12. Bulk Crystal Growth: Methods and Materials

Peter Capper

This chapter covers the field of bulk single crystals of materials used in electronics and optoelectronics. These crystals are used in both active and passive modes, that is, to produce devices directly in/on bulk-grown slices of material, or as substrates in epitaxial growth, respectively. Single-crystal material usually provides superior properties to polycrystalline or amorphous equivalents. The various bulk growth techniques are outlined, together with specific critical features, and examples are given of the types of materials, and their current typical sizes, grown by these techniques. Materials covered range from group IVs (Si, Ge, SiGe, diamond, SiC), group III–Vs (e.g., such as GaAs, InP, nitrides, etc.) group II–IVs (e.g., CdTe, ZnSe, HgCdTe (MCT), etc.) through to a wide range of oxide/halide/phosphate/borate/tungstate materials. This chapter is to be treated as a snapshot only; the interested reader is referred to the remainder of the chapters in this handbook for more specific growth and characterization details on the various materials outlined in this chapter. Neither does this chapter cover the more fundamental aspects of the growth of the particular materials covered; again the reader is referred to relevant chapters within the handbook, or to other sources of information in the general literature.

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12.1 Background

Despite the widespread progress in several epitaxial growth techniques for producing electronic and optoelectronic device-quality material, various bulk growth methods are still used to produce tens of thousands of tons of such materials each year. These crystals are used in both active and passive modes; i. e., to produce devices directly in/on bulk-grown slices of material, or used as substrates in epitaxial growth, respectively.

This chapter covers the field of bulk single crystals of materials used in electronics and optoelectronics. Single-crystal material usually provides superior properties to polycrystalline or amorphous equivalents. The various bulk growth techniques are outlined, together with the specific critical features, and examples are given of the types of materials, and their typical current sizes, grown by these techniques. Materials covered range from group IVs (Si, Ge, SiGe, diamond, SiC), group III–Vs (e.g., GaAs, InP, InSb, GaSb, nitrides, etc.) group II–IVs (e.g., CdTe, ZnSe, HgCdTe (MCT), ZnO, etc.) through to a wide range of oxide/halide/phosphate/borate/tungstate materials. This chapter is to be treated as a snapshot only; the interested reader is referred to the remainder of the chapters in this

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handbook for more specific growth and characterization details on the various materials outlined in this chapter. Many of the crystals grown at a small size mainly for R&D purposes, particularly in Universities, are not discussed, and neither, in general, are organic materials. Neither does this chapter cover the more fundamental aspects of the growth of the particular materials covered; again the reader is referred to the relevant chapters within this book, or to other sources of information in the general literature.

12.2 History

Several very useful studies on the history of crystal growth in general can be found in the literature [12.1–9]. There were many significant contributions made to the fundamentals of crystal growth during the 18th and 19th centuries, including the development of thermodynamics, undercooling, and supersaturation [12.6, 7]. In terms of crystal growth techniques, it is accepted that the first to produce usable crystals on a large scale was that of flame fusion by *Verneuil* [12.10].

Before World War II, synthetic crystals (other than ruby) were mainly used in scientific instruments. However, between 1900 and 1940 there were enormous advances in both the theoretical aspects and in producing samples for scientific study. The diffusion boundary layer was applied by *Nernst* [12.11], while ideas on the growth of perfect crystals were proposed by *Volmer* [12.12], *Kossel* [12.13], and *Stranski* [12.14]. Also during this period many of the growth techniques now used were also initially developed. The flame fusion of *Verneuil* [12.10] was followed by hydrothermal growth [12.15, 16], crystal pulling [12.17], *Kyropoulos* [12.18], *Bridgman* growth [12.19–22], and vertical gradient freeze (VGF) [12.23].

During World War II, synthetic crystals were used as piezoelectric transducers (in sonar) as resonant devices (in radar) and as infrared detectors. However, it was the invention of the transistor (announced in 1948) that heralded the modern era of crystal growth for practical purposes rather than for pure scientific interest. *Teal* and *Little* developed crystal pulling of Ge in 1950 [12.24] and *Dash* [12.25] improved this with the *necking* technique to produce dislocation-free material. A key aspect at this stage was that of impurity levels and means to measure them. The semiconductors that were used for such solid-state devices as transistors work because they have desired dopants incorporated selectively in them. Techniques were developed at this time to improve the purity of materials, for example, zone refining [12.26] and float-zone (FZ) refining [12.27, 28]. Theoretical aspects developed in this period include the role of screw dislocations in growth [12.29] and the generalized theory of *Burton* et al. [12.30]. Reducing melt inclusions in crystals was discussed by *Ivantsov* [12.31, 32] in terms of diffusional undercooling, and by *Tiller* et al. [12.33] in terms of constitutional supercooling. Similar work was carried out in solution growth by *Carlson* [12.34], who studied flow effects across crystal faces, and *Scheel* and *Elwell* [12.35], who derived the maximum stable growth rate and optimized supersaturation to produce inclusion-free crystals. Seg-

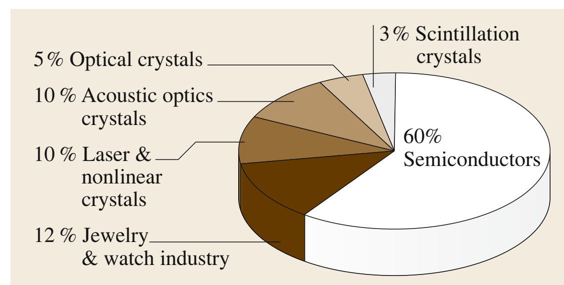

Fig. 12.1 Estimated share of the world production of 20 000 t of bulk crystals. (After [12.1], copyright Elsevier Science, used with permission)

Table 12.1 Estimated worldwide annual production rates of crystals (as at 1986, [12.5]). Some materials are mainly used for non-(electronic/optoelectronic) purposes, for example, cubic zirconia and much of the ruby are used in jewelry, watches, etc. (Items in *brackets* are small in volume but high in value)

Crystal	Rate (t/yr)	Growth methods
Silicon	4000	Czochralski, float-zone, (vapor phase epitaxy VPE)
Metals	4000	Bridgman, Strain anneal
Quartz	800	Hydrothermal
III–V compounds	600	Czochralski, Bridgman (VPE, liquid phase epitaxy LPE)
Alkali halides	500	Bridgman, Kyropoulos
Ruby	500	Verneuil
Germanium	400	Czochralski, Bridgman
Garnets	200	Czochralski
Lithium niobate	100	Czochralski
Phosphates	50	Low-temperature solution
Lithium tantalate	20	Czochralski
Cubic zirconia	15	Skull melting
TGS	10	Low-temperature solution
Diamond	10	High-temperature solution
II–VI compounds	5	Vapor, Bridgman

regation effects, which are related to mass and heat transfer, were studied by *Burton* et al. [12.36] for melt growth and by *van Erk* [12.37] for solution growth, while experimental conditions to produce striation-free material were established by *Rytz* and *Scheel* [12.38]. Forced convection in diffusion-limited growth was recognized as being beneficial for open systems with stirrers [12.39–42], while stirring in sealed containers was accomplished using the accelerated crucible rotation technique [12.43].

In 1986, *Brice* [12.5] estimated the annual production rates of crystals and Table 12.1 reproduces that data. Semiconductor materials clearly dominated at that stage, in particular silicon and III–V compounds. Later, *Scheel* [12.6] gave estimates of 5000 t in 1979, 11 000 t in 1986 (from [12.5]) and approximately 20 000 t in 1999 (Fig. 12.1), with a similar total quoted by *Scheel* in 2008 [12.8]. By 1999, the balance had shifted somewhat from the earlier estimates, but semiconductors continued to dominate, at $\approx 60\%$. There were roughly equal percentages of scintillator, optical, and acousto-optical crystals, at around 10–12%. The remainder was made up of laser and nonlinear optical crystals and crystals for jewelry and the watch industries.

A recent book edited by *Capper* [12.44] gives a comprehensive update on the bulk growth of many of the materials used in the electronic, optical and optoelectronic fields.

12.3 Techniques

12.3.1 Verneuil

This is the fastest growth method and was the first to be capable of controlling nucleation and thus producing large crystals of high melting point oxide crystals, for example, sapphire and ruby. Currently, a large number of high melting point materials have been grown by this technique, including ZrO_2 (2700 °C), SrO (2420 °C), Y_2O_3 (2420 °C), etc., but the largest use is still Al_2O_3 (often doped to produce ruby, sapphire, etc.). Figure 12.2 shows a schematic of the equipment used. Many different heat sources have been used, for example, solar furnace, glow discharge, plasma torch, arc image and radio frequency heating, but the original gas-flame technique is still the most popular. An oxy-hydrogen flame heats the seed crystal placed on a ceramic pedestal. Powder from a hopper is shaken through the flame and melts, forming a melt surface on the seed. During growth the seed is lowered, controlling the linear growth rate, while the volume growth rate is governed by the powder feed rate. The balance of these two rates controls the crystal diameter and the crystal is normally rotated slowly. Ruby crystals up to 200 mm diameter can be grown. Drawbacks of the technique include high dislocation densities and concentration variations.

12.3.2 Czochralski

Czochralski is a fast growth method and is widely used for both semiconductors and oxide/fluoride materials for optical applications. It also normally produces the most nearly perfect and homogeneous crystals. However, it is only really applicable to those materials that melt congruently or nearly congruently, that is, the solid and the melt compositions are the same at equilibrium. Normally a crucible material is needed that is compatible with the melt, however, the most common crucible material used for silicon, that is, silica, dissolves slowly in the melt and this raises certain process issues in the growth of this material. Capital costs for Czochralski pulling are higher than most other techniques, but it is used when the greatest perfection of grown material is required.

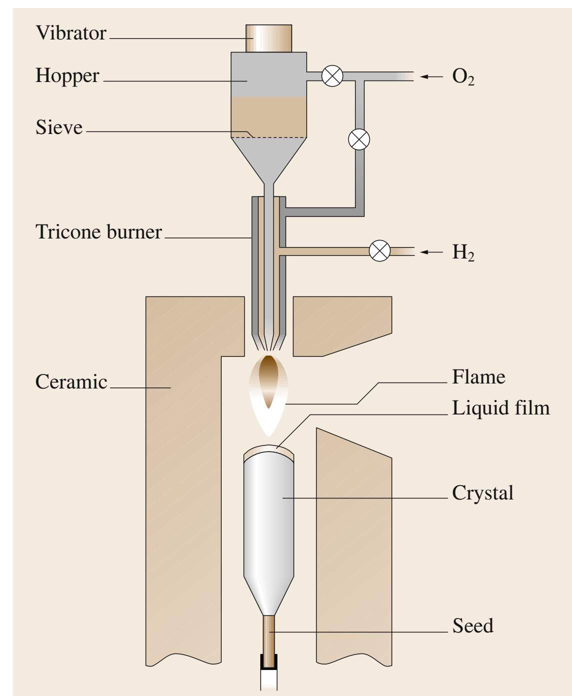

Fig. 12.2 Schematic of Verneuil growth equipment. (After [12.5])

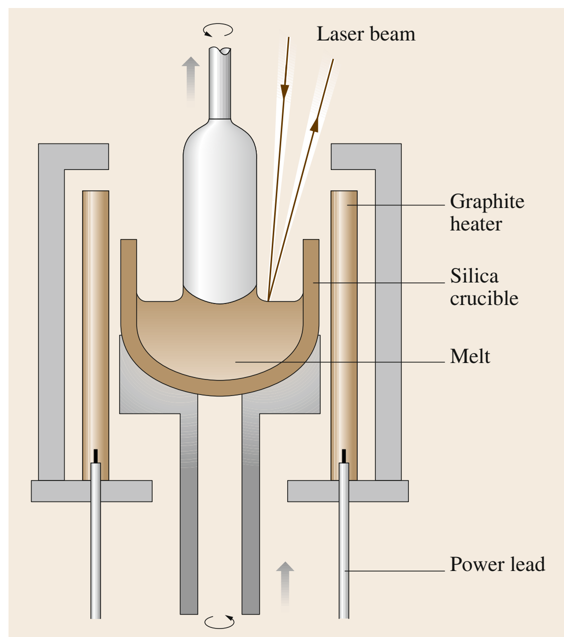

Fig. 12.3 Schematic of Czochralski growth equipment. (After [12.5])

The largest use is clearly for silicon, but probably ≈ 100 materials are commercially grown using this method, while many more are at the research stage. As the diameter of the crystal increases, in silicon for example from 200 to 300 mm, dislocation control becomes more difficult due to larger radial temperature gradients. Figure 12.3 shows a schematic of a Czochralski growth equipment. The basic method is relatively simple: The solid charge is placed in the crucible and heated to a temperature several degrees above the melting point. The seed crystal, rotating slowly, is lowered to contact the melt and the seed then slowly melts. After a short delay (a few minutes) pulling is commenced and new material (with slightly reduced diameter) begins to grow. A long narrow *neck* region is grown to reduce dislocations, then the melt temperature is reduced to increase the diameter. When the crystal attains full diameter growth is maintained until the desired length of crystal has grown, and growth is terminated by sharply increasing the pull rate or increasing the melt temperature so that the diameter reduces to zero.

A constant diameter is maintained by adjusting the power input to the melt. This is done automatically either by directly monitoring the diameter optically, that is, by observing the bright ring around the crystal periphery, or by indirectly measuring the diameter via weighing methods. Crucibles are normally round based for semiconductors but should be relatively flat for oxide/halide growth, that is, ionic materials.

Hurle [12.45] discusses the effects, in detail, of convection, flows in melts, heat transport, mass transport, solute segregation, use of magnetic fields, systems dynamics and automatic diameter control, morphological stability, and defect control. In general, as melt sizes have increased natural convective flows have increased, leading to turbulence, which causes growth rate fluctuations leading to dopant concentration variations (so-called striations).

For growth of III–V compounds, liquid encapsulated Czochralski (LEC) was pioneered by *Mullin* [12.46] for GaAs and GaP. Suppression of the volatility of As and P was crucial to the successful growth of these types of compounds. This technique involves the use of an inert layer of a transparent liquid, usually B_2O_3, which floats on the melt surface and acts as a liquid seal. Most importantly, the encapsulant should wet both the crucible and crystal so that a thin film adheres to the crystal as growth proceeds. The latter prevents dissociation of the hot crystal. Pyrolytic boron nitride (PBN) crucibles are now often used and either resistance or r.f. heating is employed. Semi-insulating GaAs is produced in a high-pressure puller (100–200 atm). The main advantage here is that elemental Ga and As can be used as the starting materials. Diameter is often control by crystal-weight measurements, rather than meniscus observation. Pull rates are typically < 1 cm/h. Axial or transverse magnetic fields can again be used to control melt turbulence and dopant segregation.

Precious metal (Pt, Ir) crucibles are used for oxide crystal growth as high temperatures are used. To prevent reduction of oxide melts, a partial pressure of oxygen is needed. Normally, the crucible is not rotated or translated and the growth rate is greater than the pulling rate as the melt height decreases. Growth rates are a few mm/h, at best, so growth times are normally > 1 week. Large temperature gradients can lead to melt turbulence, which in turn produces a banded structure of solute concentration and varying stoichiometry in the crystals. Control of convection in these systems is therefore of critical importance. *Rudolph* and *Kakimoto* [12.47] have outlined various means of controlling uniformity and stability of crystal growth from the melt by complementing internal parameters (e.g., temperature field, pressure, growth velocity, etc.) by external influences, for example, mechanical, electrical, and mechanical fields. Stirring during crystal growth can often be essential to enhance solute transport through the growth fluid, to homogenize the solute concentration in the fluid and solid, and to reduce the thickness of the solute diffusion boundary layer (in order to prevent constitutional supercooling and hence the morphological instability of the crystal). The question that obviously arises then is why are the properties of the crystal not

markedly affected by the periodic disturbances applied to growth fluids? The answer lies in a comparison of the time scales involved. Movement of solute species in melt growth is normally of the order of hundreds of cm/s. With growth rates in the region of 10^{-2} cm/s, and induced fluctuations in the region of cm/s solute movement dominates. In addition, if the characteristic ratio of D/δ^2 (with D the diffusion coefficient and δ the boundary layer thickness) is less than the frequency of any hydrodynamic changes and their related temperature oscillations then mass diffusivity cannot follow the thermal changes.

12.3.3 Kyropoulos

This simple technique is used where a large diameter is more important than length, for example, for windows, prisms, lenses and other optical components, and for scintillator materials. The set-up and method of growth are similar to those of Czochralski (Fig. 12.4) but after the seed is brought into contact with the melt it is not raised much during growth. As in Czochralski, a short necked region is still grown but then the seed removal is stopped and growth proceeds by reducing the input power to the melt. The resulting crystals normally have diameters of ≈ 80–90% of the crucible diameter. Although the control systems in these equipments are relatively simple, the temperature distribution over the crucible is critical. For alkali halides, the crystal density is greater than the melt density so the melt level decreases with growth and the desired temperature distribution is one of the increasing temperature as the base of the crucible is approached. Average linear growth rates are a few mm/h, corresponding to cooling rates of $< 1\,°\mathrm{C/h}$. The only other process parameter of concern is the seed rotation rate, which is normally low or zero.

While the method appears to be economically very attractive there are technical deficiencies. The isothermal surfaces are curved, resulting in high dislocation densities and the growth interface is composed of different crystal faces, with consequent inhomogeneities in impurities and vacancy concentrations. High levels of impurities result from the majority of the not well-stirred melt being consumed. Despite these drawbacks many tons of alkali halides for optical applications are grown each year by this technique.

12.3.4 Stepanov

In this technique, a crystal is pulled from a crucible containing a crystal-shaped aperture (Fig. 12.5). Crystals can be pulled vertically upward, downward, or even horizontally. Growth rates are below those of the normal Czochralski technique, but dislocation densities can be reasonably low.

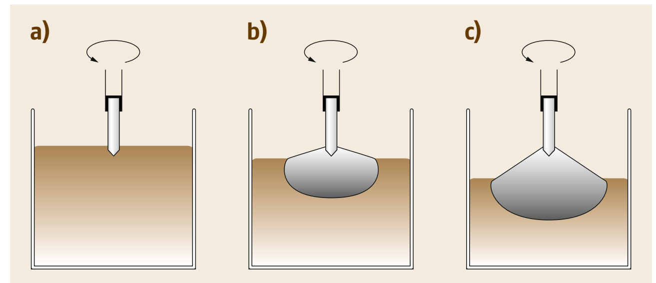

Fig. 12.4a–c Schematic of Kyropoulos growth equipment. **(a)** The seed crystal contacts the melt, a small amount melts, and then cooling is commenced to produce **(b)** and **(c)**. (After [12.5])

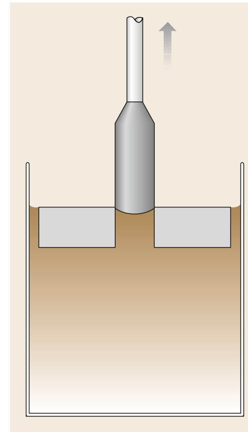

Fig. 12.5 Schematic of Stepanov growth equipment, in which a crystal is pulled through an aperture that defines its shape. (After [12.5])

12.3.5 Edge-Defined Film Growth

A die with a central capillary is placed on the surface of the melt (Fig. 12.6). Surface tension forces cause the melt to wet the die and be drawn up the capillary. A pointed seed crystal is lowered to contact this melt and then pulled upward. The melt is cooled slightly to increase the crystal diameter until it reaches the size of the die. Die can be designed to produce various shapes of crystals, for example, tubes, sheets, etc. Rapid growth is possible, but crystal quality normally suffers. One product is alumina tape (1 mm thick by several cm wide) used as a substrate for the production of high-frequency circuits. In this technique, however, purity can be limited.

12.3.6 Bridgman

In essence, this is a method of producing a crystal from a melt by progressively freezing it from one end to the other (Fig. 12.7). Crystals can be obtained with good

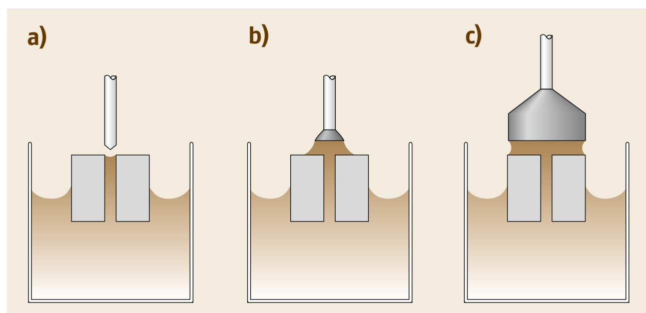

Fig. 12.6a–c Schematic of edge-defined film growth equipment. **(a)** The melt wets the die and is drawn up the capillary; **(b)** the seed is contacted to the melt and pulled up and cooling starts to increase the crystal size; **(c)** the crystal reaches the size of the die. (After [12.5])

dimensional control and the method uses relatively simple technology requiring little supervision. However, as the diameter increases, controlling heat flow becomes progressively more difficult. A wide range of materials have been produced by this technique, including sapphire at a melting point of $\approx 2370\,°\mathrm{C}$. One major requirement is that neither the melt nor its vapor must attack the crucible material significantly. Dislocation densities can also be limited to $> 10^4\,\mathrm{cm}^{-2}$, and many materials contain low-angle grain boundaries.

Growth rates can be in the range $0.1{-}30\,\mathrm{mm\,h^{-1}}$. Either the crucible or the furnace can be moved to achieve movement of the freezing isotherm, and both vertical and horizontal orientations are used. Crucible materials include silica (for covalently bonded crystals), graphite, and some metals (e.g., Mo for sapphire growth). Traditionally, crucibles have tapered tips to try to restrict nucleation to one crystal, although seed crystals can also be used. If spurious nucleation occurs it usually forms at the crucible walls, but this can be suppressed by making the growth face concave into the melt. Baffles are often used to separate upper and lower parts of the furnace to ensure thermal isolation. A low radial temperature gradient is needed to reduce dislocation densities. Calculating the temperature distribution is possible [12.48]. The most obvious requirements are a large temperature gradient at the growth interface and low-temperature gradients in the radial direction.

Impurity distributions in crystals are, in general, governed by the type of mixing in the melt. In stirred melts, so-called normal freezing, the relevant equation is

$$C_\mathrm{s} = k_\mathrm{eff} C_0 (1-x) k_\mathrm{eff} - 1\ ,$$

where C_s is the concentration in the solid, C_0 the initial concentration, k_eff is the effective distribution coefficient, and x is the fraction solidified. In unstirred melts,

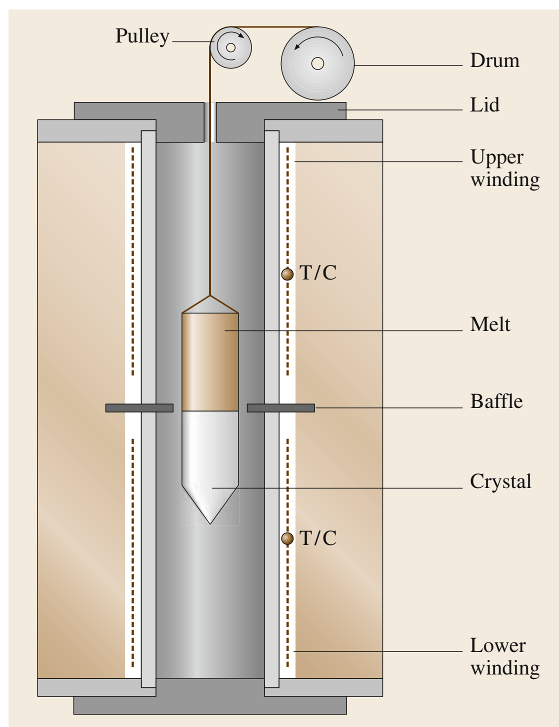

Fig. 12.7 Schematic of Bridgman growth equipment. (After [12.5])

the interface segregation coefficient k^* governs the segregation behavior

$$C_\mathrm{s} = k^* C_0 \left[1 - \frac{(1-k^*)}{k} \times \left(1 - \exp\left[-\frac{(1-k^*)k^* f_z}{D_\mathrm{L}}\right]\right)\right],$$

where f is the growth rate, z the axial distance, and D_L is the diffusion coefficient. For a molten zone of length L, the equation is

$$C_\mathrm{s} = C_0[1 + (k_\mathrm{eff} - 1)\exp(-k_\mathrm{eff}\,x)]\ .$$

For materials with a volatile component, there are several possible refinements of the basic process, for example, sealed ampoules, overpressure, and liquid encapsulation (e.g., using B_2O_3). Normally in sealed-ampoule growth there is a lack of control over stirring. For vertical systems, the accelerated crucible rotation technique (ACRT) can be used, and this author has developed this refinement for the growth of mercury cadmium telluride (MCT) up to 70 mm in diameter [12.49]. Faster stable growth rates are possible with ACRT [12.50], as are larger diameter crystals, improved uniformity and better crystallinity.

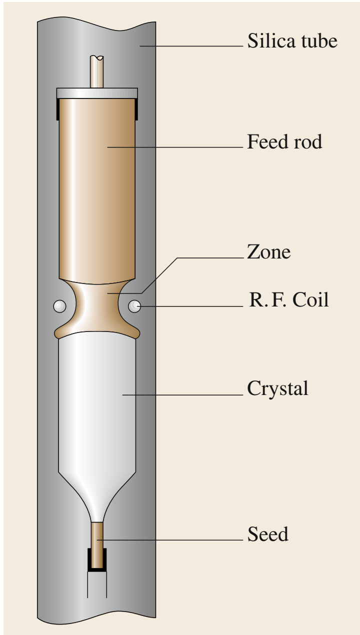

Fig. 12.8 Schematic of float-zone growth equipment. (After [12.5])

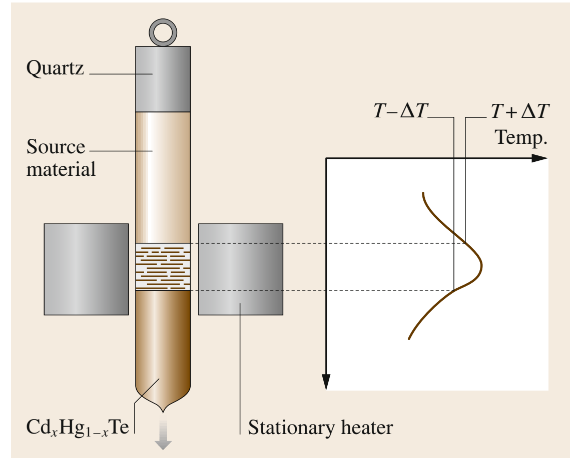

Fig. 12.9 Schematic of THM growth equipment. (After [12.5])

Zharikov [12.9, Chap. 3] discussed how axial vibrational control can be used to control the heat and mass transfer and growth kinetics during growth from liquids. Low-frequency, small-amplitude vibrations allow growth of high-quality crystals at high growth rates, and also provide control of stoichiometry and dopant distribution. This technique suppresses temperature oscillations at the interface and improves radial and axial distributions of impurities. It can also be used for non-electroconducting melts and liquids with high Prandtl numbers. Applications range from semiconductors to dielectrics produced from Bridgman, TSSG, Czochralski, and float-zone techniques.

12.3.7 Vertical Gradient Freeze

The vertical gradient freeze (VGF) technique involves the progressive freezing of the lower end of a melt upward. This freezing process can be controlled by moving the furnace past the melt or, preferable, by moving the temperature gradient in a furnace with several independently controlled zones. Low-temperature gradients are normally obtained, leading to reduced dislocation densities, and the crystal is of a defined shape and size. Difficulties include furnace design, the choice of boat material, and the issue of seeding.

The majority of melt-grown crystals are produced by the Bridgman and Czochralski techniques (and their variants). In general, if no suitable crucible can be found then other methods are required, for example, Verneuil.

12.3.8 Float Zone

In this technique, a molten zone is maintained between two solid rods (Fig. 12.8). By moving the zone relative to the rods, one of them grows, and a single crystal can be grown if a seed is used. Silicon is the only material grown on a large scale by this technique. The only other use for it is in the small-scale growth of very pure crystals, as no crucible contact is involved. For silicon, r.f. heating is used, with frequencies of 2–3 MHz for diameters > 70 mm. There is a steep temperature gradient that induces flows in the molten zone, and if both the seed and feed rods are rotated then the shape of the solid/liquid interface can be controlled. The molten zone normally moves upward.

12.3.9 Traveling Heater Method

The traveling heater method (THM) technique was developed for II–VI alloy growth (Te-based) by *Triboulet* [12.51]. In this technique, a molten zone is made to migrate through a homogeneous solid source material. This is normally accomplished by slowly moving the ampoule relative to the heater (Fig. 12.9). The key requirement here is to obtain the appropriate temperature profile, also shown in Fig. 12.9. Matter transport is by convection and diffusion across the solvent zone under the influence of the temperature gradient resulting from the movement. For alloy growth, a steady state can be reached where the solvent dissolves a solid of composition C_0 at the upper growth interface and deposits, at near-equilibrium conditions, a material of the same composition at the lower growth interface. Growth occurs at a constant temperature below the solidus temperature and hence shows all the advantages

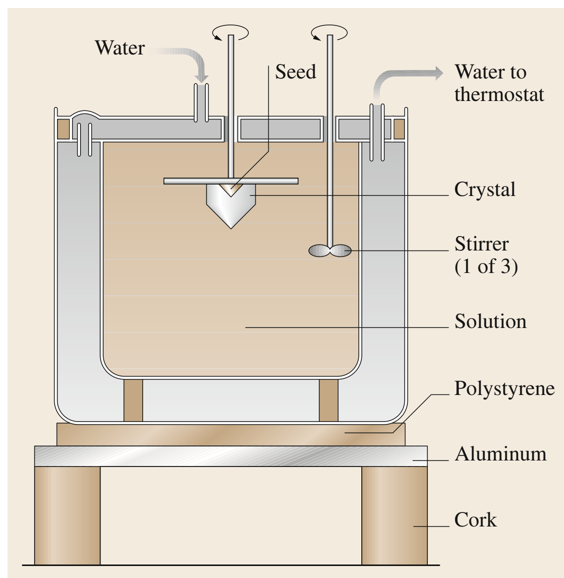

Fig. 12.10 Schematic of low-temperature solution growth equipment. (After [12.5])

of low-temperature growth. When tellurium was used as a molten zone there was a marked purification effect. Seeding was also found to be possible with the technique, as was growth of larger diameter material than with the other common melt techniques used for these compounds.

Problems with THM include the availability of suitable feed material with the required composition and dimensions, although several different routes have been used to overcome this problem. Natural convection is the dominant mechanism of material transport, which led to the addition of ACRT to the basic THM method for some of the ternary alloys.

By producing two bevelled cylinders of binary compounds graded-composition alloys were also produced. These were then used to assess the effects of composition on various electrical and optical properties in the given system. Other modifications to the basic process included the *cold THM* process, in which the relevant metallic elements were used as the source material. This produced a process that accomplished synthesis, growth, and purification at low temperature all in a single run. To avoid the problems resulting from solvent excess in the crystal *sublimation THM* was developed in which an empty space of the same dimension as the molten zone is used. This method was successfully applied to the growth of ZnSe. To improve the purification effect, repeated runs on the same material were used. A drawback of this is one of repeated handling, which in turn was solved by using the *multipass THM* technique, which can be thought of as a variety of the classical zone-melting method.

12.3.10 Low-Temperature Solution Growth

Most of the crystals grown by this technique are water soluble. This limits their use to applications in which moisture can be excluded. Growth rates are low (0.1–10 mm/d), as the growth faces are unstable. This is due to the concentration gradient near the growth face, in addition to which the crystal is normally totally immersed in the solution so that latent heat evolution increases the adverse supersaturation gradient (Fig. 12.10).

Water (both light and heavy) is used in $\approx 95\%$ of the cases, and must be highly pure. All equipment must be carefully cleaned and protected from dust and the solutions must be stirred vigorously while being prepared. Both slow cooling and solvent evaporation techniques are used. Large volumes of solution (> 100 l) are needed for very large crystals of, e.g., KH_2PO_4 (KDP). These large volumes imply very long thermal time constants, which can be increased by adding thermal insulation, up to a limit. Large time constants make it easy to obtain good temperature control. The growth equipment is normally held in temperature-controlled rooms. Although temperature stability is key, other parameters, such as fluctuations in stirring, can lead to large changes in growth rate too.

Solvent evaporation simplifies the temperature control system and makes it more reliable. However, it is difficult to ensure a constant acceptable rate of loss of solvent. This can be approached by using a water-cooled condensation region. One drawback of this technique is that concentrations of impurities increase as the growth proceeds.

12.3.11 High-Temperature Solution Growth (Flux)

This method is used for those materials that melt incongruently; the solvent (flux) reduces the freezing point below the relevant temperature to produce the desired phase of the compound. Both liquid metals (Ga, In, Sn) used in semiconductors and oxides/halides (e.g., PbO, PbF_2) used for ionic materials are employed as solvents. Often, an excess of one of the components will be used (e.g., Ga for GaAs and GaP for instance) or a common ionic material (e.g., K_2CO_3 for $KTa_xNb_{1-x}O_3$). Alternatively, the solvents contain large atoms, such as Pb and Bi, which are too large to enter the lattice of the desired crystal. Mixed solvents, for example, alkali metal ions, break the chains that exist in B_2O_3, SiO_2, and

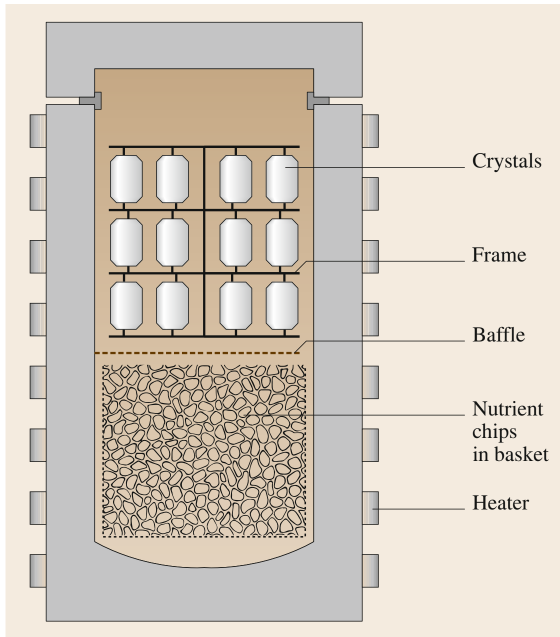

Fig. 12.11 Schematic of hydrothermal growth equipment. (After [12.5])

Bi_2O_3, lowering viscosities and surface tensions. The book by *Elwell* and *Scheel* [12.4] contains much useful information in this field.

Slow cooling of high-temperature solutions was used between 1950 and 1970 to produce hundreds of different materials. Small crystals were normally obtained but these were sufficient to obtain useful measurements of magnetic, optical, and dielectric properties. Later, seeded growth and stirring using ACRT led to much larger crystals. A Czochralski-type pulling technique can also be used in high-temperature solution growth to produce larger crystals.

12.3.12 Hydrothermal

This is growth from aqueous solution at high temperature and pressure. Most materials grown have low solubilities in pure water, so other materials (called mineralizers, for example, NaOH and Na_2CO_3) are added to increase the solubility. Quartz is the only material grown on a significant scale by this method, although ZnO is also produced commercially by this technique.

Natural quartz crystals are used as seeds, as they have lower dislocation densities. Growth proceeds in the temperature-gradient transfer mode. Nutrient is held in the lower part of the liquid in an autoclave. This region is held at between 5 and 50 °C above the upper portion of the autoclave. Convection carries the hot su-

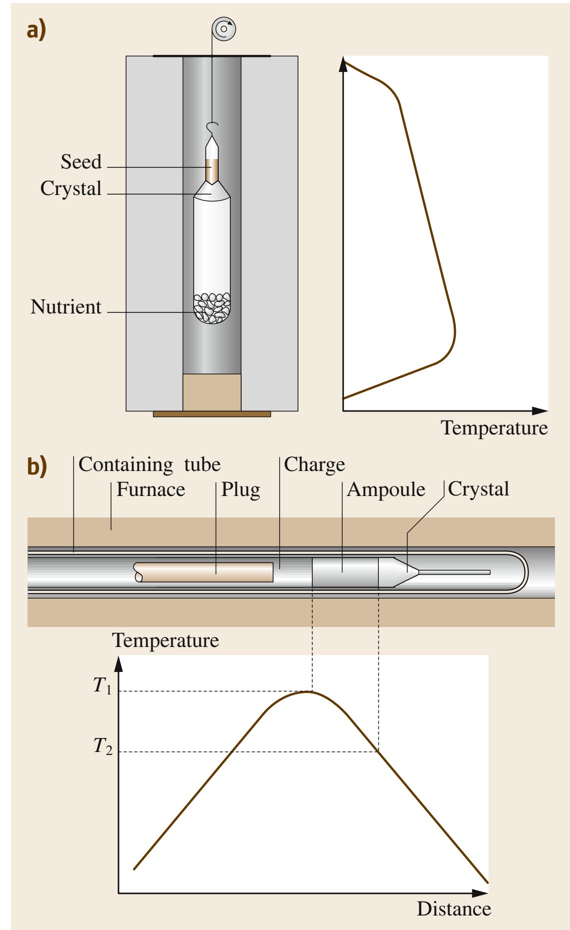

Fig. 12.12a,b Schematic of vapor growth equipment. **(a)** Seeded growth; **(b)** Piper–Polich set-up. (After [12.5])

persaturated liquid to the cooler upper regions, where deposition occurs on the seed crystals (Fig. 12.11). These autoclaves can be operated at up to 400 °C and 2000 atm pressure for ≈ 10 yr without degradation. Autoclaves can be up to 1 m in diameter and 2.5 m high for low-pressure growth from Na_2CO_3 solution, while 40 cm diameter and 8 m high autoclaves are typical for growth from NaOH.

Resistive heating elements are strapped to the outside of the autoclave and connected to two control systems, allowing independent control of the temperatures in the solution and growth zones. *Brice* [12.5] presents a table that shows some typical hydrothermal growth conditions for a wide range of materials.

The essential problem in the growth of quartz is to produce useful devices with reasonable yields with OH concentration (measured by IR absorption) of $<$ 100 ppma. Several parameters restrict the maximum growth rate to ≈ 0.5 mm/d.

12.3.13 Growth from the Vapor

Vapor growth has some applications, particularly in high melting point materials and in II–VI compounds such as ZnSe and ZnS (Fig. 12.12). High-temperature vapor transport, or sublimation, of SiC has progressed recently to producing 1–2 in crystals. Growth proceeds by sublimation of a SiC source at 2000–2500 °C in near-vacuum conditions onto a seed held at ≈ 1000 °C lower than the source. 6H-polytype material oriented at ⟨0001⟩ is produced. Growth rates are ≈ 2 mm/h. Problems remaining include impurities (≈ $10^{16}\,cm^{-3}$), voids, high dislocation densities, and mixed polymorphism.

12.3.14 Multicrystalline Si Growth for Solar Cells

Green [12.52] discusses the production of multicrystalline Si slices for photovoltaic applications and notes that in 2011 approximately 48% of the world production was based on this material. Advantages over the Czochralski process are noted as lower capital costs, higher throughput, and a higher tolerance to poor feedstock quality. Basically, the process involves the controlled solidification of molten silicon in a container to give silicon ingots with large columnar grains, normally propagating from the container base (Fig. 12.13a). These rectilinear ingots can be very large, up to 400–600 kg, and they are sawn into smaller more manageable sections, ≈ 150 mm in size (Fig. 12.13b), before being sliced into wafers by continuous wire sawing. This material is capable of producing solar cells with ≈ 90% of the performance of single-crystal Si, but due to the higher packing density possible due to the square geometry, this difference is masked at the module level where the overall performance is equivalent.

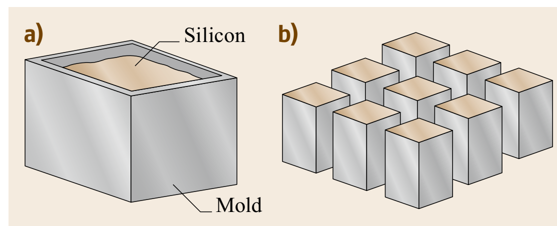

Fig. 12.13 **(a)** Direction solidification of silicon within a mold: **(b)** smaller sections are sawn from the main ingot. (After [12.52])

12.4 Materials Grown

This section summarizes the position regarding the wide range of materials used in electronics and optoelectronics. Again the reader is referred to the following relevant chapters for more in-depth coverage of a particular material. The section is subdivided roughly into group IV, group III–V, group II–VI, oxides, halides, and finally phosphates/borates.

12.4.1 Group IV

Silicon (Germanium)

The growth of silicon still dominates the electronics industry in terms of size of activity. *Hurle* [12.45] describes in detail the growth of silicon by the Czochralski method. In essence, a polysilicon charge is placed in a high-purity quartz crucible mounted in pre-baked graphite supports. Chains or cables are used in the pulling system, rather than rods, to limit the height of modern pullers. Both the crystal and the crucible can be rotated, although the details of this aspect vary from manufacturer to manufacturer and are proprietary. As the growth proceeds, the crucible is raised to maintain the position of the melt surface in the heater.

Silicon has two major advantages from a crystal growth perspective: a high thermal conductivity (which permits removal of latent heat of solidification) and a high critical resolved shear stress (which allows high thermal gradients without dislocation generation). These two factors enable high growth rates, leading to economic benefits. Heat is provided by *picket-fence*-type graphite heaters. Most commercial pullers are highly automated with full computer control. In most cases, diameter control is achieved via monitoring of the *bright ring* around the meniscus of the growing crystal. Oxygen is a particular problem and is introduced via erosion of the silica crucible by the melt. Convection moves the oxygen within the melt toward the crystal, where it is incorporated. A similar situation arises with carbon monoxide loss from the melt. Problems with convection have increased as the diameters of silicon crystals have increased over the past several decades. This convection controls concentrations and distributions of oxygen, carbon, and other unwanted impurities.

Although current production of large-diameter material is at the 300 mm level, there have been reports of 400 mm diameter material [12.53] and even 450 mm (≈ 450 kg) [12.8, Chap. 6]. In this case, it was necessary to grow a secondary neck below the Dash dislocation-reducing one as the thin Dash neck could not hold the

weight of the crystal. One report [12.54] shows how codoping Si with B and Ge can obviate the need for this narrow-neck region, while maintaining dislocation-free growth. *Rudolph* and *Kakimoto* [12.47] report how the use of a 0.35 T magnetic field can reduce turbulence in such large melts.

The highest grade of silicon i. e., the highest purity, is probably still produced by the floatzone (FZ) method, rather than the Czochralski technique [12.55, 56]. The higher purity (particularly regarding carbon and oxygen) and better microdefect control result in higher solar cell efficiencies in FZ material. Faster growth rates and heating/cooling times together with the absence of crucibles and hot-zone consumables also give FZ material an economic advantage over Czochralski material.

Table 12.2 summarizes the present position on sizes of various crystals, including silicon and germanium and silicon/germanium. The author does not claim that this list is complete nor is it authoritative, it merely serves to show the range of crystals and sizes currently being grown by bulk growth techniques. The information is taken from a number of published conference proceedings [12.57–66] and other sources [12.8, 9, 44, 49, 67–69].

Silicon Carbide

The growth of SiC for semiconductor devices, as opposed to abrasive applications, became successful when substrates could be reproducibly grown up to large sizes [12.70–72]. Currently, substrates up to 50 mm diameter are commercially available and 100 mm diameter substrates have been reported by *Talalaev* et al. [12.9, Chap. 2]. The current method is that of seeded sublimation growth. A water-cooled quartz reactor enclosure surrounds a graphite crucible, which is heated by r.f. means. Crucible sizes are slightly larger than the required crystal size and SiC powder (particle size 20–200 μm) and/or sintered polysilicon is used as the source. Typically a distance of 1–20 mm between the seed and the source is used. At the high process temperatures of 1800–2400 °C, volatile species of Si_2C, SiC_2, and Si evaporate from the source and deposit on the seed. The source temperature determines the rate of evaporation, and the temperature difference between the source and the seed determines the diffusion transport rate; together these two temperatures govern the growth rate. The Si : C ratio is a key control parameter for proper growth of the desired material. Sublimation is normally performed in vacuum or inert gas, such as argon. The pressure of this gas also controls the growth rate to an extent. Growth rates can reach up to 0.5–1.0 mm/h, and crystal lengths of up to 20–40 mm are achieved. Doping can be accomplished via nitrogen and aluminum addition for n- and p-type material, respectively.

Polytype control is obtained by carefully choosing the seed orientation, with growth on the (0001) Si face giving 6H material, while 4H material grows on the $(000\bar{1})$ face. Both growth temperature and pressure and intentional/unintentional impurities can also affect the polytype obtained. One remaining problem is that of micropipes within the material. These are hollow core defects of 1–10 μm diameter, although their density has been reduced from 1000 to 1 cm^{-2} in the best samples. Maintaining good control over the nucleation conditions can reduce micropipe density.

Diamond

High-pressure diamond is produced under conditions where it is thermodynamically more stable than graphite [12.73]. However, very high temperatures and pressures are required for growth, unless catalysts are also employed. Clearly a detailed knowledge of the diamond–graphite pressure–temperature phase diagram is a prerequisite for successful growth. For example, in static compression, 8–20 GPa of pressure and temperatures of 1000–3000 °C are needed. Carbon sources include graphite, amorphous carbon, glassy carbon, and C_{60}. Dynamic compression techniques employ pressures of 7–150 GPa. A wide variety of catalysts have been used ranging from conventional ones, for example, transition metals, to carbide-forming elements (Ti, Zr, etc.), to Mg, to oxygen-containing materials (carbonates, hydroxides, etc.), to inert elements (P, Cu, Zn, etc.) to hydrides.

Crystals above 1 mm size are grown by the temperature gradient method. Growth temperature, temperature gradient, growth time, type of catalyst, and impurities all affect the growth. Crystals up to 10–12 mm in size are commercially available from high-temperature–high-pressure growth, see *Sumiya* [12.74]. Growth rates can reach 10 mg/h and are governed by the growth temperature and the temperature gradient. If a high-quality diamond seed is used crystals free of major defects, such as inclusions, stacking faults and dislocations, can be obtained. Impurities, mainly form the catalysts used, are still an issue, as is their nonuniform distribution.

More recent work on CVD techniques has led to diamond crystals up to 100 mm in diameter and 1–2 mm thickness [12.75]. This book also gives details of the use of diamond in a very wide range of device applications, including radiation/neutron detectors, electronic devices, for example, field effect transistors (FETs), electrochemical, and biological sensors and microelectromechanical devices. It even describes the area of superconductivity in diamond films.

Table 12.2 Typical sizes (i. e., diameter) of a selection of bulk-grown crystals (in mm and/or weight in kg) currently in production and in R&D

Crystal	Commercial	R&D
Silicon (Cz)	300 (250 kg)	450 (450 kg)
Silicon (FZ)	100	
Silicon (multicrystalline)	680 × 680 mm (400–600 kg)	
Germanium	75	200–300
Silicon/Germanium		35 (120 mm long)
SiC	50	100
Diamond	100 (1–2 mm thick)	100
GaAs	200 (50 kg)	200
InP	150	150
GaSb	50	75
GaInSb	50	
InSb	75	100
InAs	50	
InGaAs		10
GaInAsSb		30
GaN (sublimation)	50	
AIN (physical vapor transport, PVT)	25 (5 mm thick)	40 (core in 50 mm slices)
MCT	50	70
CdZnTe	140 (10 kg)	140 (12 kg)
Bi_2Te_3	12	28
ZnSe (vapor, LEC)	60	
ZnTe	80	
ZnO	50	75 (10 mm thick)
HgMnTe	30	
CdMnTe		40
HgZnTe	30	
$LiNbO_3$		40
$YCa_4O(BO_3)_3$	80	
$PbZnNbTiO_3$		75
YAG	20	75
GGG	110 (25 kg)	
$LiTaO_3$	100	125
Ruby	200	
Sapphire	350 × 500 × 40	500
BGO	140	
$La_3Ga_5SiO_{14}$	100	
Quartz	15–30 × 150–250, (0.5–18 kg)	
β-BaB_2O_4		60
CaF_2	385 (100 kg)	
Alkali halides	520 (550 kg)	1000 (poly)
BaBrI	400	
Ce:$Li_6Lu(BO_3)_3$	30	
KDP	660 × 500 (380 kg)	
$Ca_5(PO_4)_3F$	70	
TGS	40	

12.4.2 Groups III–V

Gallium Arsenide

Mullin [12.46] provided a comprehensive discussion on all aspects of the growth of III–V and II–VI compounds. He starts his treatment with the early work done on purification in Ge and Si, which highlighted the need for both high purity and for single-crystal growth. He notes that *Pfann* [12.76] initiated zone melting, in which, in the simplest case, a horizontal molten charge is progressively frozen from one end. Both zone leveling, in which a liquid zone within a solid bar is moved through

the bar in one direction and then in the reverse direction, thus producing a uniform distribution of a dopant, and zone melting, in which liquid zones are repeatedly passed through a solid bar to force impurities to segregate to the ends of the bar and then these are subsequently removed before the bar, are used in growth. Horizontal techniques were also used to produce single-crystal material by slight back-melting of a seed crystal, followed by progressive freezing. These various horizontal techniques were subsequently applied to the purification of both elements and compounds in the materials from groups III–V and II–VI.

Table 12.3, taken from [12.46], summarizes the growth techniques that have been used for the various compounds in the groups III–V and II–VI. There has been much debate about the relative advantages and disadvantages of these techniques as applied to compound crystal growth.

GaAs is the most important group III–V compound. Horizontal growth can be used to produce low-temperature gradients at the solid/liquid interface, which reduces stress-induced slip and hence dislocations. This is particularly beneficial for the use of GaAs in laser diodes, where dislocation densities are required to be very low. However, there is a potential problem in using these low-temperature gradients and that is constitutional supercooling, which may result in unstable growth and second-phase inclusions. In addition, there is the issue of impurity uptake from the crucible and nucleation of twins, grain boundaries, and even polycrystalline growth from the crucible walls. These problems can be minimized by taking care in experimental detail but they still make horizontal growth unattractive where large-area uniformity is required, particularly as scaling up to ever larger diameters is difficult.

Early efforts to produce this material by the vertical Czochralski method failed due to dissociation of the melt. This problem was solved by the LEC technique [12.46]. A layer of boric oxide floats on the melt and the seed crystal is dipped through this to contact the melt (Fig. 12.14). PBN crucibles are normally used and heating can be by resistance or r.f. means but commercial systems use graphite heaters. Most semi-insulating GaAs, which is required for integrated circuits, is produced at pressures of 100–200 atm. The advantage of this modification is that elemental As and Ga can be used as the source. Diameter control is normally via crystal weighing. Currently, LEC produces material of 150 mm diameter [12.77] from 28–40 kg melts using 400 mm diameter PBN crucibles. Also reported were modifications to the basic Czochralski technique to reduce stresses, and hence dislocations, in crystals up to 100–150 mm diameter. These are vapor-pressure-controlled Czochralski (VCZ), fully encapsulated Czochralski and hot-wall Czochralski. The reader is referred to the reference for more details of these techniques. Friedrich et al. [12.8, Chap. 5] note that 200 mm diameter crystals have also been grown.

An alternative to Czochralski is that of vertical gradient freeze. For reproducible growth of large-diameter crystals by this technique it was found necessary to use B_2O_3 in a PBN crucible. Freezing is accomplished by moving the temperature gradient via furnace-controller changes, rather than movement of the furnace itself. This naturally produces low-temperature gradients, which give low dislocation densities, and it pro-

Table 12.3 General applicability of growth techniques to compound semiconductors. (The more *asterisks* there are the more appropriate the technique; P: potentially applicable; C: conventional VGF; L: LEC VGF.) (After [12.46])

Technique/ compound	Zone melting, horizontal Bridgman	VGF, vertical Bridgman	Conventional vertical pulling	Liquid encapsulation pulling	Vapor growth
InSb	***	P	***		P
GaSb	***	P	***		P
InAs	***	P		***	P
GaAs	***	C***: L***		***	P
InP	*	C*: L**		***	P
GaP	*	C*: L**		***	P
HgSe		**			P
HgTe		***			P
CdSe	*	**			***
CdTe	***	***			***
ZnSe		**			***
ZnTe		**			***
HgS					***
ZnS					***
CdS					***

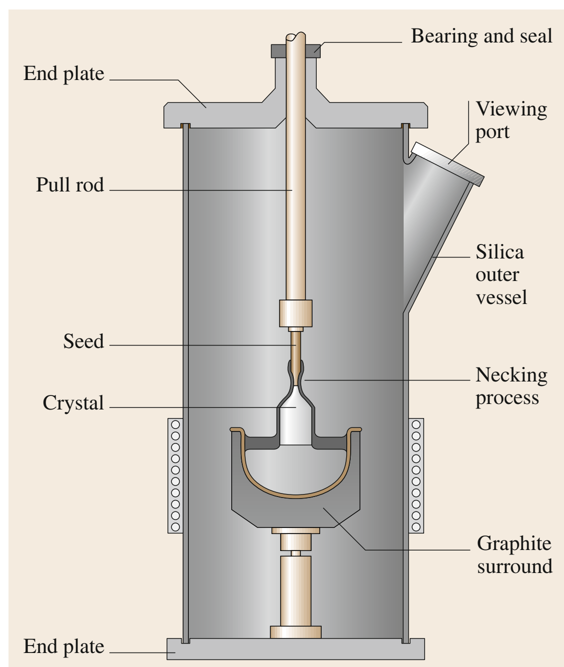

Fig. 12.14 Schematic of liquid-encapsulated Czochralski growth equipment. A silica outer vessel with viewing port is held between end-plates. The induction heating coils couple into the graphite surround. The seed is fixed in the chuck on the pull rod that rotates and moves through the bearing and seal. The crystal grows from the seed through a necking process, and on withdrawal pulls out a layer of B_2O_3 over its surface. (After [12.44], copyright Wiley-VCH (1998), used with permission)

duces a crystal of the right size and shape for subsequent slicing and processing. *Rudolph* [12.77] reports that in 1999 LEC growth of GaAs accounted for ≈ 90% of all SI GaAs, with the remaining 10% via vertical Bridgman or VGF growth. By 2000, he puts the figures at ≈ 50% LEC and ≈ 50% VGF. Rudolph also notes that VGF has been reported to grow up to 150 mm diameter material. *Rudolph* and *Kakimoto* [12.47] have shown how application of a magnetic field in VGF growth can produce nearly striation-free material.

Indium and Gallium Phosphides

As for GaAs, high-pressure LEC growth of both InP and GaP is normally used [12.46]. The problems were analogous to those of GaAs, with the major addition of an increased tendency to twinning. Loss of phosphorus (P_4) is still a problem and leads to deterioration in crystal quality. Dislocation densities are still seen to be high. *Asahi* et al. [12.78] report that some of these problems have been alleviated by modifications to the basic LEC process, for example, thermal-baffled LEC, phosphorus-vapor-pressure controlled LEC, and VCZ. Dislocations tend to increase with crystal diameter, although crystals up to 100 mm with low-disclocation densities have been grown by VCZ. Lower dislocation densities are produced by the VGF method, at a given crystal diameter. High-pressure VGF growth of InP is difficult and temperature fluctuations cause twinning. By improving the temperature control (to within $\pm 0.03\,^{\circ}$C). Asahi et al. show that twin-free ⟨100⟩ InP single crystals of 100 mm diameter and 80 mm length can be obtained. Temperature gradients of $< 10\,^{\circ}\mathrm{C/cm}$ reduced the etch pit densities below those of comparable LEC material. *Friedrich* et al. [12.8, Chap. 8] report that crystals of InP up to 150 mm diameter have also been produced.

Indium and Gallium Antimonides

Mullin [12.46] has detailed the early work on InSb; much less work has been done on GaSb. The low melting point combined with the negligible vapor pressure of Sb over the melt make zone-refining methods attractive. However, certain impurities render this route troublesome, although means to overcome this issue were found. Crystal-pulling methods were preferred for their versatility, although twinning was seen as a major issue. Growth on the (111) Sb face produces this twinning and it is recommended that growth takes place instead on [211] Sb or [311] Sb faces.

Micklethwaite and *Johnson* [12.79] summarized the position for InSb production for IR detector applications. InSb expands by ≈ 13% on freezing, leading to a net flow away from the growth interface. This *density effusion* must be accounted for in modeling this system. Hydrogen is used as the atmosphere, as it reduces floating InO_x. The basic Czochralski method is used for commercial production and 75 mm diameters are routine. Defect densities can be as low as $10\,\mathrm{cm}^{-2}$. Many of the details of the growth process are proprietary. Growth proceeds without a liquid encapsulant, and as such resembles Si growth more closely than its arsenide and phosphide cousins. However, there are significant differences from the silicon case in terms of reduced radiative heat transfer and increased convective flow in the hydrogen atmosphere. Fluid mechanics in the melt are complicated both by the *density effusion* and the facet effect [12.46].

Dutta [12.8, Chap. 12] reports on the VB and VGF (+ACRT) growth of ternary III–V crystals, for example, GaInSb, up to 50 mm diameter and discusses the reasons why ternaries are so much more difficult to grow than binaries. Later, he described the growth of sev-

eral other III–V ternaries, for example, GaInAs, from quaternary melts by VB/VGF, including the addition of melt replenishment during growth [12.9, Chap. 9].

Group III Nitrides

There was an increase in interest in these compounds following successful development of blue laser diodes. Ideally, epitaxial thin films of these nitrides would be grown on bulk substrates of similar compounds, to minimize lattice mismatch. However, growth of these compounds by the more normal Czochralski and Bridgman techniques is not possible due to the high melting temperatures (2200–3500 K) and high-decomposition pressures (0.2–60 kbar) [12.80, 81]. One growth method that can be used is high-pressure solution growth. In this technique, liquid Ga (plus 0.2–0.5 at % Mg, Ca, Be or Zn) is held in a high-pressure chamber with a N_2 atmosphere. The maximum pressure is $\approx$ 20 kbar and the maximum temperature is 2000 K. Both pressure and temperature are controlled within tight limits and in situ annealing in vacuum is also allowed for. A temperature gradient of 2–20 °C/cm is maintained along the crucible axis and the N_2 dissolves in the hotter end and GaN crystallizes in the cooler end. No seeding was used and after 120–150 h of growth hexagonal needles or platelets are produced of size 10×10 mm. Growth by metal-organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) of GaN and InGaN multi-quantum wells (MQWs) on these bulk GaN samples was also reported by *Grzegory* et al. [12.81]. Light emitting diodes (LEDs) and laser diodes based on these epitaxial layers were also described.

This technique only produces very small crystals of both AlN and InN.

Nishino and *Sakai* [12.82] describe the sublimation growth of both GaN and AlN. Initially, the source powder is synthesized by heating Ga metal in NH_3. This powder is then annealed in NH_3 before loading into the growth chamber. Temperatures are 1000–1100 °C but atmospheric pressure can now be employed. Both NH_3 and N_2 are introduced into the growth chamber. Either small, 3 mm × several hundred μm, *bulk* crystals or free-standing films (10–30 μm thick) on sapphire substrates are produced. Thicker samples (up to 500 μm thick) can be produced by the sublimation sandwich method in which the distance from source to substrate is reduced to 2–5 mm. A hot-pressed polycrystalline source of AlN and a SiC-coated graphite crucible was used to grow 0.3–1.0 mm thick films on the 6H-SiC seed (10×10 mm in size) at temperatures of 1950–2250 °C. *Talalaev* et al. [12.9, Chap. 2] note the growth of 50 mm diameter AlN substrates with a central 40 mm diameter single-crystal core, plus totally single-crystal high-purity 25 mm AlN substrates.

12.4.3 Groups II–VI

Several reviews of the growth of a wide range of binary and ternary II–VI compounds have been published [12.46, 67, 83, 84]. One of the key concepts in the growth of these compounds is the ease with which phase transitions occur. This imposes limits on certain growth techniques for particular compounds.

There are two main types of bulk growth techniques, namely growth from the liquid and growth from the vapor. Most narrow-gap II–VI compounds are characterized by high melting points and/or high component partial pressures and early work concentrated on various forms of vapor growth, particularly for S- and Se-containing compounds. Problems of low growth rate and/or small crystal size and purity led to a switch to melt growth techniques, although there have been some significant developments in the growth of larger crystals from the vapor.

Many techniques have been used to grow narrow-gap II–VI compounds. Solid-state recrystallization (SSR) was used for ternary systems where there is a wide separation between solidus and liquidus, for example, MCT. Other names that have been used for this process are quench anneal (QA) and cast recrystallize anneal (CRA). The term anneal is used in the first case to define a high-temperature grain growth process while in CRA it is a low-temperature process to adjust stoichiometry. Strictly speaking SSR is crystal growth from the solid phase at temperatures close to the melting point but is included here for convenience.

Bridgman growth is the most widely used of the bulk growth techniques applied to narrow-gap II–VI compounds. It is the only technique that has produced crystals of all the binary and ternary compounds studied. Numerous modifications have been applied to the basic process but the three principle means of achieving growth are to move an ampoule through a temperature gradient, to move the furnace past a stationary ampoule and to move a temperature profile from high to low temperatures with both the furnace and ampoule stationary, the so-called vertical gradient freeze (VGF) method.

Usually, silica ampoules are used but various coatings have been applied and the use of other materials such as PBN has been reported [12.85]. Charges are prepared either using the appropriate elements or, for ternaries and quaternaries, pre-formed compounds of the binaries. Both vertical and horizontal configurations have been used and large crystal sizes coupled

with a relatively high growth rate (1–2 mm/h) make the basic technique relatively cheap and versatile. Marked segregation of both matrix elements, in ternaries and quaternaries, and impurities can occur. Difficulties in controlling component vapor pressures can be overcome by employing a reservoir of one of the components at a temperature lower than that of the growing crystal. High partial pressures in Hg-containing compounds can cause ampoule failure but means have been developed to cope with this situation [12.86].

The traveling heater method (THM) has mainly been used for Te-based binary and ternary compounds. Growth by THM combines the advantages of low-temperature solution growth with steady-state conditions, as in zone melting. A homogeneous alloy can be used as the starting ingot or segments of the binaries can be employed. If the Te zone height is made equal to the ring heater size then a flat interface is obtained, for particular geometries of crystal and furnace and growth parameters [12.87]. Very low growth rates (0.1 mm/h) are typical but diameters up to 40 mm have been accomplished. As in Bridgman, many variations on the basic THM method have been attempted. These include multipass-THM [12.88] and *cold* THM [12.89].

Hydrothermal growth has mainly been applied to S- and Se-based binary compounds and was reviewed by *Kuznetsov* [12.90]. The main advantages are in reducing growth temperature (to 200–250 °C) and dealing with the high partial pressures. Growth rates are very low (0.05 mm/d), and crystals are small (few mm) and contain subgrains and inclusions, but can still provide useful fundamental data.

Growth from the vapor is usually carried out at much lower temperatures than growth from the liquid, hence below unwanted phase transition temperatures, and can lead to less defective crystals. However, growth rates are generally much lower and uncontrolled nucleation and twinning are more prevalent. Techniques can be split essentially into unseeded and seeded methods. The simplest technique is that of chemical vapor transport (CVT), usually using iodine as the transport agent. The compound to be grown is reacted at a high temperature with the iodine, transported to a cooler region and deposited. The reverse reaction produces iodine, which diffuses back to the high-temperature region and the process repeats itself. The method uses a 2-zone furnace but has the disadvantages of iodine incorporation and small crystal sizes. *Mimila* and *Triboulet* [12.91] experimented with sublimation and CVT using water as a transporting agent for ZnSe and Triboulet has succeeded in the growth of CdTe by this means.

Most other vapor techniques are in some sense a derivative of the Piper–Polich method (Fig. 12.12b). Although this was developed originally for the growth of CdS [12.92], the technique may be applied to the vapor growth of any compound that sublimes readily below the melting point temperature. The crystal is grown in a closed crucible that is moved through a steep temperature gradient, such that the source material is always hotter than the growing surface and mass transport occurs from source to crystal.

Vapor growth under the controlled partial pressure of one of the constituents has been obtained by including small quantities of one of the elements in an extended part of the capsule located in a cooler part of the furnace [12.93]. The technique, termed *Durham*, is a vertical unseeded growth procedure, where the source is sublimed from bottom to top in an evacuated silica capsule over several days. Constituent partial pressures are independently controlled by placing one of the elements in a separately heated reservoir connected to the main capsule via a small orifice.

The vertical unseeded vapor growth (VUVG) method differs from the Durham technique in that the partial pressures are controlled by the initial deviation from stoichiometry of the charge material. It was initially developed to grow CdTe. The crystal is grown in an evacuated cylindrical silica capsule in a vertical furnace. A long quartz tube, which extends outside the furnace, is attached to the top of the capsule providing a heat pipe to create a cooler area for nucleation, which is closely monitored to ensure that the nucleus is single grained.

The sublimation traveling heater method (STHM) was developed from THM by *Triboulet* and *Marfaing* [12.88]. The Te-rich molten zone in conventional THM is replaced by an empty space or vapor zone. A problem arises in that the constituent partial pressures are not only functions of the temperature. However, the vapor can be maintained near the stoichiometric $P_{\min}$ condition if a small capillary, one end of which is at room temperature, is connected to the vapor chamber [12.94]. Excess species are sublimed down the capillary, preserving the relative constituent partial pressures and hence the growth rate.

In one version of the seeded technique, an oriented seed is placed on top of a long sapphire rod inside a sealed quartz capsule. The source material is placed in a basket above the seed and sublimation is top-down. The sapphire rod is carefully centered within the growth capsule to ensure a narrow gap between it and the walls of the capsule. The crystals grow clear of the container walls and generally consist of two or three large grains, some of which maintain the seed orientation. This *Markov* technique has been adapted for commercial production by the ELMA Research and Development Association of Moscow (cited in *Durose*

et al. [12.95]). Large crystals of CdTe, 50 mm in diameter and up to 10 mm in length have been grown.

HgS is grown by vapor means or by hydrothermal techniques, both of which are at low temperatures and hence low S partial pressures. HgSe has been produced by vapor growth and also by the Bridgman technique. Thick-walled silica ampoules are required in the growth of the Hg-containing compounds to contain the high Hg partial pressures. More details of the growth of the Hg-based binaries can be found in [12.89] for vapor and Bridgman growth, while Kuznetsov has reviewed the hydrothermal growth of HgS [12.90].

Early work on the growth of the Cd-based binaries was summarized by *Lorenz* [12.96]. Vapor growth was favored for CdS and CdSe, although hydrothermal growth was also discussed. The latter technique, as applied to CdS, was discussed in [12.90]. CdTe was grown by various melt growth techniques, including seeded zone melting and Bridgman, and by vapor growth methods. *Zanio* [12.97] reviewed the growth, properties and applications of CdTe, including radiation detectors. By that time, vapor growth had been essentially supplanted by both Bridgman and THM growth. A more recent review of CdTe can be found in *Capper* and *Brinkman* [12.98]. The main uses of CdTe (and CdZnTe/CdTeSe) are as a substrate material for the epitaxial growth of MCT and, more recently, as radiation detectors [12.99]. *Triboulet* et al. [12.100, 101] applied SSR to the growth of both CdSe and CdTe.

A wide variety of techniques for growth from the liquid have been used to produce crystals of CdTe. These include solvent evaporation [12.102], liquid encapsulated Czochralski [12.103], zone refining [12.104], VGF [12.105, 106], solution growth [12.107], heat exchanger method [12.108], float-zoning [12.109], Bridgman [12.98] and THM [12.51], and *Triboulet* et al. [12.100] have reviewed these materials as substrates for MCT epitaxial growth and compared them to the alternatives based on GaAs, sapphire, and Si. Problems with the growth of CdTe include low thermal conductivity, difficulty in seeding due to the need for superheated melts, ease of twin formation, tilts and rotations in the lattice, stoichiometry control, and impurities. However, *Triboulet* et al. [12.101] concluded that despite the progress made in the alternative substrate materials, lattice-matched substrates based on CdTe produced MCT epitaxial layers that gave the best device performance at that time.

Within the Bridgman growth technique, many alternatives have been attempted. These include holding excess Cd at a lower temperature in a separate reservoir [12.110], vibration-free growth [12.111], vibrational stirring [12.112], horizontal growth [12.113], low-temperature gradients [12.114], high-pressure (100 atm) growth [12.115], and the addition of the accelerated crucible rotation technique (ACRT) [12.116]. Work in the United States [12.113] aimed at improving both the horizontal and vertical techniques and scaling-up to large melts, up to 8 kg (horizontal). *Szeles* et al. [12.117] showed that crystals up to 140 mm diameter and 10 kg in weight can be grown by careful control of the temperature fields.

In the Bridgman process, elemental Cd and Te are loaded into a clean carbon-coated silica ampoule, homogenized by melting/rocking, heated to temperatures in excess of 1100 °C, and then frozen at rates of a few mm/h in a vertical or horizontal system. Single crystals or, more normally, large-grained ingots of size ≈ 75 mm in diameter and 10–15 cm in length are produced.

Growth by variations on the basic THM process have included the addition of ACRT [12.118, 119], focused radiant heating [12.120], sublimation-THM and multipass-THM [12.88], and *cold* THM at 780 °C [12.89]. Crystals are grown either from the precompounded binaries or the elements (as in cold THM). Growth rates tend to be low, few mm/d, but crystals are very pure due to segregation effects and high-resistivity material results (10^7 Ωcm in [12.88]). This makes THM material ideally suited for gamma- and x-ray detectors.

The vast majority of work on bulk growth of MCT has been from the melt. Although rapid progress has taken place in the epitaxial growth techniques for MCT, material grown by several bulk methods is still in use for infrared detection, particularly for photoconductive detectors (this is the case in this author's lab and others worldwide, for example, SPITFIRE in New Zealand). Several historical reviews of the development of bulk MCT have been published [12.121–123]. Many techniques were tried in the early years but three prime techniques survived: SSR, Bridgman and THM.

Two fundamentally different approaches have been followed to improve the basic Bridgman process. These are based on control of melt mixing and of heat flows, respectively. The former has been studied by this author and coworkers [12.124] while the latter includes the work of *Szofran* and *Lehoczky* [12.125] among others. Marked segregation of CdTe with respect to HgTe occurs in the axial direction but this leads to an advantage of the Bridgman process over other techniques, that is, material in all ranges of interest (1–2, 3–5 and 8–12 μm, for $x = 0.7$, 0.3 and 0.2 regions, respectively) is produced in a single run.

A means of stirring melts contained in sealed, pressurized ampoules was needed and the ACRT of *Scheel* and *Shulz-Dubois* [12.43], in which the melt is subjected to periodic acceleration/deceleration at rotation rates of up to 60 rpm, was chosen. The first report

of ACRT in MCT Bridgman growth was given in a patent [12.126]. These effects were developed and discussed in more detail in later papers, which are reviewed in [12.124]. Crystals were produced up to 20 mm in diameter and with x values up to 0.6 in the tip regions of some crystals (this has recently been increased to ≈ 0.93 at 20 mm diameter in this author's lab, *Capper* et al. [12.44, 49, 127], up to 0.4 in 40 mm diameter crystals, while the size has also been increased up to 70 mm).

Triboulet [12.51] developed the THM technique for MCT where diameters up to 40 mm were accomplished and x values up to 0.7 [12.128] for optical communication devices. *Durand* et al. [12.129] employed seeds to produce large, oriented crystals, an advantage of this technique over other bulk methods. *Gille* et al. [12.130] adopted a slightly different approach. A pre-THM step is carried out to quench a Te-rich (53–60%) MCT melt. The entire growth procedure takes several months but gives uniform material. This group also used rotation in the horizontal growth by THM with some success [12.131]. Two groups have applied ACRT to THM and obtained enhanced material properties. *Royer* et al. [12.132] used a saw-tooth ACRT sequence and obtained improved radial and axial compositional uniformity. *Bloedner* and *Gille* [12.133] used ACRT although no significant dependence of crystallinity on rotation sequence was seen. They did, however, achieve an increase in growth rate from 1.5 to 8.5 mm/d.

Bridgman is the main melt growth technique for the Hg- and Cd-based ternary and quaternary compounds while work on the vapor growth of these compounds has been limited. The various Hg-based ternaries (e.g., HgZnTe and HgMnTe) have been studied as potential alternatives to MCT for infrared detectors (*Rogalski* [12.134] gave more details including phase equilibria plots). This work was initiated by a theoretical prediction that the Hg–Te bond is stabilized by the addition of Zn, in particular. Rogalski concluded that THM produced the best quality HgZnTe while Bridgman growth of HgMnTe was described as being similar to MCT growth but with reduced segregation. Crystals of HgMnTe up to 40 mm diameter were produced. *Triboulet* [12.135] discussed alternatives to MCT. He concluded that HgMgTe, HgCdSe, and HgZnSe were not suitable, for a variety of reasons, but that HgMnTe and HgZnTe were potentially suitable.

The main Cd-based ternaries are CdZnTe and CdTeSe, which are used as substrates for epitaxial MCT growth by LPE and MBE. A vast literature exists on these compounds and it is still a very active area of research. Vertical and horizontal Bridgman are the main techniques used [12.98] although VGF has been used [12.98] as has THM [12.51]. High-quality crystals up to 100 mm (and even 125 mm) diameter can be produced by VGF [12.78, 106]. Even larger crystals are being grown by horizontal Bridgman [12.117, 136]. Two main problems remain in these compounds. These are uniformity of Zn, or Se, and impurities.

Pelliciari et al. [12.137] showed how solvent evaporation from a Te-rich solution of CdTe in an open tube system can produce large-grained and even single crystals of CdTe up to 300 mm diameter. This large-area material is aimed at the fabrication of x-ray and γ-ray detectors.

Dilute magnetic semiconductors (DMSs) are a class of semiconductor where the semiconducting properties are changed by the addition of a magnetic ion (e.g., Mn^{2+} or Fe^{2+}). These materials therefore display normal electrical and magnetic properties, and novel ones such as large Faraday rotations and giant magnetoresistance. *Pajaczkowska* [12.138] gave an early review of the phase diagrams, lattice parameters, and growth of many of the Mn- and Fe-based DMS compounds. Vapor growth and hydrothermal growth were mainly used, although the Te-based compounds were grown by the Bridgman technique. The most comprehensive review of DMSs is given in [12.139]. In that book, Giriat and Furdyna review the crystal structure of, and growth methods used for, the Mn-based compounds. The majority of the compounds, particularly the Te-based ones, were grown using Bridgman, or unspecified modifications of it. CdMnS was grown in graphite crucibles under high inert gas pressure, or by CVT (using iodine as transport agent). HgMnS was grown hydrothermally, yielding 2 mm diameter crystals. For Fe-based compounds similar preparation methods to those used for the Mn-based compounds were applied but less Fe can be incorporated in the lattice.

Bismuth telluride (strictly speaking a V–VI compound) is used in thermoelectric applications close to room temperature [12.140]. This material is also grown by the Bridgman technique. Both n-type and p-type materials are required to make the thermoelectric devices, and these can be achieved either by stoichiometric deviations or deliberate doping. In this author's lab bismuth telluride is grown at similar rates of 0.5–2.9 mm/h for 12 mm diameter ingots up to 100 mm length using antimony and iodine as acceptor and donor dopants, respectively.

12.4.4 Oxides/Halides/Phosphates/Borates

Oxides

Hurle [12.45] summarized the issues of the growth of oxides by the Czochralski technique. The high melting points of most oxides of interest necessitate the use

of precious metal crucibles, for example, iridium, platinum, although molybdenum and tungsten ones can be used for lower melting point materials. Extensive and efficient thermal insulation is required, using alumina, magnesia, zirconia, and thoria. Some materials require a partial pressure of oxygen in the growth chamber to prevent reduction of the melt. However, this can lead to oxidation of the crucible, which in turn enters the melt. Careful management of the oxygen pressure and gas flow is needed, together with physical baffles. Heating is normally by r.f. means. Mounting of the seeds is problematic and long seeds are necessary to avoid thermal degradation of the seed holder and pull rod. Rotation or translation of the crucible is normally not used, so the rate of growth has to be above the pulling rate to account for the fall in melt height. Crystals are normally limited to less than half the crucible diameter for stable growth. Growth rates are low, a few mm/h or less, to avoid unstable growth. Afterheaters are also employed to reduce the built-in stress in the crystal during the later stages of growth and subsequent cool down. Growth runs are several days so automatic diameter control, in this instance using weighing techniques, is mandatory. The high temperatures lead to high-temperature gradients and thus strong bouyancy-driven convection that is turbulent by nature. This turbulence gives rise to nonuniformities in the crystals. In addition, catastrophic failure can result from coupling between this turbulent flow and the flow due to the crystal rotation. Thus, understanding the convective flows in oxide growth is critical if large-diameter highly perfect crystals are to be produced.

Fukuda et al. [12.141, 142] have presented detailed reviews of the growth of a wide range of oxide materials of interest for optical and optoelectronic applications. They note that only $LiNbO_3$ (LN), $LiTaO_3$ (LT), and $Y_3Al_5O_{12}$ (YAG) have as yet reached production status. Many of the other materials exhibit superior properties but are not available in large quantities at sufficient perfection to warrant them being used in devices. In general, the growth methods are based on liquid–solid transitions, either from the melt or from high-temperature solutions (flux), for congruently and incongruently melting materials, respectively. Czochralski growth is still the mainstay of oxide growth, although problems with shape (diameter) control of some oxides (rare-earth vanadates, rutile, etc.) necessitate the use of edge-defined film-fed growth (EFG). Growth from fluxes is used for a range of oxide materials, although some incongruently melting materials can be produced from melts of the same composition as the crystal by a micro-pulling down technique.

In the micro-pulling down technique the melt is held in a Pt crucible and a micro-nozzle (die) is arranged at the bottom of the melt. Below this arrangement is placed an afterheater. This combination produces a steep temperature gradient (300 °C/mm), which ensures stable growth at high rates. Single crystals of 0.05–1.0 mm diameter are produced onto seeds. LN crystals, for example, are grown at 12–90 mm/h from stoichiometric melts up to 100 mm in length, assumed only to be limited by the melt volume used. Dislocations are introduced if the diameter of the crystals exceeds 0.8 mm. Growth of $K_3Li_2Nb_5O_{12}$ (KLN), which has outstanding electro-optic and nonlinear optical properties, is problematic by either Czochralski or Kyropoulos methods due to segregation effects at the solid/liquid interface and cracking. This material was grown by the micro-pulling down technique at rates of 20–80 mm/h with diameters of 0.15–0.5 mm. The crystal composition was found to be near to the melt composition and crystals were single domain.

Crystals in the $KTiOPO_4$ (KTPO) family were grown by the flux method using slow cooling from 1100 to 800 °C. Crystals of a few mm in size were obtained for second-harmonic generation measurements.

Crystals from the langasite family ($La_3Ga_3SiO_{12}$) are used for lasers. These were grown by the Czochralski method at 50 mm diameter and 130 mm length. High-purity oxide powders were used as starting materials and an Ar/O_2 mixture was used to suppress evaporation of the gallium suboxide. A pulling rate of 1.0 mm/h was used together with a crystal rotation rate of 10 rpm. The resulting crystals were single phase and crack free. These crystals show superior properties, as filters, to quartz. A range of langasite-type crystals up to 100 mm diameter have also been grown by both Czochralski and VB techniques ([12.8, Chap. 15], [12.143]).

Another means of overcoming problems in Czochralski growth of these materials is to use the EFG method. Rutile (TiO_2) is used as a polarizer in optical isolators and prisms for optical communication systems. Crystals of this material can be grown by Verneuil and float-zone methods but growth by Czochralski is difficult. Iridium is used for the die material and crystals up to 8×1 cm and 0.5 mm thick were grown. A modified die was used to grow a rod of 15 mm diameter and ≈ 40 mm length. A double-die system was shown that was used to produce a core-doped crystal of LN, using Nd^{3+} and Cr^{3+} as the dopants. A 5 mm diameter crystal some 60 mm in length was produced. Such crystals have potential in optical applications where pumping energy is only absorbed in the core region, reducing heat-induced energy losses.

Quartz is used in both piezoelectric and in various optical applications [12.144]. *Balitsky* [12.145] noted

that some 2500 t were produced per year at that time. Hydrothermal growth is the main growth technique used in order to keep the growth temperature below the β- (nonpiezoelectric) to α-quartz (piezoelectric) phase transition. Growth at temperatures of 250–500 °C and pressures of 50–200 MPa are used in both alkaline and fluoride solutions. Growth rates of 0.5–1.0 mm/d are achieved on (0001) or (1120) seeds and crystals up to $200 \times 70 \times 60$ mm in size weighing from 1–18 kg.

Various oxide materials are used widely in scintillator applications. The most common are $Bi_4Ge_2O_{12}$ (BGO), up to 140 mm diameter and 400 mm long [12.8, Chap. 8] and $PbWO_4$ (PWO) [12.146, 147]. These materials are grown by normal Czochralski and Bridgman techniques and the requirement is for thousands of each for large high-energy/astrophysics projects in several centers throughout the world. For example, some 85 000 PWO crystals were required for one application at the Large Hadron Collider at CERN. High-purity starting materials are important as are certain growth parameters and post-growth annealing, for example, in oxygen, to reduce stress in the material.

Sapphire is grown by several techniques for a wide variety of optical, microwave and microelectronics applications [12.148]. Verneuil [12.149] and Czochralski and EFG [12.45] have been used extensively to produce large single crystals, particularly for laser rods, and shaped pieces using various forms of dies. In addition, the horizontal directional solidification crystallization (HDC) technique [12.148] has been used. A molybdenum boat filled with the charge is simply moved through the temperature gradient. Low-temperature gradients lead to crystals with low stress and low-dislocation densities (compared with the Verneuil and pulling techniques. The growth rate is high at 8 mm/h and crystals up to 10 kg and up to $30 \times 30 \times 2.5\,cm^3$ and even $50 \times 35 \times 4\,cm^3$ [12.150] can be produced. Even larger crystals, up to 20 kg with a diameter of 200 mm) can be produced by a modified Kyropolous method [12.151] and 500 mm diameter crystals were noted by *Friedrich* [12.8, Chap. 5].

Another technique used is the heat exchanger method, which is a solidification technique from the melt [12.152]. By independently controlling the heat input and the heat output, large crystals can be grown onto seeds. The seed is prevented from melting by a helium gas flow at the bottom of the melt. By progressively increasing the helium flow, following partial melting of the seed, and/or decreasing the furnace temperature growth is progressed. After complete solidification, an annealing step is performed prior to cooling to room temperature. The submerged solid/liquid interface damps out any thermal and mechanical variations and also produces a low-temperature gradient at the interface. There is impurity segregation into the last-to-freeze parts of the crystal that form near the crucible walls. These areas are removed before machining takes place. Crystals up to 340 mm in diameter (65 kg) have been produced in this way. Slabs cut from these crystals are used as optical windows, between 5–25 mm thick. *Demina* et al. [12.9, p. 213] note that in 2007 the total volume of 2 in equivalent wafers for all applications was $\approx$ 5 000 000.

Bruni [12.9, p. 267] reports on the growth of a 110 mm GGG crystal weighing 25 kg, which was used in laser applications.

There has been renewed interest recently in the growth and applications of ZnO [12.153, 154]. It is shown that 50 mm and even 75 mm diameter crystals (up to 10 mm thick) can be grown by both vapor and hydrothermal techniques.

Halides

Another class of scintillator materials are halides. These are used in a range of applications from high-energy physics, nuclear medicine, environmental monitoring and security systems [12.155]. Both large diameter, comparable with the human body, and large numbers, for the high-energy physics applications, are required. The simple Bridgman growth process is still used for many of these materials, although problems do arise due to the contact between crystal and crucible. Insufficient melt mixing also leads to inclusions and striations in crystals. The alternative technique for growth is that of continuously fed Czochralski/Kyropolous growth. A melt-level sensor is normally used to control the diameter over the tens/hundreds of hours of growth of large halide crystals. Replenishment of the melt by molten material from a closed feeder enables purification of the starting materials, and a conical crucible that is not too deep is used. Crystals of CsI up to 500 mm diameter and 750 mm height, weighing $\approx$ 550 kg have been produced [12.156] and CdF_2 up to 400 mm diameter [12.8, p. 140]. The ultimate aim is to produce crystals $>$ 1 m in diameter so that entire crystals can be used to monitor the human body.

Phosphates, Borates and Tungstates

Nonlinear optical materials are very important for laser-frequency-conversion applications. One of the most important of the phosphates is potassium dihydrogen phosphate (KDP) that is used for higher harmonic generation in large laser systems for fusion experiments [12.105, 157]. Growth takes place at room temperature to 60 °C and growth rates can be as high as 10–20 mm/d with sizes of $\approx 40 \times 40 \times 85$ cm [12.157] or $45 \times 45 \times 70$ cm [12.105] or $50 \times 50 \times 50$ cm [12.158], the latter weighing some 300 kg, some taking over

a year to grow! *Schaffers* et al. [12.9, p. 229] noted that the National Ignition Facility required some 75 such large-scale crystals weighing over 100 t. They also reported on the production of 70 mm diameter crystals of $Ca_5(PO_4)_3F$ and 80 mm diameter crystals of $YCa_4O(BO_3)_2$ for laser applications, for example, frequency-conversion materials.

Another important phosphate is potassium titanyl phosphate (KTP) used to get green light by frequency doubling a Nd:YAG laser. Growth in this case is from high-temperature solution at about 950 °C [12.105]. Sizes up to $32 \times 42 \times 87$ mm (weight 173 g) can be grown in 40 days.

Borates, including barium borate, lithium borate, cesium borate and coborates, for example, cesium lithium borate are used in UV-generation applications. Crystals are again grown by the high-temperature solution method up to $14 \times 11 \times 11$ cm in size, weighing 1.8 kg, in 3 weeks [12.105]. Crystals of β-BaB_2O_4 have recently been produced up to 60 mm diameter [12.159], while $YCa_4O(BO_3)_2$ (YCOB) material up to 100 mm diameter for SHG have also been grown [12.160].

Crystals of $CaWO_4$ up to 40 mm diameter weighing 1.8 kg are currently being used in dark-matter research [12.161].

12.5 Conclusions

This chapter has summarized the current position on bulk growth of crystals for optoelectronic and electronic applications. It is not intended to be a completely comprehensive view of the field, merely serving to introduce the reader to the wide range of materials produced and the numerous crystal growth techniques that have been developed to grow single crystals. An historical perspective has been attempted to give the reader a feel for the scale of some of the activities. The sections on specific materials try to summarize the particular growth techniques employed, and those that cannot in some cases, and outline the typical sizes currently produced commercially and in the R&D areas. For more details on current developments see the books [12.8, 9, 44, 49, 69].

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