

**MATERIALS PROCESSING
THEORY AND PRACTICES
Volume 7**

Series Editor F.F.Y. Wang

**III-V semiconductor
materials
and devices**

Volume Editor

R.J. Malik

north-holland

III-V SEMICONDUCTOR MATERIALS AND DEVICES

MATERIALS PROCESSING – THEORY AND PRACTICES

VOLUME 7

Series editor

F.F.Y. WANG



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III–V SEMICONDUCTOR MATERIALS AND DEVICES

Edited by

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USA



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INTRODUCTION TO THE SERIES

Modern technological advances place demanding requirements for the designs and applications of materials. In many instances, the processing of materials becomes the critical step in the manufacturing processes. However, within the vast realm of technical literature, materials processing has not received its proper attention. It is primarily due to the lack of a proper communication forum. Since the materials processing is intimately concerned with specific products, those who are experts have no need to communicate. On the other hand, those who are involved with a different product will develop, in time, the technology of materials processing when required.

It is the objective of this series, *Materials Processing – Theory and Practices*, to promote the dissemination of technical information about the materials processing. It provides a broad prospective about the theory and practices concerning a particular process of material processing. A material process, intended for one technology, may have an applicability in another. This series provides a bridge between the materials engineering community and the processing engineering community. It is a proper forum of dialogues between the academic and the industrial communities.

Materials processing is a fast-moving field. Within the constraints of time and printed spaces, this series does not aim to be encyclopedic, and all-inclusive. Rather, it supplies an examination of material processes by the active workers. The view will be, by necessity, subjective. But the view will include both near-term and long-term prospectives. It is the fondest hope of this general editor that the volumes in this series can serve as first reference books in the field of materials processing.

Franklin F.Y. WANG
Stony Brook, New York.

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PREFACE TO VOLUME 7

Since the discovery of microwave oscillations in bulk GaAs by Gunn in 1963 and the international race to make the first successful solid-state laser in the late 1960's, III-V semiconductor materials and devices have been the focus of ever-increasing research activity. Although the major promise of III-V technology has yet to be realized, its impact is starting to be seen today. From microwave and fiber optic lightwave communications systems to the commercially available digital audio compact disc players, III-V semiconductors are beginning to change our lives. If the old saying 'Gallium Arsenide is the material of the future ... and always will be' remains true, then surely part of the future is here today. The present state-of-the-art III-V materials technology enables semiconductor layers to be grown essentially atom by atom as if they were bricks in the construction of a building. The ability to form semiconductor multilayers with thicknesses of the order of atomic dimensions profoundly alters the electronic and optical properties of these materials from their constituents due to quantum size effects. This has allowed the study of the basic physical properties of these materials along with the ability to precisely tailor these properties by 'band-gap engineering' to form new types of devices.

It is the objective of this volume to provide a general reference guide for researchers in the field of III-V semiconductors. Although no work can be completely authoritative, I do believe that this volume outlines the basic principles and understandings of III-V materials and device technologies, together with an extensive listing of references which are scattered throughout the literature. Although this work was intended to be as up-to-date as possible at the time of its printing, unanticipated delays in the publication schedule may have led to some omission of very recent work in the literature. In this regard the editor assumes total responsibility.

To date the majority of research activity has concentrated on GaAs and the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy system due to their technological use in microwave, high-speed electronic, and opto-electronic devices and circuits. More

recently the use of InP and lattice-matched $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ alloys in lasers and photodetectors for use in long-wavelength fiber optic communications has received a good deal of attention. The antimony-based III–V semiconductors have received relatively little attention beyond fundamental studies and a few experimental devices. This bias in research activity is naturally reflected in their respective coverage in the chapters of this review volume.

This book is organized into the following chapters. Chapter 1 deals with bulk crystal growth of binary III–V semiconductors. From large bulk boules thin wafers are cut and polished which are used either as a template for epitaxial growth of device layers or for direct ion implantation. The quality of the starting III–V wafers has a significant effect on subsequent processing and final device performance. Chapters 2–5 are concerned with the major epitaxial growth techniques: liquid phase epitaxy, vapor phase epitaxy, metal organic chemical vapor deposition, and molecular beam epitaxy. The evolution of the various epi-growth techniques is discussed along with the principal chemical and physical models used to describe these processes. The relative merits and limitations of the epi-growth techniques as they apply to film purity, thickness control, uniformity, heterojunction and doping profile abruptness, device fabrication, and potential scale-up for production purposes are also discussed. Chapter 6 describes the technologically important technique of ion implantation in III–V semiconductors. Ion implantation has played a critical role in the success of the silicon integrated circuits technology and as such holds great promise in III–V device manufacture. The current understanding and use of ion implantation in III–V semiconductors and a critical comparison vis-à-vis silicon is offered. The electrical and optical characterization of III–V semiconductors is covered in chapter 7. The techniques described in this chapter are used in fundamental studies of the transport and optical properties of III–V semiconductors. They are also used for evaluating doping and alloy composition in III–V epilayers, for process monitoring in device manufacture, and for completed device testing and screening. Finally, chapter 8 provides a comprehensive review of the status of III–V device technology. The basic concepts and properties of III–V semiconductors which are used to design devices are described as well as current state-of-the-art device results. Some of the electronic and opto-electronic devices discussed in this chapter include p/n junction and Schottky barrier diodes, heterojunction field effect and bipolar transistors, Gunn and IMPATT diodes, heterojunction laser and light emitting diodes, photodetectors, and solar cells. The interplay between the materials growth, processing technology, and device design is also revealed.

I would like to thank all of the authors for their outstanding contributions to this volume. I would like to acknowledge some of my expert colleagues at AT & T Bell Laboratories who anonymously reviewed the manuscripts. I would also like to thank North-Holland Physics Publishing and general series editor Professor F.F.Y. Wang for their courteous support, encouragement, and patience throughout the course of this work. Finally, I would like to thank my wife, Linda, who has provided me with invaluable assistance and support to complete this book.

Roger J. MALIK
Murray Hill, NJ, USA

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CHAPTER 1

MELT-GROWTH OF III-V COMPOUNDS BY THE LIQUID ENCAPSULATION AND HORIZONTAL GROWTH TECHNIQUES

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1. Introduction

International interest in the semiconducting properties of the III–V compounds began around 1949 (Welker, 1952, 1953), the dawn of semiconductor science and technology. Transistor action had been discovered in germanium two years earlier as a result of the work of Bardeen and Brattain (1948) and Shockley (1949). It was soon realised from this work and related studies that crystal quality was vital to effective device operation. This created a requirement to prepare semiconductor crystals to standards of physical and chemical perfection never previously considered possible. A new concept of quality emerged, that of semiconductor quality. Crystals were required that were free from electrically active impurities generally to levels below ten parts per billion atomic (10 ppba). Equally stringent specifications were required of lattice perfection. Completely single crystals, substantially free from defects including dislocations, were required. The specification of semiconductor quality resulted in an ever increasing materials effort devoted to purification and crystal growth. At the forefront of this materials work was an intense activity associated with the science and technology of melt-growth. In less than a decade the melt-growth of germanium developed from an art to a science (Tanenbaum, 1959). In the case of the III–V compounds the timescale of that evolution was similar for compounds like InSb, but for the intrinsically more difficult compounds GaAs, GaP, and InP over three decades have elapsed and the melt-growth of these compounds continues to be an extremely active field of research.

In considering the science and technology of melt-growth our focus of interest will be on the principal binary semiconductors InSb, GaSb, InAs, GaAs, InP and GaP. Special reference, however, must first be made to the early work on Ge and Si. Indeed the framework of the melt-growth of the semiconductors was created by the pioneering work of Pfann (1966) on zone melting and by Teal and Little (Teal, 1958) on the vertical pulling of single crystals of Ge. Pioneering work on III–V compounds is reviewed in the book *Compound Semiconductors* by Willardson and Goering (1962).

Two horizontal growth processes resulted from the zone melting concept: zone refining which is used to produce exceptionally pure bulk Ge and zone

levelling which is used to produce high-quality uniformly doped single crystals. But although these processes were very successful the lack of an effective working theory for convection and hence solute transport and segregation at the solid-liquid (S/L) interface has restricted the scientific development of our knowledge of horizontal growth.

This is not the case in vertical pulling. Here the theory of Burton, Prim and Slichter (BPS) (1953b) has provided an analytical description of solute transport and segregation at the S/L interface of a pulled rotating crystal. The theory has enabled one to predict the effects of doping on crystals and crystal growth. An example is that of constitutional supercooling. This growth phenomenon can lead to gross non-uniformities in heavily doped crystals (Bardsley et al., 1962). Hurle (1961) has been able to predict conditions for the onset of the effect during growth using a theory based on BPS theory. The avoidance of constitutional supercooling is particularly important in the growth of III-V compounds since it can readily develop when the melt is non-stoichiometric (Hurle et al., 1961).

Germanium is a particularly convenient material for studying melt-growth phenomena generally on account of its relatively favourable materials properties. It melts at 937°C, has negligible vapour pressure at its melting point and is substantially inert to both vitreous silica and graphite, the standard crucible and boat container materials for the element. The situation is very different for Si and the III-V compounds. Silicon is highly reactive at its melting point (1417°C) and will even gradually dissolve vitreous silica, the standard crucible material. Also, frozen silicon sticks tenaciously to a silica crucible causing stress and cracking. As a consequence there has not been any significant technological development of the horizontal growth of Si. On the other hand, the vertical pulling of Si is well established. It has a very intensely researched science and technology (Zulehner and Huber, 1982).

Silicon materials growth is dominated by the need to satisfy the enormous market for integrated circuits. The pulling technique is currently the basic technology for the production of wafers for large-scale integrated circuitry. In a new development the oxygen content of Si has become a critical parameter in device fabrication. Oxygen precipitates can be used to getter transition metals, and, since it is possible to create an oxygen-free surface region on Si containing oxygen precipitates, it is possible to produce a surface region free from transition metals. This is an essential requirement (Kishino, 1982) for high-quality device fabrication. Five years ago one could not have predicted that a phenomenon like oxygen precipitation would be responsible for the choice of a particular growth technology for the fabrication of the material used in integrated circuits. The pulling technique can be used to

introduce controlled amounts of oxygen into Si, whereas the float zone technique generally removes oxygen.

The crystal growth and preparation problems presented by the III-V compounds range in difficulty from being easier than Ge to being more difficult than Si. These problems will be considered in the following sections. However, since the III-V compounds can be grown both by the horizontal and the vertical pulling techniques an important question of basic interest is what dictates the choice of melt-growth technology for application considerations. As one might suspect there is no simple answer. It is rarely possible to predict the course of technological development. This is because new critical specifications or phenomena concerned with the use of a semiconductor in a device application can emerge and change the course of the evolution of that material. In the commercial development of materials cost and/or unique device specifications are generally the deciding parameters. In the case of Ge, the manufacture of individual diodes and transistors was possible using material grown by either of the two melt-growth techniques and both were used initially. However, the economics of production—Ge can be reduced from its ore and grown as a single crystal, appropriately doped, using horizontal growth technology—ultimately dictated the development and more general use of that technique. It is interesting, however, that current interest in large diameter infrared windows has dictated a resurgence of interest in the vertical pulling system. This is partially due to the shape requirement for lenses, but mainly due to the better physical and chemical perfection that can be obtained by the pulling technique.

In the case of the III-V compounds there is a wide variety of materials and device applications which has resulted in the development of a range of different materials, growth and device fabrication technologies. For example, the emergence of epitaxial techniques—vapour phase epitaxy (VPE), liquid phase epitaxy (LPE), metalorganic vapour phase epitaxy (MOVPE) and molecular beam epitaxy (MBE)—has significantly increased the variety of choice in device fabrication. Nevertheless melt-growth remains a primary underlying technology since it can be used directly in the fabrication of devices, that is the bulk material forms part of the active device, or it can be used indirectly as a substrate on which epitaxial material is deposited in order to form the active device. A further stage is often the fabrication of the whole device in epitaxial material, often with the complete removal of the substrate by etching.

Owing to its relatively easier materials technology InSb reached an advanced stage of development before the advent of epitaxial technologies. Discrete devices can be made in either horizontally grown or vertically pulled

material. The range of devices include infrared detectors, Hall effect and related devices, magneto-resistance devices, p-n junction devices and transistors. The low melting point and consequently the relatively insignificant contamination that occurs from silica boats ensure the growth of a very high purity material by melt-growth (Murray et al., 1966). Thus the advantage of epitaxy would tend to lie in the need for specialised fabrication technologies rather than in the need for creating significantly better active device material.

Gallium arsenide (Hollan et al., 1980), however, has a high melting point (1237°C) and significant contamination with silicon (~ 1 ppma) and also with other elements can occur if it is grown in contact with vitreous silica. As a result the trend in device technology, especially for minority carrier devices, has been to grow epitaxial layers onto bulk material. But the choice of bulk material is also significant. Unlike Si and Ge, GaAs has an energy band structure that permits suitable p-n junctions to emit radiation in a stimulated form as in a laser or simply as a light emitting diode (LED). The life of such devices is extremely sensitive to dislocations. Further, at this period of evolution horizontal boat-grown GaAs generally has dislocation densities of 10^2 – 10^3 , significantly less than in pulled crystals. Hence devices such as lasers, photodetectors (discrete and array), photodiodes, photocathodes etc., tend to be fabricated using a base of boat-grown material. Solar cells, however, may be fabricated in MOVPE material grown on Liquid Encapsulated Czochralski (LEC) grown material (Akai et al., 1983). For integrated circuits using field effect devices (FET) the current trend is also to use LEC crystals. Here the size and circular shape of the material are critical in order to establish compatibility with standard Si fabrication equipment. Aspects of the materials technology for integrated circuits, a very important area of current development, will be discussed later.

What is apparent in this brief survey is that the choice of materials technology is not only complicated but, perhaps more significantly, evolves in an apparently random fashion stimulating and being stimulated by the new device concepts. The inevitable advances made in a very dynamic materials field create new, often unpredictable, applications which can lead to new areas of science and technology.

2. Melt-growth techniques

2.1. Technical constraints

The primary properties of the III–V compounds which determine their growth technology are their melting points, the vapour pressure of their

Table 1
Melting point vapour pressure data for the III-V compounds.

Compound	Melting point (°C)	Vapour pressure (atm)	Reference
InSb	525	4×10^{-8}	Muller and Jacob (1984)
InAs	943	0.33	Van der Boomgaard and Schol (1957)
InP	1062	27.5	Bachmann and Buehler (1974)
GaSb	712	1×10^{-6}	Muller and Jacob (1984)
GaAs	1238	0.976	Arthur (1967)
GaP	1465	32	Nygren et al. (1971)

group V constituents and the reactivity of their component elements. Aspects of the properties for the more developed compounds are shown in table 1. It is evident that one may classify the compounds broadly into those with significant dissociation pressures, that is the phosphides and arsenides, and those with insignificant dissociation pressures—the antimonides. The binary aluminium compounds have been omitted from table 1 since they are not now actively researched. However, some of the alloys containing aluminium are very important materials. Gallium aluminium arsenide, for example, is widely used in heterojunction formation and finds application in lasers, photocathodes, solar cells etc. The active regions are grown epitaxially. The problem with the binary aluminium compounds is that they oxidise in the atmosphere in a way that causes the break-up of the compound. The aluminium binaries still represent an intriguing and technically difficult melt-growth challenge. Practical prudence, however, may indicate that vapour growth is currently the more reliable way to prepare them.

Our main considerations then concern the antimonides, arsenides and phosphides of gallium and indium. The framework of our consideration will be exclusively the growth of single crystals but, where appropriate, reference will be made to other technologies.

2.2. The vapour pressure problem

The antimonides can be grown as single crystals using the same basic technologies that were developed for germanium. Thus both horizontal growth and vertical pulling techniques are suitable, although vitreous silica boats and resistance heating are more often used than the conventional graphite boat and induction heating that is generally used for germanium. In the case of the phosphides and arsenides the crystallisation concepts in both

technologies are still applicable but the vapour pressure problem posed by the group V element must be taken into account. Thus a GaAs melt in a crucible in a standard germanium puller will rapidly lose arsenic creating a non-stoichiometric melt and a messy arsenic-coated system. There are two types of technology which have evolved to overcome this problem, the so-called hot wall technology and Liquid Encapsulation technology.

In hot wall technology the walls of the containing vessel surrounding the charge of the III-V compound are kept sufficiently hot to prevent the condensation of arsenic or phosphorus on the vessel walls; this requires temperatures of $\sim 600^{\circ}\text{C}$ or $\sim 700^{\circ}\text{C}$ respectively for the two elements. Clearly this constraint is much easier to apply in the case of horizontal crystal growth involving the use of a sealed silica tube than in a case of a vertical pulling apparatus. The simplicity of the former approach is the reason why it was used and effectively developed in the initial period of the evolution of GaAs (Willardson and Goering, 1962). In the case of vertical pulling a variety of techniques have been developed in an attempt to overcome the pressure problem, albeit with varying degrees of success. They are syringe pulling and magnetic pulling which have been reviewed by Gremmelmaier (1962) and Fischer (1970), and pulling using a pressure balancing technique which has been discussed by Mullin et al. (1972). These techniques all tackle the crucial problem created by highly reactive vapours of arsenic or phosphorus. The pull rod, its bearings and the pull rod seal are all at risk even when exposed to arsenic or phosphorus at the minimum temperature necessary to avoid condensation. Conventional metals and seals are inadequate and are corroded by such an environment. In syringe pullers which may be used for GaAs and InAs, a ceramic pull rod is made a close fit to a long ceramic bearing. It is not a perfect seal but the loss of arsenic can be minimised. The magnetic puller is a tour de force in which the whole of the ceramic pulling and rotation assembly is maintained within the growth chamber. Translation and rotation are achieved by magnetic coupling to suitably sited and protected magnetic material attached to the pull rod. This is a very difficult, demanding and expensive technology. Neither syringe pullers nor magnetic pullers have achieved any significant following. Pressure balancing is a concept which was first used by the author (Mullin et al., 1972) as a potential solution to the problem. The essential feature of this technology is a long ceramic boron nitride (BN) bearing in which is cut a screwed channel like an extended nut. A reservoir at the top of the bearing is used to hold a liquid seal (B_2O_3) against the ceramic pull rod. The rotation of the pull rod acts as an Archimedes screw and prevents the B_2O_3 draining down the rod. The internal and external pressures are balanced against the B_2O_3 seal. This is so

designed that it allows only a minimum minute amount of vapour passage in order to maintain pressure equilibrium. The system works well but has not been fully exploited, probably because of the success of Liquid Encapsulation technology which has transformed the whole of III-V pulling technology for the arsenides and phosphides. Our principal considerations will therefore be directed at Liquid Encapsulation and horizontal crystal growth.

3. Liquid Encapsulation

The concept of Liquid Encapsulation is elegantly simple. It is illustrated in fig. 1 which shows a crystal C, being pulled using a seed S from a melt, say of

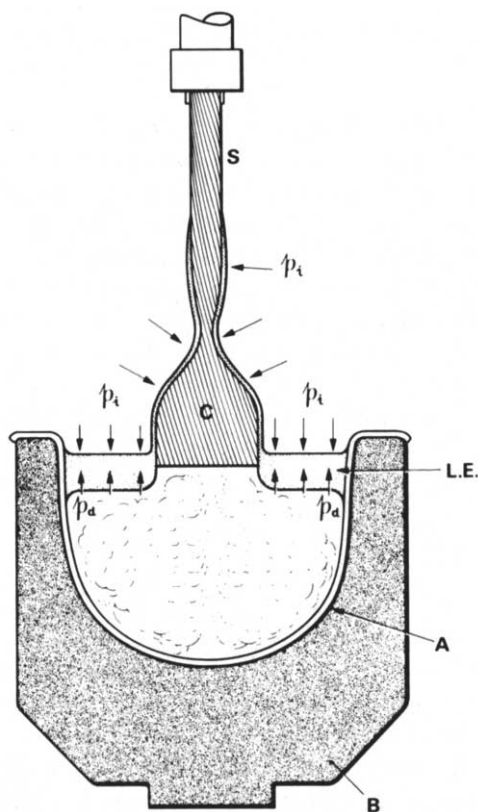


Fig. 1. Diagram illustrating the concept of Liquid Encapsulation: A, silica crucible; B, graphite susceptor; C, crystal growing on seed S; LE, Liquid Encapsulant (B_2O_3); p_i represents inert gas pressure; p_d represents dissociation pressure of the melt.

GaAs, using a conventional Ge-type crystal puller. A low melting point transparent liquid (encapsulant LE) floats to the surface of the melt. Provided the inert gas pressure p_i is greater than the dissociation pressure p_d exerted by the components of the melt, the encapsulant will act as a liquid seal and prevent vapour loss from the melt. The ideal encapsulant should possess additional properties. It should be immiscible with the melt and chemically unreactive towards it and the crucible A. But, most importantly, the encapsulant should wet the crystal and the crucible. Further, its viscosity and the temperature dependence of this viscosity should be such as to allow it to be drawn up and coat the emerging crystal with a thin film and be retained as such throughout the growth process. This latter requirement is to prevent the decomposition of the hot crystal. In spite of a detailed study of very many glass-like systems, only B_2O_3 and related mixtures fulfil sufficiently well these ideal characteristics. Many of the inorganic fluorides, chlorides etc. simply do not wet the crystal.

The application of the concept of Liquid Encapsulation to the growth of III-Vs was initially reported for the growth of InAs and GaAs by the author and his colleagues (Mullin et al., 1965). The use of B_2O_3 , however, is well known metallurgically and has a long history of use in protecting molten metals from oxidation and vapour loss. In the case of the group IV-VI semiconductors Metz et al. (1962) used B_2O_3 in the crystal growth of volatile compounds like PbTe and PbSe. However, the most significant advance in III-Vs came with the application of Liquid Encapsulation to the concept of high-pressure pulling in steel pressure vessels. Liquid Encapsulation high-pressure pulling was initially applied to the growth of InP and GaP (Mullin et al., 1968) and represented a breakthrough in the growth of these materials as high-quality uniformly doped single crystals. This work is discussed in section 3.2.

3.1. Low-pressure LEC technique

The application of Liquid Encapsulation to InAs and GaAs and similar materials that have dissociation pressures not greatly in excess of atmospheric pressure is often referred to as low-pressure technology. In such cases the growth apparatus such as that shown diagrammatically in fig. 2 can be used with a transparent silica tube (N) as a growth chamber for containing the controlled growth environment.

3.1.1. Application to GaAs and InAs

The LEC growth of these compounds as single crystals is similar to crystal pulling of germanium crystals. The B_2O_3 can cause visibility and control

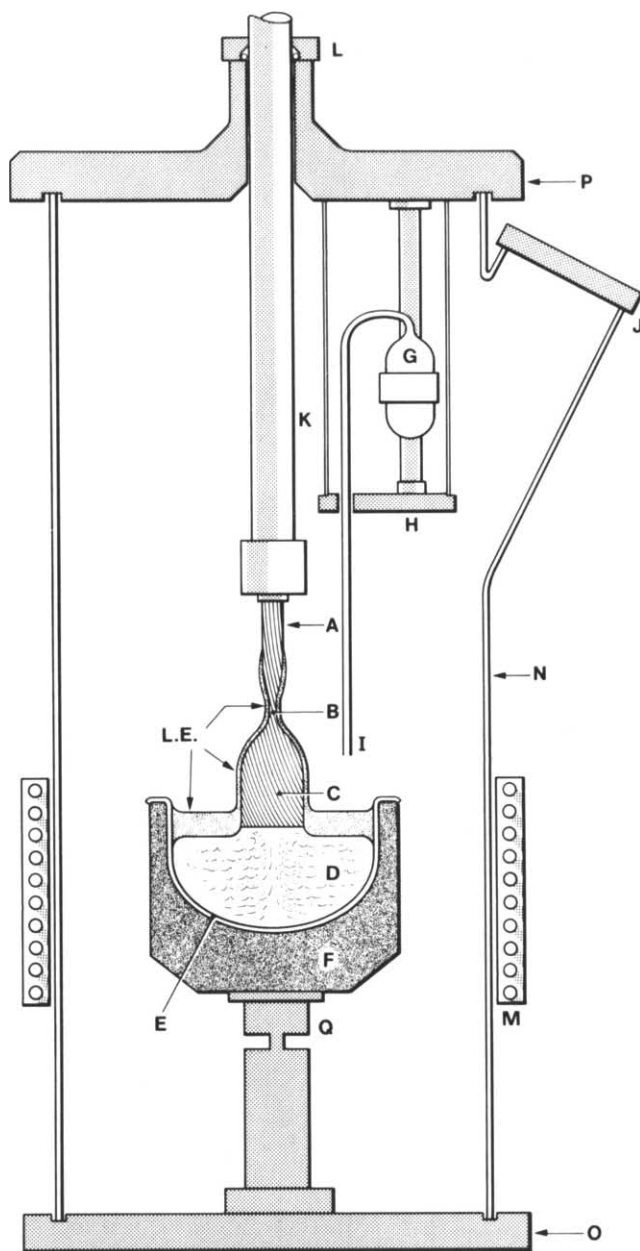


Fig. 2. Diagrammatic representation of the low-pressure LEC technique for compounding GaAs in-situ. See text for description.

problems but these can be eliminated with careful preparation and thermal design. The quality of the B_2O_3 —especially its water content—is very important. Conventional B_2O_3 needs to be dried and recommended drying procedures involve vacuum baking or bubbling dry N_2 (Chang and Wilcox, 1971) through the molten glass. The water content of the B_2O_3 controls the reaction and hence contamination between the melt and its containing crucible. This is discussed in section 6. It is also important to minimise As loss from the starting charge. The use of preshaped B_2O_3 designed to fit the crucible above the compound is useful in this connection. As the temperature is raised during melting the B_2O_3 seals in and flows over the charge preventing As loss. The starting charge in this situation, of course, entails the use of GaAs preformed in a separate, usually Bridgman-type, system. An alternative procedure is to compound the starting material in-situ from the elements in the crystal grower (Pekarek, 1970). A diagram illustrating the formation of GaAs in a low-pressure puller is shown in fig. 2. The essential requirement is a small reservoir G that holds the initial charge of As. A tube I leads from the reservoir and dips through the encapsulant LE into the heated pool of Ga. The diptube and reservoir are raised in temperature in a carefully controlled manner so as to distill all the As into the Ga. Great care is needed since the reaction is exothermic. With skill, suck back of Ga into the As reservoir can be avoided. The system needs to be pressurised to a few atmospheres to avoid loss of As from the melt. The diptube is withdrawn when a stoichiometric melt is formed and the crystal can then be grown in a standard LEC fashion. One of the merits of in-situ low-pressure formation of GaAs is the elimination of a separate compounding apparatus. This can minimise Si contamination, which can be a feature of the formation of GaAs in horizontal growth systems (see section 3.2.1).

3.1.2. *Application to InSb and GaSb*

These compounds do not require the use of liquid encapsulation technology since their dissociation pressures are sufficiently low at their melting points. Both can be pulled in germanium-type pullers. However, twinning and facet formation can be problems and the growth of InSb as a completely single crystal in directions other than the $[111]$ Sb type direction is not easy. Facet formation is also very troublesome in creating extreme non-uniformity problems (see section 5.5.2).

3.2. *High-pressure LEC technique*

3.2.1. *Concept*

The pressure limit in the low-pressure technology just discussed is set by the

strength of the silica containing chamber and is generally 2 or 3 atmospheres. However, Liquid Encapsulation has been combined with the concept of high-pressure pulling using a steel pressure chamber in order to give a unique technology for the growth of highly dissociable compounds InP (Mullin et al., 1968) and GaP (Mullin et al., 1968; Bass and Oliver, 1968). As we shall see later, it has also been applied to the growth of GaAs and has potential for the growth of other highly dissociable compounds. In Liquid Encapsulation, dissociation and vapour loss from the melt can be avoided if the inert gas pressure p_i is greater than the dissociation pressure p_d (fig. 1). The essential requirement then is a pressure chamber that will withstand the pressure p_i . The value of p_i must be ~ 30 atm for InP and ~ 40 atm for GaP. The equilibrium vapour pressure p_e over the stoichiometric melt at the melting point T_m of the compounds has been published and the values are 27.5 atm for InP (Bachmann and Buehler, 1974) and 32.3 atm for GaP (Nygren et al., 1971). The experimental values of the dissociation pressure p_d during growth generally differ from the equilibrium p_e values. This can arise from changes in the stoichiometry of the melt caused by differential solution of the melt components in the B_2O_3 encapsulant. Another source of variation in the value of p_d occurs during the melting and seeding process when temperatures significantly in excess of T_m can occur. Values of p_i which are 1–15 atm in excess of p_e are generally used. Too high an excess pressure can cause deleterious gas convection.

The technical success of the LEC high-pressure technology lies in the confinement of the chemically-active elements to the region of the crucible within the liquid encapsulant and away from the chamber wall, the pull rod assembly, bearings, seals etc. Indeed, the pressure chamber pull rod seals etc. need only be compatible with the inert gas pressure and are required to conform only to standards of high-pressure engineering. The relative simplicity of the technology thus makes the growth of InP and GaP comparable with that of the growth of Ge or Si, although it must be emphasised that the B_2O_3 is a complicating factor in growth control. The overall effect of the technology has been to revolutionise the growth of these materials.

3.2.2. Application to InP, GaP and GaAs

High-pressure LEC technology was applied first to the growth of InP and GaP using starting materials compounded in a separate apparatus. The growth procedure is relatively straightforward and the whole process is normally monitored by closed circuit TV. It is essential, particularly in the case of GaP, to have very good quality B_2O_3 that is quite dry otherwise there is a tendency for the B_2O_3 to become opaque. This can make seeding-on difficult. Whilst electrical contacts between the melt and an electrically

insulated pull rod can be used to register seeding-on this is not essential once the characteristics of the system are known. Nevertheless the use of a weighing cell in the growth of these materials is a great asset. Examples of crystals grown by this technique are shown in fig. 3.

A significant technical development has been the application of the technique in a high-pressure system to the growth of GaAs. As noted earlier the formation of GaAs by the distillation of As into liquid Ga held at an elevated temperature in a silica boat can lead to significant silicon contamination in the crystal due to the reaction of Ga with SiO_2 (Hicks and Greene, 1971). A similar problem occurs during the growth of epitaxial GaAs using the $\text{AsCl}_3\text{:Ga:H}_2$ system. Here the HCl that forms reacts with the SiO_2 (Di



Fig. 3. Single crystals of (left) InP; (right) GaP grown by the LEC technique. Note, crystal appears red from transmitted light.

Lorenzo and Moore, 1971). The use of boron nitride (BN) liner tubes (Ashen et al., 1975) has been shown to eliminate the problem. A similar solution involving the use of pyrolytic boron nitride (PBN) crucibles has been demonstrated by Swiggard et al. (1977, 1979) for the in-situ compounding of GaAs. Arsenic, if unreacted, would have a pressure of 80 atm at the melting point of GaAs, 1238°C, hence reacting the elements together under an inert gas pressure of 100 atm is a perfectly feasible way of forming a stoichiometric melt. Since the starting elements are generally more than 7/9's pure with respect to significant impurities the avoidance of contact with vitreous silica results in a very high-purity compound which can be grown as a reliable semi-insulating ($10^8 \Omega \text{ cm}$) crystal. More importantly, however, wafers cut from these crystals are found to be thermally stable on cycling at temperatures (850°C) used in annealing ion-implanted material (Stolte, 1984). High-pressure LEC compounding of GaAs in BN from the elements is now a major route to the growth of semi-insulating GaAs used in the development of integrated circuits in GaAs (Coin et al., 1979; Thomas et al., 1981; Fairman et al., 1981; Duncan et al., 1983).

The in-situ compounding of InP and GaP by melting the bulk elements together is not readily achievable because of the very high pressures that are required in achieving complete reaction and avoiding phosphorus loss. However, it is possible to distill phosphorus into either indium (Farges, 1982a) or gallium melts using a technology similar to the low-pressure technology for the in-situ compounding of GaAs discussed previously. It may also be possible to distill phosphorus vertically up into a melt held in a crucible which has a base comprising a sintered frit. The technical details of this technology appear to be confidential, for commercial reasons.

The growth of crystals by the pulling technique, and the LEC technique in particular, demands considerable skill by the operator in manipulating the power, pull rate and rotation rate controls so as to grow out satisfactorily from the neck of the crystal and then maintain a constant diameter crystal. In the case of LEC crystals the combination of visibility and system time lags frequently conspired to produce a crystal with periodically varying diameter (see fig. 4). The development of automatic diameter control and, as a consequence, automatic crystal growth have been developed in the last decade and have been a major development in the field. A variety of techniques have been tried with varying degrees of success in order to control the growth of crystals and some of these are reviewed by Hurle (1977). A technique that has found considerable success at RSRE and worldwide has been the use of the so-called weighing technique. Either the crystal itself (together with the pull rod) or the melt (together with its crucible) are weighed continuously as a function of the amount of crystal pulled. The



Fig. 4. LEC-GaAs crystal. The variation in crystal diameter illustrates the problem with manual control.

change in weight can then be used as a monitor of crystal diameter. The basic science and control parameters behind the process are discussed in section 5.4. A diagrammatic example of a weighing cell is shown in fig. 5 and an engineered version as used in combination with a research high-pressure LEC system is shown in fig. 6. High-pressure LEC technology has now taken the growth of InP (Rumsby et al., 1980), GaP and GaAs to an advanced stage of commercial development. The growth of 2 inch and 3 inch diameter crystals is now commonplace. The growth of such crystals requires the development and use of very large high-pressure crystal growers like the one shown in fig. 7.

Two new aspects of vertical pulling which are currently attracting significant research are magnetic Czochralski—aimed at reducing or

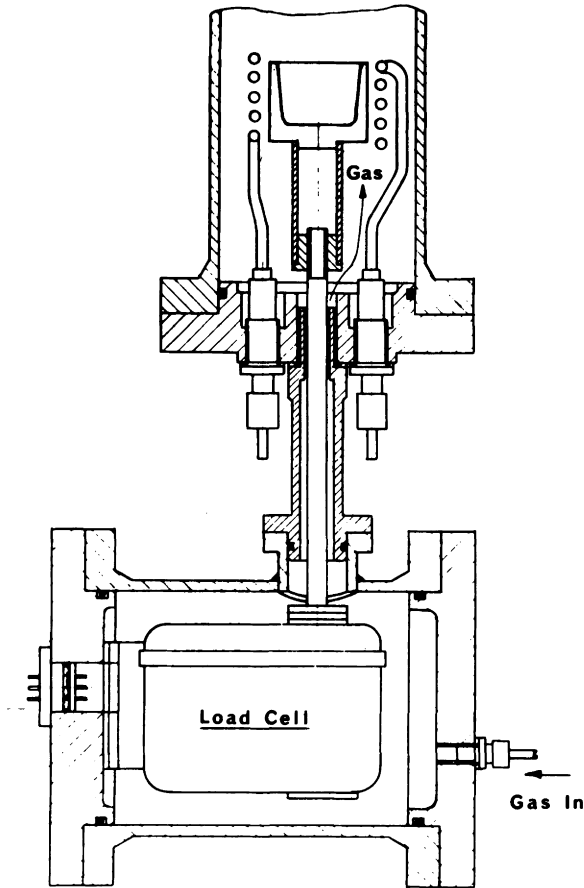


Fig. 5. Diagram of a load cell, part of an automatic diameter control system, used for sensing weight changes in the melt during crystal growth.

eliminating striae—and isoelectronic doping—aimed at reducing or eliminating dislocations. These are discussed in sections 5.5.1 and 6.3.3 respectively.

4. Horizontal growth

The term Horizontal Growth (HG) is used here to cover all crystallisation techniques as discussed by Pfann (1966) on Zone Melting, but carried out horizontally. Thus Horizontal Bridgman (HB) is a normal freeze (NF) process achieved by moving a boat of molten material out of a furnace

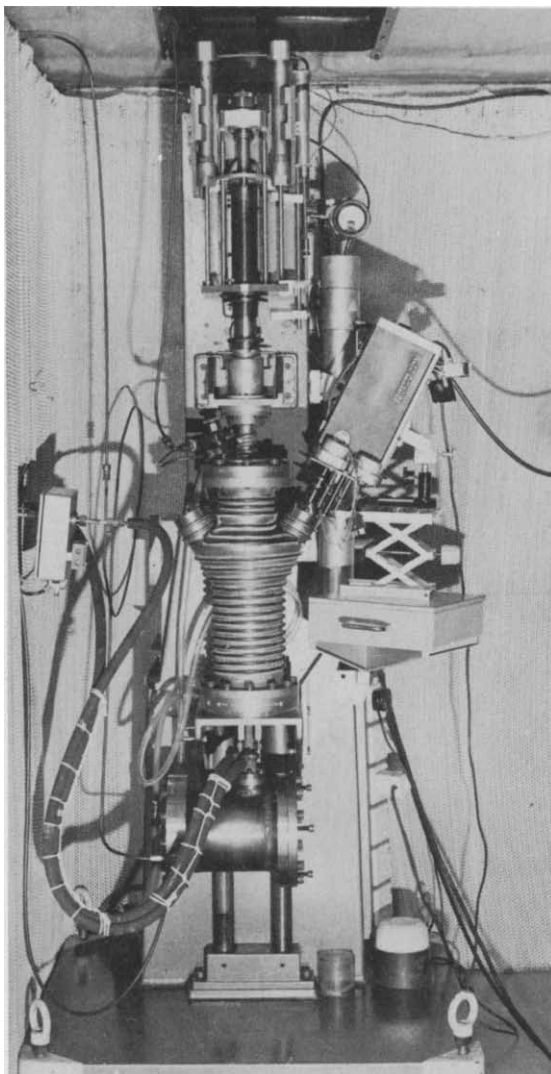


Fig. 6. RSRE-designed high-pressure crystal puller fitted with an automatic diameter control system involving a load cell as shown in fig. 5. The steel pressure chambers are designed for operation at up to 200 atm pressure. Two viewing ports can be seen. One is for remote viewing using a TV system.

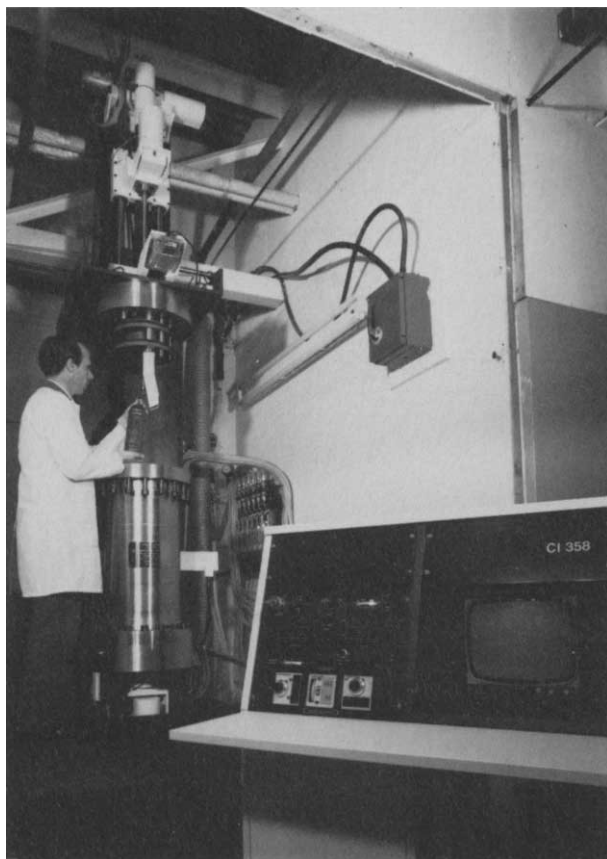


Fig. 7. A commercial high-pressure LEC pulling system. The system is designed for growing as standard 3 inch diameter GaAs, InP or GaP crystals. It can be used for in-situ synthesis of GaAs. Illustrated is a 3 inch diameter GaAs crystal that was grown from an 8 kg charge using the CI 358 system. (Courtesy of Cambridge Instruments Ltd., UK.)

whereas Gradient Freeze (GF) achieves the same crystallisation process with a stationary boat by suitable programming of the power to the heater or heaters. To avoid the confusion of names we will identify the normal freeze processes as carried out by moving (i) the boat by HNF-B, (ii) the thermal gradient by HNF-G, or (iii) the heater by HNF-H where appropriate. The Vertical Bridgman (VB) or Bridgman Stockbarger process involving vertical growth in a closed tube (VNF-B) has been used for the growth of III-Vs but the large expansion of these compounds on freezing (7–13%) (Muller and

Jacob, 1984) can create a serious strain problem during crystallisation in a confined volume.

The attraction of horizontal growth for the III-Vs stemmed initially from its relative simplicity and ease of automation, at least for the antimonides and arsenides. For the phosphides the concept is also simple but the technology is difficult because of the high operating temperatures and pressures. Horizontal growth apparatus is also used for preparing the compounds from their elements. This in-situ compounding was originally considered to confer on the HG technique an advantage over the pulling technique since it could be combined with a crystal growth process in the same apparatus. This advantage is now being eroded by the in-situ compounding LEC techniques just discussed. The main advantage of the HG technique which is currently both technically and commercially important for GaAs is the naturally occurring low temperature gradients in the growth environment. Low temperature gradients enable the growth of GaAs crystals with dislocation densities of the order of 10^2 to 10^3 cm^{-2} which are a factor of 100 less than are currently found in conventional crystals grown by routine LEC techniques. A development discussed in section 6.3.3 uses iso-electronic doping to harden the crystal lattice. This reduces the dislocation density and may yet erode this advantage of horizontal growth. However, this technology has yet to be proved.

Horizontal growth is the preferred method for the growth of GaAs crystals used in the fabrication of laser diodes. Low temperature gradients however can create problems. Thus with heavily doped crystals or with melts that are not close to stoichiometry it is often very difficult, if not impossible, to avoid the effects of constitutional supercooling and the consequent non-uniformity and often polycrystallinity that this confers on the resulting ingot (see section 5.5.3). A potential problem with the HG technique is the constraint imposed by the boat on the crystallisation process and the crystal. The stresses created by expansion on solidification and sticking combined with contraction on cooling can give rise to dislocation generation and polycrystallinity. However provided non-wetting surfaces are used for the containing boats and a non-confining boat shape is used, this problem can be minimised.

The main limitations then of the HG technique lie in the prolonged contact of the crystal with the boat material, in the difficulties associated with providing single crystal seeds and in the lack of controlled stirring which can affect doping and uniformity. These disadvantages are qualitative rather than absolute. They detract from the versatility and universality of the technique. In certain cases, such as in the growth of high or low resistivity GaAs, they may not be significant. This applies particularly to the growth of crystals

which are subsequently sliced and diced for the fabrication of small discrete-type devices like lasers etc. However, for integrated circuit applications where large area uniformity is becoming increasingly important as device sizes diminish, horizontal growth looks less attractive. Indeed, the D-shape of HG ingots alone appears to have ruled them out for integrated circuit applications, although it is possible to cut even large diameter (3") circular sections from horizontally grown ingots (Akai et al., 1983).

In summary, then, the application of the HG technique to InSb, GaSb, InAs, GaAs, InP and GaP increases in technical difficulty in the order as written. This difficulty correlates simply with the rise in melting points and dissociation pressures as one goes from InSb: melting point 525°C, dissociation pressure 10^{-8} atm to GaP: melting point 1465°C, dissociation pressure 32 atm. Indeed the technical difficulties in the application of the HG techniques to GaP are so great that this application is no longer actively researched.

4.1. Application to InSb and GaSb

The application of the HG technique to InSb and GaSb is relatively straightforward. Their vapour pressures are sufficiently low at their melting points that the loss of antimony is quite insignificant, unless of course the growth is attempted under vacuum conditions. Crystal growth can be carried out in a suitably-treated silica boat in the type of apparatus shown in fig. 8. Compound formation can simply be achieved by melting lumps of the mixed elements together en masse or by passing a zone through the mixture. There is no need for a separate boat C for the antimony. Growth of a single crystal is normally carried out by propagation from a single crystal seed using a single zone normal freeze (NF) process.

Indium antimonide has attracted considerable scientific study (Hulme and Mullin, 1962; Murray et al., 1966) not only on account of its role as an infrared detector material but also as a consequence of the interesting properties associated with its low energy gap (0.17 eV at 300 K). Gallium antimonide has an energy gap (0.67 eV at 300 K) which is very close to that of Ge (0.66 eV at 300 K). It has not attracted such detailed study as InSb although its growth phenomena appear to be similar. It is interesting that with the lower melting point compounds one finds more definitive and more easily characterised relationships between the conditions of crystal growth and the resulting crystal quality. Detailed studies on growth of InSb have revealed a wealth of factors affecting the twin formation, faceting, anisotropic segregation, uniformity, dislocation density, lineage and polycrys-

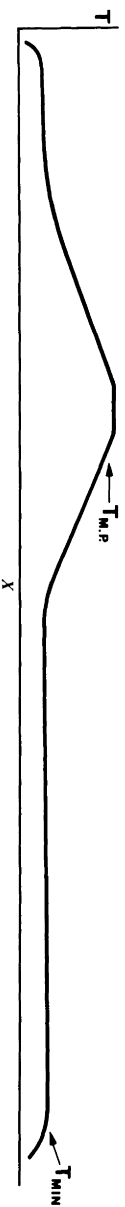
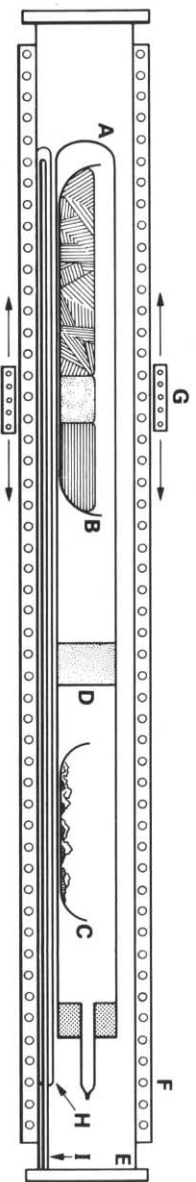


Fig. 8. Horizontal apparatus used variously for synthesis, zone refining, zone levelling and crystal growth of the III-Vs. A, sealed hot wall growth chamber; B, boat used for III-V synthesis or growing a crystal with or without a seed; C, reservoir container for group V element; D, porous plug—acts as vapour/thermal anticonvection baffle; E, outer jacket; F, heater for maintaining hot wall temperature; G, heater for zone formation; H, slider; I, thermocouple sheath.

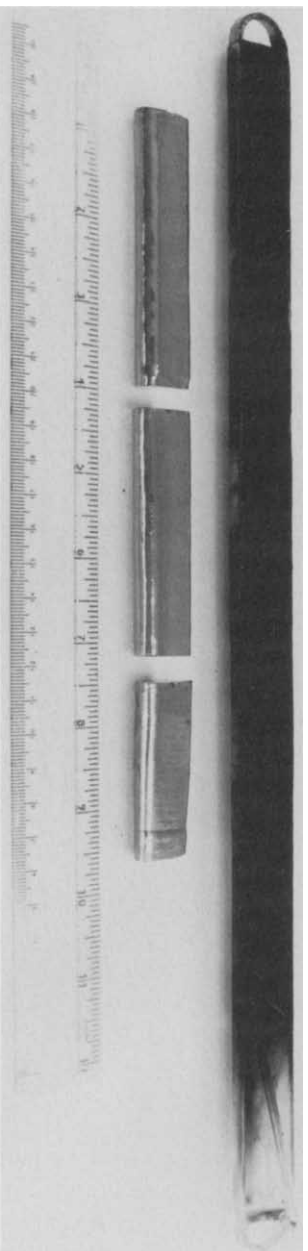


Fig. 9. Horizontal single crystal of InSb grown using a carbon-coated silica boat as illustrated.

tallinity. The phenomenological relationships between these phenomena and the growth conditions will be considered here and the basic science will be considered in section 5.

The most troublesome growth problem is the prevalence of twin formation. Two parameters appear to be important: firstly, the nature of the boat surface and, secondly, the orientation of the crystal growth surface relative to the growth direction. The former parameter appears simply to be associated with wetting. If the crystal wets the boat the probability of nucleation occurring on the walls of the crucible is considerably enhanced. The propagation of wall initiated nuclei gives rise to separate grains and twins. It is interesting that the inter-grain relationships in InSb (Hulme and Mullin, 1962) are normally twin relationships rather than mis-orientations associated with grain boundaries. Whilst low angle grain boundaries can occur in III-V compounds in, for example, large diameter GaAs and InP crystals they are generally uncommon. This contrasts with the situation in II-VI compounds where they are endemic in all melt-grown crystals. The optimum non-wetting conditions have been found from empirical studies. The best surfaces appear to be those resulting from grinding the inside surface of the silica boat with, for example, carborundum powder and then rubbing in either carbon, graphite or colloidal silica.

The frequency of twin formation undoubtedly correlates with the growth direction. The probability of growing a completely single crystal is greatest in the $[111]$ Sb direction and least in the $[\bar{1}\bar{1}\bar{1}]$ In direction. The probability of twin formation is intermediate for growth in between these two directions. The formation of the growth twins whose composition plane is of the $\{111\}$ type correlates with $\{111\}$ Sb or $\{\bar{1}\bar{1}\bar{1}\}$ In type facet development. This phenomenon is discussed later in the growth of vertically pulled crystals. The gaseous ambient also appears to be important. Hydrogen significantly improves the probability of the growth of single crystals and is to be preferred to the use of inert gases. It has been suggested that oxygen or water vapour could be implicated in the twin formation.

Whilst growth in the $[111]$ Sb direction is preferred on singularity grounds it is not on dopant uniformity considerations. As will be discussed later (section 5.5) the growth surface at the solid-liquid interface has a marked tendency to develop $\{111\}$ Sb or $\{\bar{1}\bar{1}\bar{1}\}$ In type facets on a flat singular surface where the isotherms become tangential to the low index planes. Impurity or dopant incorporation appears to be kinetically controlled on these flat surfaces compared with the non-faceted surfaces and an effect known as the Facet Effect (section 5.5.2) occurs which for most impurities gives rise to significantly enhanced dopant incorporation on these singular surfaces

compared with the non-singular surfaces. The changes of interface shape which can be quite marked in horizontal growth give rise to varying facet size and position on the growing surface of the crystal. The resultant effect is to distribute the dopant or residual impurities in a very non-uniform way throughout the grown crystal. The avoidance of facet formation is very difficult, it is a matter of growth orientation and carefully-controlled interface shape brought about by very good thermal engineering. Growth in, say, a $[221]$ or $[331]$ direction with a controlled interface shape can normally restrict facet formation to the edges of the growth surface but the probability of growing twinned crystals then increases with growth on the $\{111\}$ Sb type facets. The reasons for this have become apparent in the growth of pulled crystals of InSb and will be discussed later. Apart from non-uniformities associated with facet formation, dopant and residual impurity incorporation is also a function of crystal orientation irrespective of facet formation.

The control of dislocation formation in horizontally grown crystals appears to be even more complex than the control of twinning. Dislocations can be introduced into the grown crystal either by propagation of dislocations from a seed or by stress-induced deformation which generally takes the form of a slip process. The confinement of the crystal in a defined container shape can be a cause of stress and hence strain, even if the crystals do not stick to the surfaces of the container. However, shallow boats with well-rounded sides and non-wetting surfaces (see fig. 9) can minimise these problems. The growth of crystals in a non-uniform thermal environment can also be a prominent cause of dislocation formation. The cooling of the crystal causes non-uniform stresses and this can give rise to slip in the crystal. It is clearly very important to have planar growth surfaces not only from the point of uniformity of dopant distribution but also in order to minimise dislocation formation.

It has been noted that the gaseous environment is also important for controlling dislocation formation in the case of InSb. Hydrogen appears to have a beneficial effect compared with inert gases. This might be associated with the fact that hydrogen is a good thermal conductor and can reduce temperature gradients and hence stress in the material. But it would appear that its effect is more subtle. It has been noted that the introduction of hydrogen in growth systems can immediately prevent the propagation of dislocations from dislocated seeds. The mechanism of this process is not understood. Finally, there is strong evidence that the orientation of growth is important in dislocation propagation. The zinc blende lattice has a polar character, and growth in the $[hkl]$ direction might be expected to be different from growth in the reverse $[\bar{h}\bar{k}\bar{l}]$ direction. It has been found (Murray et al.,