping into supercooled melts and the growth rate was determined as a function of the rotation rate, or of time in unstirred melts. The measured growth rates depend strongly on the substrate rotation rate  $\omega$ , and the data of Giess *et al.* (1972), Blank *et al.* (1973) and Knight *et al.* (1974) indicate a linear dependence of the growth rate  $v$  on  $\omega^{1/2}$ , provided that a correction is made for the growth prior to the establishment of steady state conditions. The influence of the interface kinetic mechanism is not appreciable except at rotation rates above 160 r.p.m. where the rate of solute flow by diffusion becomes relatively rapid. Using the Burton, Prim and Slichter (1953) approximation for the boundary layer thickness, the data of Blank *et al.* give a solute diffusion coefficient between  $9 \times 10^{-7}$  and  $6 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for different temperatures and supercooling. A plot of  $v\omega^{-1/2}$  versus  $v^{1/m}$  (Eqn 4.21) gave a more nearly linear variation for  $m=2$  than for  $m=1$  but the range of values of  $v$  and  $\omega$  is insufficient for this result to be interpreted with confidence, and additional uncertainty is introduced by the effect of the initial transient. The data for zero rotation rate (Fig. 2 of Blank *et al.*) indicate a value of  $D=7 \times 10^{-6}$  to  $3 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> if the Carlson (1959) expression is used for the boundary layer thickness, with the solution flow velocity estimated at 0.1–1 cm s<sup>-1</sup>.

Ghez and Giess (1973) extended the data of Giess *et al.* (1972) and performed a detailed analysis of results in the transient regime and in the steady state. Their data also indicate that the growth rate is primarily limited by solute diffusion although evidence is presented for a kinetic limitation of the growth rate. A correction to the observed data is required because of the effect of a non-uniform lead impurity on the refractive index, so that a film of thickness 0.62  $\mu\text{m}$  (as determined by SEM) had an apparent thickness of 0.74  $\mu\text{m}$  by optical measurement. The authors subtracted a value of 0.12  $\mu\text{m}$  from all measured thicknesses, but this procedure is not valid for very thin films, and a more accurate interpretation is likely if the data points are multiplied by the ratio 0.62/0.74. With this amendment a plot of  $v\omega^{-1/2}$  versus  $v^{1/m}$  from Fig. 1 of Ghez and Giess (1973) gives a linear variation for  $m=1$ , but also gives an approximately linear relation for  $m=2$ . The analysis of Ghez and Giess assumes a first order reaction, but more data are required before the order of the kinetic process can be determined with confidence. Additional evidence for a partial kinetic limitation of the growth rate is obtained from a plot for growth at zero substrate rotation of the thickness  $h$  versus  $t^{1/2}$ , which has a small negative

intercept on the  $t=0$  axis. With the correction mentioned above, the intercept has a value of about  $0.06 \mu\text{m}$ . This value is probably significant in view of the care taken in these experiments to achieve a reproducible process with accurate determination of the time for which the substrate is immersed.

With the modified correction for the refractive index, and assuming a first order kinetic process with  $v = C(n_i - n_e)$ , Ghez and Giess' data for rotating substrate gives  $D = 6 \times 10^{-6} \text{ cm s}^{-1}$  and  $C = 3 \times 10^{-2} \text{ cm}^4 \text{ g}^{-1} \text{ s}^{-1}$ . (The supersaturation is taken to be  $0.032 \text{ g cm}^{-3}$ , in agreement with the phase diagram of Blank and Nielsen, 1972.) The unstirred melt data give  $D = 3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $K = 1 \times 10^{-3} \text{ cm s}^{-1}$ . The mean value of  $C$  corresponds to a growth rate of  $20,000 \text{ \AA s}^{-1}$  for a 1% supersaturation at the interface, which is very rapid compared with growth on a habit face.

Knight *et al.* (1974) introduce a term linear in time to the expression for the film thickness to correct for growth due to convection in the unstirred case and find a value of  $(5 \pm 1) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  for the diffusion coefficient at about  $850^\circ\text{C}$ . This value for  $D$  is in good agreement with that obtained for growth on a rotating substrate, where the correction due to growth prior to establishment of the boundary layer is relatively minor.

The data quoted are in substantial agreement in that they demonstrate the dominant effect of solute diffusion. The discrepancies in the calculated values of the diffusion coefficient probably reflect the inevitable problem of correcting for the initial transient, in addition to differences in interpretation. The values found for the diffusion coefficient are rather low in relation to values for alkali halides but this is not unexpected for the diffusion of complex ions. Knight *et al.* (1973) estimate the radius of the diffusing species to be about  $2.8 \text{ \AA}$ .

It is clear from the above data that the interface kinetic process is extremely rapid and nucleation may be expected to occur uniformly over the whole area of substrate. LPE deposition of garnet films differs from the growth of bulk garnets in that the growth normally occurs in the fast  $\langle 111 \rangle$  directions rather than on the  $\{110\}$  or  $\{211\}$  habit faces. As in LPE growth of semiconductors, it appears that screw dislocations are not necessary for growth on  $\{111\}$  substrates. The energy required for the generation of dislocations is, in fact, very high in the garnets and substrates are often dislocation-free (Brandle *et al.*, 1972). Defects in the substrates which give rise to etch pits are normally inclusions, for example of iridium from the crucibles used for Czochralski growth, but Plaskett (1972) claims that such defective regions do not give rise to preferential local growth.

The use of time markers in growth rate studies has been applied to LPE growth by Kumagawa *et al.* (1973) and this technique is likely to lead to improved understanding of the growth process.

The incorporation of impurities such as Pb and the composition of solid solution garnet films are governed by the same principles which are described for the growth of bulk crystals in Section 7.1.3. An additional factor which may affect the composition as well as the growth rate is the lattice parameter mismatch between film and substrate and different considerations will apply in many cases according to whether the film is in tension or in compression. (See, for example, Plaskett *et al.*, 1972.) Giess *et al.* (1972) noted a tendency for the effective distribution coefficient of gallium to change with time at constant growth rate and constant temperature, and this may be due to the transition from hetero-epitaxial growth in the initial stage to homoepitaxial growth as the thickness of the deposited film increases. A rapid variation in lead concentration across the films has been confirmed by Robertson *et al.* (1974). A gradation in lattice parameter or other properties across the film-substrate boundary is to be expected on some scale, even if this is difficult to detect, for all epilayers and this variation must be considered in interpreting results on epitaxial film growth.

### 8.6. Important Factors and Future Trends

In this section an attempt is made to specify those aspects which are of greatest importance in the preparation of high quality, uniform, homogeneous epilayers with a high degree of reproducibility. As with all statements on crystal growth processes, generalizations are dangerous. Also there may be overriding economic factors which influence a decision in favour of some particular technique or procedure.

A factor which is stressed throughout the literature of LPE is the importance of cleanliness in the preparation of the substrate and holder. As an example of the necessary precautions, Giess *et al.* (1972) clean the substrate and holder, after mounting, in Alconox† alkaline solution for 15 min. at 80°C. The holder is then rinsed in deionized water, boiled in deionized water for 15 min. and finally rinsed with a jet of ethanol. According to Blank and Nielsen (1972), defects arising through handling of the substrate are amongst the most troublesome in garnet film preparation, and transfer of the wafer from the polishing stage to the furnace should occur under clean conditions which may be obtained by the use of laminar air flow cabinets.

Contamination from the crucible must be avoided in semiconductor preparation where low impurity concentrations are vital for device performance. This problem has been considered particularly by Wolfe and Stillman (1971), who refer to studies using both graphite and silica crucibles for the growth of GaAs. Silicon contamination in the latter case was studied in detail by Hicks and Greene (1971).

† Proprietary name, Alconox Inc., New York.

Similarly, cleanliness in the growth atmosphere is essential. The observation by Vilms and Garrett (1972) of contamination of semiconductor films resulting from air leaks has already been mentioned in Section 8.4.1. Dean *et al.* (1968) found that silicon contamination of GaP from Ga solution could be reduced by adding water to the hydrogen gas stream.

Substrate preparation is also of fundamental importance. In the case of semiconductors, many surface treatments have been used but a standard procedure has been adopted by most workers which comprises lapping, mechanical polishing and chemical polishing with a solution of 1% bromine in methanol. However, Vilms and Garrett followed this procedure by successively immersing the substrate in concentrated HCl, rinsing in water, drying in nitrogen, immersing in concentrated H<sub>2</sub>SO<sub>4</sub> followed by H<sub>2</sub>SO<sub>4</sub> with H<sub>2</sub>O<sub>2</sub>, and finally rinsing in hot water and drying.

GaAs and GaP substrates differ from the garnet substrates used for bubble films in that they often contain a high density of dislocations, introduced either during growth or during the subsequent cutting and polishing. The surface damage may be removed by the chemical polish but the residual dislocations will affect the layer growth and probably the device performance. Ladany *et al.* (1969) noted a reduction in the dislocation density from  $5 \times 10^5 \text{ cm}^{-2}$  in the substrate to  $5 \times 10^4 \text{ cm}^{-2}$  in the epilayer, and found a dependence of the efficiency of light emission on the dislocation density. Saul (1971) demonstrated a reduction in the dislocation density by etching back the wafer during growth (in addition to an initial etch-back of the substrate) since the crystal-solution interface provides a source of point defects which are required for dislocation mobility. It is not clear, however, how far this reduction in dislocation density may be taken by repeated growth and dissolution cycling. Queisser (1972) has proposed that it is the movement of layers along the surface in the earliest stages of growth which leads to the annihilation or termination of dislocations.

Generally etch-back of the substrate is to be avoided in heteroepitaxial growth since it will lead to a graded film composition. It would appear very desirable in LPE growth of the III-V semiconductors to improve the growth and handling of substrate crystals so that dislocation-free wafers could be produced for routine device fabrication, and the etch-back stage eliminated. According to Rozgonyi and Iizuka (1973), it is decorated dislocations which are important in affecting luminescent properties and these occur only when another type of defect (called a saucer or S-pit) is present.

In the growth of magnetic garnet films it is clearly established that substrate dissolution is undesirable, which is one reason for the choice of

supercooled melts with growth at relatively high supersaturation. Substrate preparation normally consists of mechanical polishing using diamond grit, followed by Syton† polishing. Robertson *et al.* (1973a) have suggested an alternative procedure which involves the deposition on the sawn slice of a homoepitaxial layer following an initial etch-back of the slice in the high temperature solution. A saw blade of good quality with internal cutting edge is required for slicing the wafer but this procedure is otherwise very rapid and convenient compared with lapping and polishing since the substrate can be easily transferred between adjacent furnaces for deposition of the magnetic garnet layer. These advantages may, however, be offset by a reduction in film uniformity (Nielsen and Blank, private communication). Glass (1972) has shown that LPE films greatly enhance surface scratches in the substrate.

Attack of the substrate by the flux vapour is possible if it is held for several minutes above the solution, particularly if the solvent has a relatively high volatility, and this etching results in a deterioration in film uniformity. Giess *et al.* (1972) found it necessary to pre-heat the substrate in a shielded enclosure prior to immersion in the solution, rather than in the furnace immediately above the solution, otherwise some etching by the vapour was observed.

One question which is not normally discussed in the literature is the accuracy of substrate orientation. The sensitivity of the growth rate and surface topography to orientation has not been established and slight misorientations in cutting and polishing may account for some of the scatter in experiments aimed at assessment of the reproducibility of a technique.

Reproducibility, film uniformity and homogeneity are extremely important criteria, particularly as regards device production, and these parameters will have a very strong influence on the technique which is preferred for large-scale production. Of the results reported in Section 8.4, dipping has given good results for garnet films, particularly if rotation is used, and the sliders have given good results in terms of reproducibility and thickness uniformity for semiconductor epilayers. An important reservation which must be expressed about slider techniques is that homogeneity is unlikely to be achieved across any film grown by slow cooling. If homogeneity is of importance to the device performance a steady-state method is desirable, and growth on a rotating substrate by temperature gradient transport (see Section 7.1.2) is recommended.

Since nucleation occurs uniformly across the surface of a film, it is particularly important to ensure homogeneity both of temperature and of solute distribution over the surface, otherwise more rapid growth is likely

† Proprietary name, Monsanto Inc.

to occur at the film edges (as discussed in Chapter 6). Stirring the solution will lead to more uniform layers, so long as turbulence with non-uniform flow patterns is avoided. If a single substrate is used, a horizontal position is more favourable but has the disadvantage that solution droplets tend to adhere to the surface after removal from the liquid. These may be removed by rapid rotation of the wafer following withdrawal, but draining of excess solution will occur more readily in the substrate holders shown in Fig. 8.9.

Assuming that a uniform layer of solution is achieved during growth, the major problem remaining is that of avoiding a supersaturation gradient. The possible techniques are to use a very thin layer of solvent or to apply a stabilizing temperature gradient. Longo *et al.* (1972) have reported major improvements in film quality on mounting the substrate in contact with a heat sink through which cooling is achieved by a flow of air.

*Future trends.* The requirement of reproducibility and close control over the properties of the epilayers will require increasingly precise control over substrate preparation, growth temperature and duration and indeed of all parameters which affect the film growth. The very large potential market for such devices as low current LED display arrays will ensure continuing interest and development in this field. Additional semiconductor devices such as solar cells (Hovel and Woodall, 1973) will be produced by LPE.

Practical production of any device will require techniques for the preparation of multiple films and for the deposition on large area substrates. Experimental techniques must be concentrated on the development of batch processes for the simultaneous production of many films, once conditions for growth of a single film have been established. Large-scale production will require the development of apparatus for automatic production of devices, preferably by a continuous flow process, and design proposals for such a system have been described by Bergh *et al.* (1973).

Further development is necessary of techniques for the reproducible preparation of very thin layers, of thickness in the region of 100 Å, for devices such as heterojunction lasers. In addition to the devices mentioned above, the growth of high quality films by LPE is certain to lead to the development of completely new devices, and investigations are taking place at present of optical devices and of novel magnetic applications of epitaxial films. For example, thermomagnetic recording has been discussed by Krumme *et al.* (1972), and a review of Bi-substituted garnet films for modulation and storage of information has been given by Robertson *et al.* (1973b). Integrated thin film optical systems have been discussed by Tien *et al.* (1972), and laser action in  $Y_3Al_5O_{12}$  films by van der Ziel *et al.* (1973).

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