

Crystal Growth through the Ages: A Historical Perspective

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Excerpt from Pliny the Elder's, *Natural History*, AD 77, "... I have prefaced these volumes with the names of my authorities. I have done so because it is, in my opinion, a pleasant thing and one that shows an honourable modesty, to own up to those who were the means of one's achievements..."

Trans. H. Rackham

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1.1 Introduction

Most scientists and engineers are aware that the basic tools they use in their daily research activities were developed by groups of researchers working in series or parallel over decades, in some cases centuries. It was often in an incremental way, one study building on another. As time went on, these earlier ideas became more refined and practical, providing future workers with a more thorough understanding of the physics and chemistry involved in different materials systems and leading to innovative new processes for making materials and devices that have affected everyone's lives. They helped define the world we live in and used their newly gained knowledge to stoke the technological revolution.

The crystal growth field (a branch of materials science, physics, chemistry and crystallography) has a rich historical background that goes back at least several millennia. It basically deals with understanding the underlying mechanisms involved in the crystallization process and the technology to produce a single crystal from some medium in a controlled fashion. One of the earliest written accounts documenting work on methods for preparing crystals was given by the Roman Pliny the Elder in 77–79 AD [1]. His collected work was a summary of knowledge going back to even more ancient times. It is probable that even prehistoric man engaged in the recrystallization of materials like salt. Among other topics, Pliny discussed the preparation of Vitriol (iron,

copper and zinc sulfate hydrates). The process involved evaporating mine or spring waters obtained from the Mediterranean region. About 1500 years later, in medieval times, Pliny's work was referred to by both Biringuccio [3] and Agricola [2]. They concentrated on preparing crystals of these compounds for medicines, dyes, fluxes and acids. The various methods employed generally began with the purification of mineral deposits, followed by recrystallization of the remaining solutions by evaporation.

The field of crystal growth encompasses a wide spectrum of scientific disciplines and includes (1) experimental and theoretical studies of crystallization processes, (2) the growth of crystals under controlled conditions for both scientific purposes and industrial applications and (3) crystal characterization. It also covers almost all classes of materials, i.e., inorganic and organic compounds, elemental materials as well as biological macromolecules. Many methods have been developed over the years for producing single crystals, the size range for which varies from the nanometer to meter scale. These crystals have in common an atomic ordering that persists throughout their bulk and without the presence of grain boundaries. The two principal scientific pillars upon which the field of crystal growth depends are thermodynamics and kinetics. The thermodynamic properties of a system describe how solid, liquid and gaseous phases behave with respect to state variables such as temperature, pressure and composition. They provide a road map, so to speak, which crystal growers use to plan growth strategies. For the preparation of crystals of a size, purity and composition required for a specific application, one needs to know what material phases will exist under various conditions of temperature, T, and pressure, P, etc., and how these phases will form under dynamic solidification processing conditions. Kinetic factors, on the other hand, influence our ability to produce a crystal at a desired growth rate and with a degree of perfection and uniformity suited to the intended application. We will explore below how interface stability and segregation behavior are influenced both by thermodynamic and kinetic factors.

In the beginning, crystal growth was not the well-defined field it is today. Work was carried out by chemists, physicists, etc., and research results were reported in various conferences and journals of these societies. The first conference to concentrate on the topic was at a Faraday Society meeting in 1949, held in Bristol, England. In spite of the growing importance of crystals for solid-state electronic applications in the early 1950s, it was almost a decade later before a second meeting concerning issues in crystal growth arose. That conference, held in Cooperstown, New York in 1958 [4], gathered together some of the most eminent crystal growth researchers to discuss a wide range of topics of interest to the crystal growth community. Conferences were also started in the Soviet Union (Moscow) as early as 1956. However, the major consolidation of the field into a viable entity was the formation in 1966 of the International Organization of Crystal Growth (IOCG) and under their aegis, the subsequent International Conferences on Crystal Growth (ICCG). These conferences have been held every three years since 1966.

The local organizers of the first ICCG conference held in Boston, Massachusetts immediately founded the American Association for Crystal Growth (AACG) under the joint chairmanship of Doctor Robert (Bob) Laudise and Doctor Kenneth (Ken) Jackson.

The AACG held their own national conferences soon afterward and other national groups formed around the world. The *Journal of Crystal* was established in 1967 under the leadership of Professor Michael Schieber, along with Sir Charles Frank and Dr Nicholas Cabrera as co-editors. Although papers on crystal growth topics are published elsewhere as well, the *Journal of Crystal Growth* has remained the major venue for papers on crystal growth theory, practice and characterization and has published related proceedings of conferences focused on various aspects of the field.

Many of the topics discussed in this introductory history are covered in much more detail in various chapters in this comprehensive, updated version of the *Handbook of Crystal Growth*. This treatment is designed to focus mainly on their historical context.

1.2 Evolution of Crystal Growth Theories

Although crystals can be grown by purely empirical means, control of their rate of growth, perfection, dimensions, composition and physical properties is greatly facilitated by having a good grasp of the fundamentals underlying crystal growth processes. Over the past century, a sound theoretical foundation has been built up through the efforts of many different scientists and engineers working in materials-related fields such as chemistry, physics and crystallography. The approach is generally two-fold: first to understand the nature of material systems (crystal structure and morphology, phase equilibrium, etc.), and second, to determine the factors that affect the crystallization process (nucleation, growth kinetics, segregation behavior, interface stability, heat and mass transport, etc.). Although remarkable progress has been made, the complex nature of the field and its changing emphasis on newer materials and structures keeps providing a constant source of challenges to our understanding of crystallization processes.

1.2.1 Early Developments (Before the Nineteenth Century)

The earliest scientific studies important to the field of crystal growth were made by natural scientists trying to understand the morphologies of mineral crystals. One of these early pioneers was the Swiss naturalist Conrad Gesner (1516–1565) who in 1564, after studying different crystals, reported that one crystal differs from another by its angles and form [5]. Later in the sixteenth century, Andreus Caesalpinus (1519–1603) wrote in “De Metallicis” [6] that the shape of crystals grown from water solution (e.g., salt, sugar and alum) were a characteristic of the material. Ichiro Sunagawa [7] proposed, however, that the science of crystal growth started with the treatise of N. Steno. Nicolas Steno, also known as Niels Stensen, (1638–1686) was a well-known Danish scientist specializing in the fields of geology and anatomy. He was also one of the founders of crystallography. In his treatise, published in 1669 [8], he observed that, although quartz crystals differ in appearance from one to another, the angles between corresponding faces are always the same. In addition, he noted that they grew by an inorganic hydrothermal process rather than through the action of bacteria [7]. Years later, Steno’s law of *constant interfacial*

angles in crystals was confirmed, first by the Italian Domenico Guglielmini (1665–1710) [9] who asserted, like Casealpinus, that every salt has its own particular shape. A century later, the Frenchman Jean Baptiste Romé de l'Isle (1736–1790) [10], concluded from his study of many hundreds of different crystals that every crystalline substance with a specific composition had a similar and particular crystal shape (1772). See [Figure 1.1\(A\)](#)). He found six different fundamental forms from which all others could be derived. Although the above work, and that of other researchers not mentioned, set the stage for our improved understanding of the nature of crystals, it was not until much later that attention turned seriously to the question of how crystals grew and which mechanisms were involved. [Figure 1.1\(B\)](#) shows the internal structure of a lithium niobate crystal revealed by partial melting.

1.2.2 The Nineteenth Century

French physicist Auguste Bravais (1811–1853), building on l'Isle's previous work, determined in 1848 that there are 14 unique "Bravais" lattices comprising three-dimensional crystalline systems [11]. This work provided the basis for understanding symmetry, crystal morphology and crystalline anisotropy. The morphology of a crystal is influenced by (1) external factors, e.g., the surrounding nutrient phase and (2) internal features, e.g., cell dimensions, atom sizes, positions, and bond energies.

Contemporary quantitative crystal growth science originated with the thermodynamic studies of the American scientist J. Willard Gibbs (1839–1903). Gibbs studied how various phases behaved in heterogeneous systems under the influence of state variables such as temperature and pressure. His seminal work, *On the Equilibrium of*

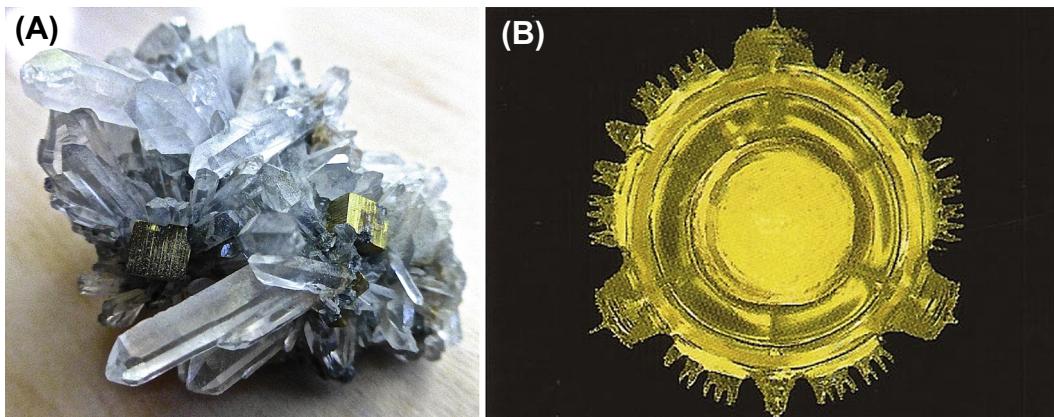


FIGURE 1.1 (A) Naturally occurring crystals of quartz (SiO_2) interspersed with pyrite (FeS_2) crystals. Their different morphologies reflect their internal crystal structures, trigonal and cubic respectively. (B) The bottom side of a c-axis Czochralski grown lithium niobate crystal that was rapidly heated to cause it to separate from the melt surface. The resulting dendritic-like structure reveals the internal three-fold symmetry along the axis of this rhombohedral crystal.

Heterogeneous Substances (1876 and 1878) [12], included both the first and second laws of thermodynamics and thermodynamic reaction tendencies in any thermodynamic system. His graphical representations, the earliest phase diagrams, have been expanded through the years to include numerous chemical systems of both academic and industrial interest. These were derived largely by experimental studies but also in recent years by numerical simulations. These “phase diagrams” are vital data sources for the crystal grower, enabling him or her to select the most appropriate growth method and produce a crystal with the desired composition and properties.

To form a crystal, a nutrient phase (i.e., liquid, gas or solid) must be in a metastable state. In other words, the free energy (at constant volume) or the Gibbs potential (at constant pressure) of this phases must exceed that of the crystal. This excess is the driving force for crystallization. This metastability is accomplished by either supercooling a melt or supersaturating a solution or vapor phase. During crystallization, latent heat is evolved. Among other remarkable contributions made by Gibbs was that nucleation phenomena resulted from heterophase fluctuations in metastable homogeneous phases. Nucleation can be either homogeneous (from within the pure matrix phase) or heterogeneous (on a foreign substance such as particles or substrates within the matrix phase or the container walls). The maximal amount of supercooling or supersaturation required depends on the thermodynamic properties of the material system, various external forces such as mechanical vibrations, and of course, the nature of the crystal surface, etc. In practice, the initial nucleation stage is often bypassed by using oriented seed crystals.

1.2.3 The Twentieth Century

In the opinion of K. Jackson [13], our modern understanding of crystal growth processes began with the research work of Harold Wilson (1874–1964) [14] and Martin Knudsen (1871–1949) [15]. Wilson’s work in 1900 concerned the velocity of solidification and viscosity of supercooled liquids, whereas Knudsen’s work involved kinetic molecular theory that much later played an important role in molecular beam epitaxy. One of the most important early growth theories was proposed in 1921 by the German physical chemist Max Volmer (1885–1965) and his student Immanuel Estermann (1900–1973) [16]. Their adsorption-layer theory (i.e., layer-by-layer growth) was deduced from measuring the tangential growth rate of plate-like mercury crystals from the vapor state at low temperatures. The proposed adsorption-layer lies between the crystal and nutrient phase, with the crystallizing species losing only part of their latent heat, while maintaining some surface mobility in the layer parallel to the crystal surface. The species are incorporated into the crystal lattice at the edges of the incomplete atomic layers (steps on the growing crystal face). Volmer was also the first to consider the role of ad-atoms (or molecules) and holes on the crystal surface under equilibrium and nonequilibrium conditions.

Walther Kossel (1888–1956) [17], a German physicist known for his theory of chemical bonding, proposed in 1928 an atomistic view of crystal growth (kinetic theory), as

opposed to a “continuum” thermodynamic interpretation. It was similar to that independently proposed by Iwan N. Stranski (1897–1979), [18] a Bulgarian physical chemist, and was based on earlier diffusion theories concerning mass transport of the crystallizing species to the growth interface with the distinction that what went on in the interface region (how the species found an appropriate lattice site) was *not* a negligible effect. Their work is often linked together as the Kossel–Stranski model. They both concluded from early work on the rock salt structure that no other planes but the cubic ones are possible and that other planes (110, 111, etc.) are not present on the surface as complete planes but are made up of alternating (001) and (100) faces several atoms thick (kinetic roughening). This work led to what is commonly referred to as the TLK (terrace-ledge-kink) model where Kossel [19] suggested that incorporation of an atom required that the steps spread laterally across the surface. Somewhat later came the work of Stranski’s younger colleague Rostislav Kaishev (1908–2002) linking the equilibrium crystal shape, i.e., the facets making this shape, with the average work required to detach a molecule from that facet, and thereby accounting for different structural positions on that facet and its edge. Stranski and Kaishev founded the famous Bulgarian school of nucleation and crystal growth (see Ref. [20]). Much of their work was on low-temperature aqueous solution growth and the crystallization of metals at room temperature in electrolyte solutions. An extensive discussion of Kossel and Stranski’s work, together with other contemporaries, is given in Buckley’s book *Crystal Growth* [21] and numerous other more recent publications.

The goal of scientific studies is the development of effective models that can explain observable physical phenomena and direct practical crystal growing via generalized predictive relationships. These activities were both based on scientific inquisitiveness and to provide guidelines for practitioners to produce material for the benefit of mankind. Basic studies on nucleation and crystal growth have greatly expanded over the years. Older theories and concepts have been refined and new concepts proposed and tested. Basic understanding has greatly benefited from important advances in crystal characterization technologies. They have provided direct evidence of crystal perfection and growth behavior down to the atomic scale. Two examples are the transmission electron microscope and in situ atomic force microscopy. The former technology makes possible the imaging of atomic structures of real crystals, allowing a study of their perfection and the nature of their imperfection. Atomic force microscopy can be used, to great effect, both to study the formation and kinetics of growth layers during solution growth (particularly biological macromolecules) and how they change upon post-growth heat treatments (surface reconstruction). Reflected beam electron microscopy has also been very useful.

The discovery of crystalline imperfections such as edge and screw dislocations, stacking faults, point defects and inclusions in an otherwise uniform crystal lattice, has had a strong impact on our understanding of crystal properties, on the one hand, and crystal growth mechanisms on the other. They are also of great technological importance for the influence they have on the electronic and mechanical properties of a material.

In 1934, Sir Geoffrey Taylor (1886–1975), a noted British physicist and mathematician, proposed that the *plastic* deformation of ductile materials could be explained in terms of the theory of dislocations developed by Vito Volterra in 1905. Some years later, the subject of dislocations occupied the thoughts of Sir Charles Frank (1911–1998), an eminent British crystallographer who spent much of his career at Bristol University. His fundamental contributions to the field of crystal growth include the laws governing dislocation branching, the existence and properties of dislocation networks, and in 1950, the Frank-Read mechanism for the generation of dislocations. In a well-documented account, the idea for this latter mechanism occurred to both Sir Charles and to W.T. Read (an American working at the General Electric Co.) independently and at the same time. Frank had shown the year before [22] that two-dimensional nucleation theory failed significantly to explain observed high crystal growth rates at low supersaturation. This discrepancy could, however, be readily reconciled if the growth face contained a screw dislocation outcrop. That this dislocation should lead to continuous step generation in the form of a “growth spiral” step on the growth face was immediately validated by experimentally observed growth spirals formed on actual crystals (i.e., Refs [23,24]).

Some of the important work on crystal symmetry in modern times was done by Donnay and Harker in 1937 [25] and later by Hartman and Perdok [26]. Hartman and Perdok’s theory [26] classified different types of faces, with only one type forming crystal facets. For ionic crystals, they defined the energy released during growth of a layer as $E(hkl)$ and were able to generate growth forms by assuming that $E(hkl)$ was proportional to the growth rate. These calculated forms were similar to natural or manmade crystals such as zircon, garnets, etc. Many researchers before and since have also observed variations from predicted or expected crystal morphologies due to impurity adsorption on a growth face. That led to methods to alter the morphologies for a specific application, one example being the purposeful poisoning of a fast-growing needle axis to make a more equiaxed crystal. Other notable contributions to our understanding of growth shapes include those of Sunagawa (1960) [7] and Bennema (1980) [27].

A major effort to control the purity and dopant uniformity in Si and Ge electronic devices was begun at Bell Laboratories in the early 1950s. The research team of Burton, Prim and Slichter came up with a relationship that described how impurities and dopants are distributed along an as-grown boule (the now well-known BPS equation). Their work was first reported in 1952, but not openly published until 1953 [28]. Measuring solute concentrations, solid–liquid distribution coefficients, diffusion coefficients and solute distributions in actual crystals, they derived equations describing what the concentration of a dopant or impurity would be in an as-grown crystal as a function of its initial melt concentration and growth rate R .

$$K_e = K_o/K_i + (1 - K_o)\exp(-R\delta_D/D) \quad (1.1)$$

where K_e is the effective segregation coefficient, K_o is the interface or equilibrium segregation coefficient, R the growth rate, δ_D is the diffusion boundary layer thickness and

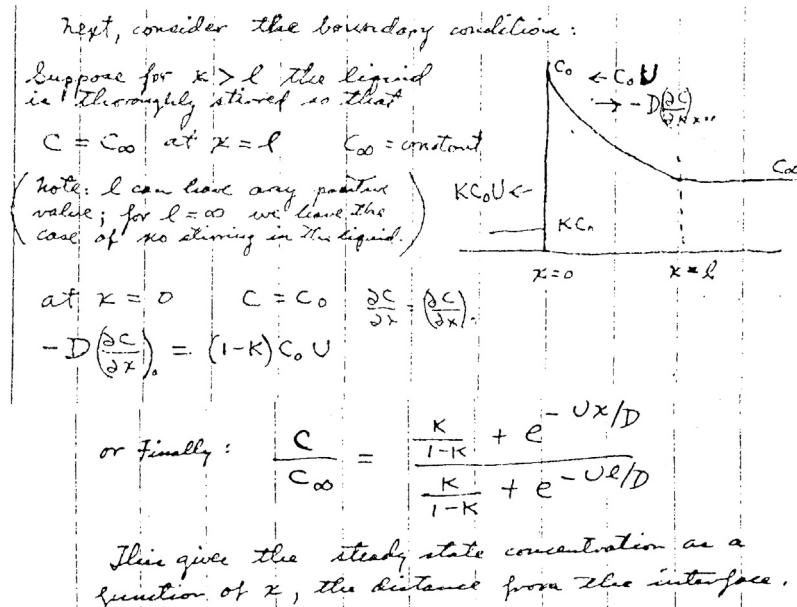


FIGURE 1.2 One of the diagrams in J.A. Burton's laboratory notebook (1951) explaining the concept of the BPS theory. The plot shows the variation of solute concentration in the solid and melt during unidirectional solidification. The $x = 0$ position is the growth interface while $x = l$ defines the width of the solute boundary layer [29].

D is the solute diffusion coefficient. Figure 1.2 shows a sketch and notes from Burton's laboratory notebook illustrating the features of the now famous segregation relationship.

This research was part of a larger effort amongst various semiconductor scientists and engineers at Bell Laboratories [29,30]. Since then, BPS segregation theory has become a particularly valuable tool for crystal growth practitioners, allowing them to control the compositional uniformity in single- and multi-component material systems via control of growth velocity, melt composition, fluid convection, etc. While BPS theory is useful for well-behaved systems, it does not work in all cases. A critical analysis of the limitations of the BPS theory and later modifications by various scientists was given by Carruthers [31] (from the standpoint of the mother liquor hydrodynamics) and by Chernov [32] (from the standpoint of equilibrium and nonequilibrium processes at the growing interface). See also Handbook chapter "Segregation and Component Distribution" for a description of the limitations of BPS segregation theory.

As mentioned in the introduction, the Faraday Society in 1949 convened one of its meetings for the sole purpose of presenting and discussing papers on crystal growth. This was the first scientific conference devoted to this topic as a separate subject. Subsequently, the proceedings of this conference, entitled *Crystal Growth*, were published in the Discussions of the Faraday Society. During that meeting, Burton and Cabrera [33] presented their research on the influence of surface structure on the rate of

growth of a perfect crystal. They considered two types of surface structures, one ordered (atomically flat) and the other disordered (stepped, containing terraces, ledges and kinks with ledge heights of atomic dimensions). Burton and Cabrera made use of the analogy between the existence of these two surface structure types and two possible states in two-dimensional systems-ordered and disordered *phases*, transferring from one to another as the temperature/binding energy ratio changes. This concept followed the 1945 suggestion by Yakov I. Frenkel that the step should be disordered and possess a kink configuration at nearly each atomic site. As a result, these steps should grow much faster than a step-free terrace. Indeed, only at the kink configuration can an atom join the crystal lattice, and thereby reduce its Gibbs potential to that of any of the bulk atoms in the crystal. In the simple cubic system, for example, only the (110) and (111) faces are flat, all others are stepped [17]. The growth proceeds by the attachment of atoms at Kossel–Stranski kinks along the step ledges [34], but not on the terraces, which do not participate in the growth phenomena. Therefore, on the flat, ordered surface of a perfect crystal, growth will not proceed until a small island or cluster nucleates on the surface, thus producing a step loop that is kinked by thermal fluctuations. The stability of such a cluster is given by the Gibbs–Thomson relationship that describes the cluster's solubility. If the cluster reaches the critical size, it may expand, generating a new lattice layer. Thus the nucleation frequency (very low at low supersaturations) determines the ordered face propagation rate. If one considers a nonperfect lattice, where the surface contains defects, such as screw dislocations [22], twins, etc., growth can proceed without the necessity for surface nucleation due to the defect providing growth steps.

Burton and Cabrera also examined the kinetics of vapor phase growth on these surfaces, considering the diffusion of the adsorbed atoms across the close-packed crystal surfaces (terraces), where secondary nucleation is required. This was a refinement of the earlier two-dimensional nucleation model proposed by Becker and Döring in which surface diffusion [35] was not taken into account. Combining their results with Frank's theory concerning the presence of spiral dislocations that can act as growth steps on otherwise atomically flat surfaces, they published together a seminal paper from which the well-known BCF theory derives [36]. In this theory, developed for vapor growth but later extended to solution growth, the boundary between the crystal and nutrient phase was considered to be sharp (interface of zero thickness), i.e., as proposed by Kossel–Stranski, rather than by Gibbs's finite layer thickness model. In this case, atoms or molecules belonged to only one or the other phase. The BCF theory of layer-by-layer growth of the crystal lattice on smooth surfaces was quantitatively confirmed in numerous studies of growth from solutions, including electrocrystallization.

In the ensuing years, interface structure and surface kinetics models have been refined to include more complex interfaces, including material systems such as biological macromolecules [37]. These and other crystals with large lattice spacings grown from room-temperature solutions have made it possible for *in situ* atomic force microscopy to capture spiral dislocation sources generating new layers during solution growth, as well as the important phenomena of step bunching, low kink density at steps,

etc. Nevertheless, this theory provided the crystal growth field with a more sound theoretical foundation together with a better understanding of experimental results. It formed an important base from which future studies could be built upon.

The roughening concept was employed in 1958 by Jackson [38] to consider the problem of why many melt-grown crystals of nonmetals had specific faceted, euhedral shapes, whereas metal crystals did not. He derived an elegantly simple theory for the solid–liquid interface structure that could successfully explain and predict experimental results. Jackson used a two-layer Bragg–Williams statistical model (rather than the BCF Onsager model) taking into account nearest neighbor bonds into the solid and lateral bonds within the solid–melt interface. The free energy for adding atoms to a singular (or atomically smooth) interface is calculated until a complete monolayer is formed. Starting with the change in excess free energy associated with randomly adding atoms to such a surface, Jackson found the following relationship for solid–liquid transitions.

$$\alpha = (L/KT_e)(\eta/v) \quad (1.2)$$

where L is the change in internal energy associated with the transfer of one atom from the bulk liquid to the bulk solid (latent heat), η is the maximum number of adatom nearest neighbors on the surface, v is the total number of nearest neighbors of an atom in the crystal, and T_e is the equilibrium temperature for the phase change. This so-called Jackson “ α factor” consists of two terms: the first is essentially the entropy of melting divided by the gas constant and is a materials parameter, and the second depends on the crystal structure and specific surface under consideration. The crystallographic term is maximum for close-packed planes, and always <1 . It has values of $2/3$ for a (100) simple cubic, structure and $1/2$ for (111) fcc and (110) bcc structures. Materials with $\alpha < 2$ grow with nonsingular interfaces, whereas materials with $\alpha > 2$ exhibit facets on the growing interface. The former are often metals, with simple centro-symmetric crystal structures, whereas the latter are materials with more complex crystal structures. Using transparent systems having different values of α , Jackson and Hunt [39] were able to demonstrate experimentally the efficacy of their model. Figure 1.3 shows the crystalline morphologies observed for high and low α factor materials. A comparison of the BCF and Jackson models was given by Woodruff [40]. In 2004, Chernov [37] discussed how interface growth kinetics has advanced during the past 50 years.

In the years following, interface structure and surface kinetics models were refined to include more realistic interfaces where each interfacial atom cannot be ascribed to one or the other phase. Instead, this disordered interface is viewed as a layer several atomic spacings thick, where all atoms move randomly and, on average over time, realizes continuous transition between the fully ordered crystal bulk and the disordered melt. This approach allowed for the prediction of a kinetic coefficient linearly connecting the supercooling ΔT at the rough crystal–melt interface to its growth rate V for simple liquids, like metals.

$$V = A\sqrt{kT/m}\Delta T/T_e. \quad (1.3)$$

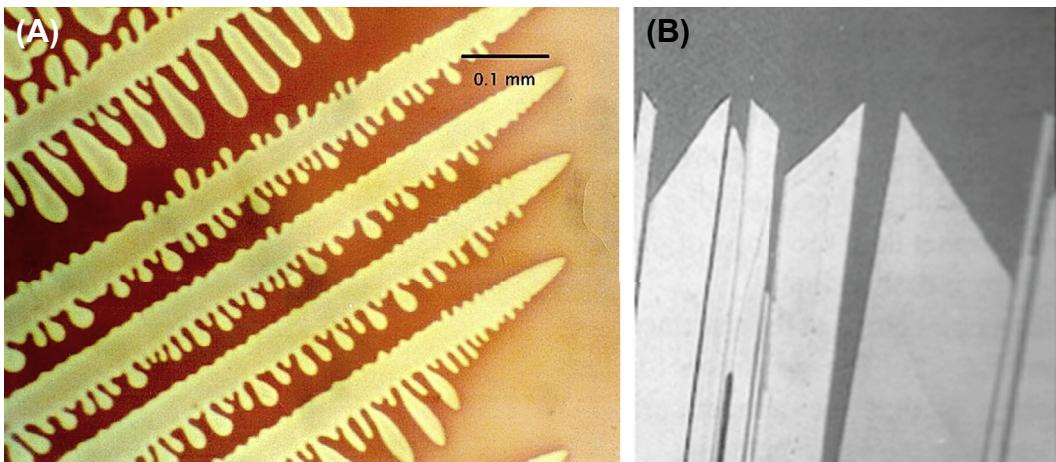


FIGURE 1.3 Comparison of crystal morphologies for (A) a transparent metal analog with an α -factor less than 2. This material grows with a dendritic structure and (B) a benzyl crystal with an α -factor greater than two showing well-developed facets.

Here m is the mass of the atom while the numerical coefficient A is determined by the structure of the liquid and is close to unity. All in all, the BCF theory and its further development provided the crystal growth field with a more stable theoretical foundation together with a better understanding of experimental results. It formed an important base from which future studies could be built upon.

In 1953, research to elucidate and quantify the nature of interface instabilities during crystal growth began with the work of Canadian metallurgists Rutter and Chalmers [41]. They postulated that the cellular (honeycomb-like) substructure that formed in solidifying metals containing a small concentration of impurities (as revealed by rapid melt decanting) was due to some type of instability at the growth interface. This led to the idea that a boundary layer containing rejected impurities develops at a growing solid–liquid interface, depressing the melting point of the liquid in that region so that it became supercooled, but at a higher temperature than the interface. The now well-known term “constitutional supercooling” was derived from Chalmers studies.¹ Shortly thereafter, William Tiller, observed banding in lead crystals arising from unintentional variations in the translation rate (hence growth rate). The structural banding was also found to be associated with the boundary layer composition. Professor Chalmers charged his group to develop a mathematical expression for what was happening at the interface to cause these interesting interfacial instabilities. Their discovery was published later the same year [42]. Their simple

¹G.P. Ivantsov working independently in Russia in the late 1940s postulated the same concept, calling it “concentrational” supercooling (Dokl. Akad. Nauk. SSSR 81 (1951) 179).

relationship for constitutional supercooling provides one of the most useful tools in the crystal grower's arsenal. The relationship, Eqn (1.4) below, shows how the ratio of temperature gradient in the liquid (G) to the growth velocity (R) must remain above some critical value to achieve stable growth. That value depends upon the material properties of the growth system, i.e., the initial melt concentration C_o (far away from the interface), the slope of the liquidus curve (m), the segregation coefficient (k_o) and the diffusion coefficient. To maintain stable growth and avoid constitutional supercooling one requires that

$$G/R > mC_o(1/k_o - 1)/D \quad (1.4)$$

For the crystal grower this means that to produce a crystal without second phases and cellular structure one *must* either decrease the growth rate for a given temperature gradient or increase the temperature gradient. Faster growth rates are typically very desirable, and so many efforts were undertaken to build special furnaces, sometimes incorporating baffling, localized cooling, etc., to achieve steep thermal gradients.

The early roughening transitions models were two-dimensional models based on the Onsager (BCF) or Bragg-Williams (Jackson) models. It was found that computer modeling was needed to study the problem in more complex three-dimensional systems. Leamy and Gilmer [43] were the first to produce simulated computer images both above and below the surface roughening transition. They also determined the free energy (F) of a growth step for various values of Jackson's α -factor [44]. They showed that F for the step goes to zero at the roughening transition and therefore does not require an energy barrier for new layer formation.

Molecular dynamic simulations have provided detailed information about the process of crystal growth at the atomic level. Its use in morphological stability problems was taken up by numerous groups over the ensuing years which, coupled with experimental work, has led to a significantly greater understanding of the crystallization process (see Figure 1.4).

Modern concepts of interfacial and morphological stability are largely based on the 1963 work of Mullins and Sekerka [45]. Whereas previous researchers knew that various perturbations during growth such as mechanical vibrations, temperature fluctuations, etc., could lead to interface instabilities such as cells and dendrites, they were unable to explain the dynamic mechanisms that were responsible. Mullins and Sekerka developed a mathematical theory of linear morphological interface stability. This was based on small perturbations (sinusoidal ripples) on the growth plane in an unstirred melt that either decay or grow with time. Their analysis led to a more refined relationship that considered the destabilizing effect of the diffusion field and the influence of surface free energy on the boundary conditions. Their results extend the constitutional supercooling criterion described in Eqn (1.3), with several extra terms affecting interface stability [42]. Linear stability theory proves that constitutional supercooling is the correct criterion in the limit of disturbances with small wavenumbers (long wavelengths). The important

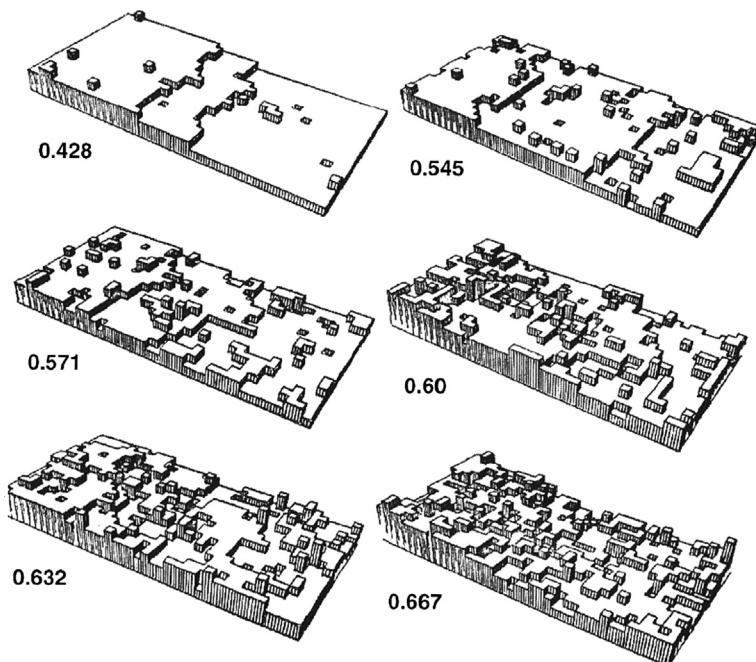


FIGURE 1.4 Monte Carlo simulations of equilibrium surface structures (microstates) for a simple cubic crystal as a function of temperature (as KT/ϵ) [44]. The surface orientation is the $(20,1,0)$ and at the lowest temperature, $KT/\epsilon = 0.428$, the step edge is clearly rough. As the temperature increases, the roughness increases. At a critical value, the thermal roughening transition, the steps become indistinguishable.

crystal growth/materials parameters affecting interface stability are the temperature gradient normal to the growing interface, the slope of the liquidus from the phase diagram, the growth velocity, latent heat, mass and interfacial energy densities and the thermal conductivities of the liquid and solid. It was also found that stability depends on whether the thermal conductivity of the melt is greater or less than that of the solid. Other researchers expanded on this research to include molecular attachment kinetic effects, interface energy anisotropy, nonlinear effects, etc., among them V. Voronkov [46] whose independent investigation on mosaic and cellular structures actually predated that of Mullins & Sekerka. John Cahn [47] was the first to treat anisotropic surface tension and interface attachment kinetics (for a spherical geometry). Coriell and Serkeka [48] studied the same types of anisotropies for a planar interface. Chernov [49] treated the case of strong anisotropies and Hurle [50] analyzed the influence of melt convection.

Historically, understanding crystal morphology has provided much of the impetus driving theoretical crystal growth studies. Aside from the regular crystalline forms found in nature (e.g., quartz) or produced during solution or vapor growth in the laboratory, other more complex crystalline morphologies such as dendrites and multiphase eutectic systems have stimulated researchers to uncover the underlying mechanisms involved in their creation.

Dendrites are “tree-like” branched crystal structures that grow in various media under unstable growth conditions. The earliest humans were sure to have noticed and pondered the reason behind the large variety and symmetry of the beautiful snowflake. Snowflakes form when microscopic supercooled cloud droplets freeze and their morphology is dependent on the ambient conditions during their growth. Dendrites also can form during the crystallization of metals, inorganic and organic compounds and even biological macromolecules from melts and solutions. They are common in metals and alloys grown from the melt in shallow temperature gradients.

Dendrites typically contain a stem terminating in a tip and side branches along the stem (see Fig 1.3a). Growth proceeds by steady-state propagation of the tip and a time-dependent crystallization of secondary and tertiary side branches. In 1947, G.P. Ivantsov [357] was the first to identify these self-reproducing crystal shapes—like paraboloids, the basis of the dendrite tip. In pure materials, growth is controlled by diffusion of latent heat away from the advancing growth interface, and in impure systems and alloys it is driven by solute buildup at the interface and where chemical diffusion dominates over thermal transport. In 1960, Temkin [51], and shortly afterward Bolling and Tiller [52], described the role of thermodynamic and kinetic driving forces in the dendritic growth of pure materials. From that time onward, theoretical and experimental dendritic growth studies have proceeded, relying on newer mathematical and computational approaches. Hamilton and Seidensticker [53] examined the role of twin planes in the rapid dendritic propagation of germanium crystals on the basis of re-entrant corner nucleation. In 2004, Glicksman and Lupulescu [54] reviewed 40 years of progress toward understanding the mechanisms involved in the dendritic growth of pure materials including low gravity experiments. An update on this subject is provided in the Handbook chapter “Dendritic Growth.”

Growth of polyphase alloys or compounds by unidirectional solidification has also been the subject of much interest to crystal growth researchers. These structures can be produced from eutectic ($L \rightarrow \alpha + \beta$), monotectic ($L_1 \rightarrow \alpha + L_2$) and peritectic ($L + \alpha \rightarrow \beta$) three-phase melt systems. A eutectic crystal can contain four types of structures within a matrix phase (1) parallel lamellar, (2) parallel rods, (3) globular particles of regular shape and (4) irregularly shaped particles. Researchers were interested in the relationship between growth velocity on lamellar spacing and interface undercooling. R. Vogel [55], in 1912, was the first to postulate that growth occurred by both phases growing simultaneously. Eutectic growth theory, however, remained largely qualitative until 1957 when Tiller [56] introduced his diffusion model of eutectic growth. This development was based on the earlier theory on eutectoid growth by Clarence Zener (1905–1993). Tiller’s work was used as a basis for Jackson and Hunt’s model of 1966 [57], a well-known model and one often used as the basis for later papers. Readers interested in this topic are directed to Glicksman’s book [58] that provides, among other crystal growth topics, an excellent review on progress in eutectic solidification.

The transport of heat and mass during crystal growth is of great importance in the design of a growth process and in understanding the resulting features found in the

crystals produced. In melt growth, the dominant factor is often heat transport, whereas in solution and vapor growth, mass transport normally dominates. As to which transport mechanism dominates, it is a matter of degree and an important consideration is what happens in the boundary layer near the interface. As a crystal grows, latent heat is evolved and the allowable growth speed depends on its removal. Therefore, the geometry of the system, the thermal properties of the crystal, the ambient atmosphere and the growth rate all comprise important factors. In addition, the growing crystal needs fresh nutrient to sustain its growth and the rates at which various species reach the interface will partly determine the maximum allowable growth rate and crystal perfection. The concentration of dopant and/or impurity species are often different in the interface region than in the bulk medium, thus influencing mass transport. Instabilities in heat and mass flow can lead to defects such as striations and interface breakdown. The degree and nature of melt convection will strongly affect both the growth process itself and the crystal produced. Many processes, for example Czochralski growth, use forced convection (crystal rotation) to enhance the growth rate and improve thermal and crystal homogeneity, whereas in other methods, for example, vertical and horizontal Bridgman growth, natural buoyant convection occurs from thermally and solutally induced density gradients. In Czochralski growth, the crystal is rotated and sometimes the crucible as well. W. Wilcox [59] and J. Carruthers and K. Nassau [60] studied the fluid dynamic behavior of such systems, as did many other researchers. The effect of fluid flow and flow instabilities are also important in other melt growth processes such as unidirectional solidification, vapor deposition and solution growth. See also Handbook chapter “Segregation and Component Distribution.”

Defects, inhomogeneities, segregation, and interface effects during crystal growth have all been the subject of numerous studies. Some useful reviews have been provided by D. Hurle and P. Rudolph [61] and C. Wang et al. [62].

1.3 Crystal Growth Methods

Crystal growth technology is mainly an applications-driven field. In the last 60 years or so, the major applications have been in the fields of electronic and optical materials. Crystals, however, can be prepared from all types of materials including elements, alloys and inorganic, organic and biological compounds. The compounds can vary from simple binary mixtures to multicomponent systems having numerous components and complex molecular or crystal structures. As a result, crystal growth methods vary widely depending on the thermodynamic and kinetic properties of the system of interest. The starting point for developing a viable crystal growth process begins with a thorough knowledge of the phase relations of the system under investigation. For example, we need to know whether the compound melts congruently, has a phase transformation below its melting temperature, has a high vapor pressure, etc. The most appropriate strategy for producing a crystal depends on the size required, purity and an ability to

control its defect structure (either by elimination, neutralization or incorporation). Crystal dimension requirements (size and shape) are a very important issue in determining the methodology. Single crystals can be grown in bulk, thin film, particulate and fiber form and from the nanometer scale up to meter dimensions. During the last decade, nanoscale wires, whiskers and quantum dots have been found to have unique properties, and this has opened up the possibility for new and improved devices for advanced applications. Classical single crystal growth methods and newer techniques have been used to create a variety of desired nanostructures.

The number of crystal growth methods available to the crystal grower is quite large and varied. The simplest approach to categorizing them is by the nutrient phase from which the crystal is grown. Single crystals can be grown from (1) a liquid phase (melt or solution), (2) from a vapor phase (condensation, sublimation or reaction) or (3) from within a strained solid. Each method has certain advantages and disadvantages that depend on both the properties of the material system involved and the application requirements. Melt growth methods are generally preferred to other methods wherever possible, while solid-state growth methods are the least useful from a commercial point of view.

The growth of a crystal from any nutrient phase requires either a seed crystal or the creation of a solid interface within the growth medium by homogeneous or heterogeneous nucleation. Homogeneous nucleation requires additional energy in the form of supercooling in melt growth or supersaturation in solution and vapor growth methods. Wherever possible, however, the use of a seed crystal or a compatible substrate (as in thin film growth) is desirable. We will explore some of the strategies that have been employed by growers to prepare very high quality, high performance materials.

The theoretical studies mentioned above range from fundamental questions about the mechanisms involved in various crystallization environments to computer simulations of actual growth systems. Issues such as growth rate anisotropy, component segregation, interface faceting, stability and morphology, fluid dynamics, thermal stability and gradient effects, etc., have been extensively studied. During the last decade in particular, computer modeling has helped growers design and modify growth systems in a more systematic way to create thermal and fluid flow environments to enhance interface shape, stability and growth rates.

1.3.1 Melt Growth

When a material melts under nearly congruent conditions and has no low-temperature destructive phase transformations, it is usually desirable to prepare a single crystal of it directly from its melt. Often seed crystals are used to control the orientation and to take advantage of growth rate and thermal anisotropies (heat and expansion). The most useful methods include the Czochralski, Bridgman–Stockbarger, Kyropoulos, Verneuil (flame fusion), and float zone methods. There are innumerable variations to these

general techniques such as the heat exchanger method (an inverted Kyropoulos configuration) and the pedestal growth and micro pull-down techniques to name a few. The discussion of melt growth will begin with the oldest technique for growing large crystals from a melt: Verneuil's flame fusion method.

1.3.1.1 *The Nineteenth Century and the Verneuil Process*

Alchemists were not only trying to transmute base metals into gold, they were also attempting to grow gemstones in the laboratory. From the beginning of the nineteenth century, various researchers were attempting to grow crystals of diamond, emerald, ruby and sapphire by various techniques, particularly by melting various oxide mixtures. These early methods, however, only produced small crystallites. A really viable commercial process did not appear until the work of Auguste Victor Louis Verneuil (1856–1913) on the growth of large ruby crystals was made public in 1902. Actually, he developed the now well-known flame fusion process a decade earlier and spent the next decade improving the method before making it public knowledge. A very thorough description of the life and work of Verneuil was given by K. and J. Nassau [63]. Verneuil (see Figure 1.5(A) below) was a French “renaissance” man and well-beloved teacher, actively interested in music performance and art and whose accomplishments spanned many different areas of chemistry. He became interested in chemistry working in his father's photography shop (his father changed careers after meeting Mr Deguerre (Louis Jacques Maude, 1787–1851), the inventor of photography. In 1873, at age 17, Verneuil went to study in the chemical laboratory of the distinguished Professor Edmund Frémy

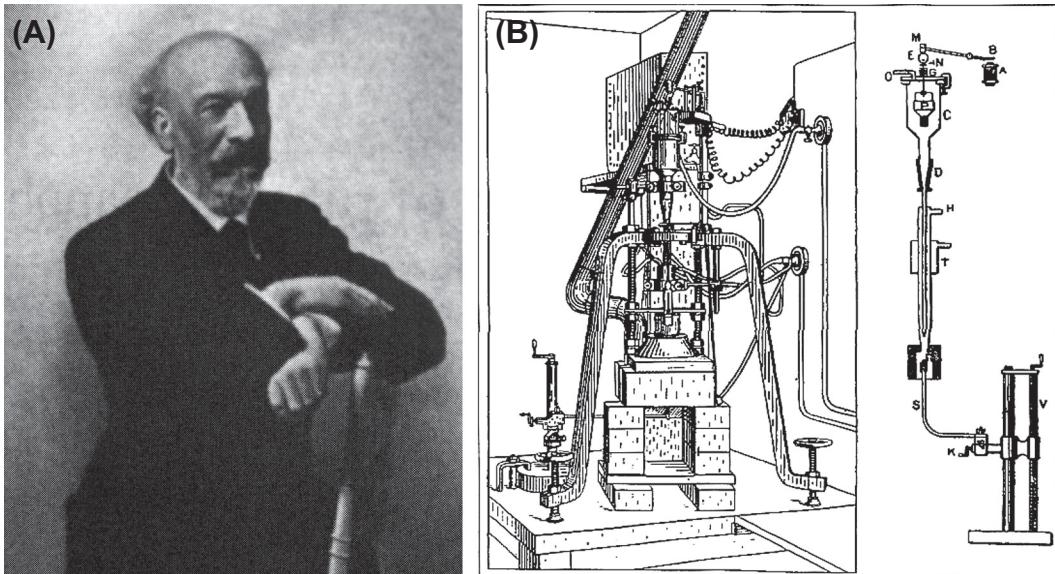


FIGURE 1.5 (A) A photograph of Dr. A.V.L. Verneuil, and (B) a schematic diagram of Verneuil's crystal growth apparatus [63].

(1817–1894). He eventually earned his doctoral degree in 1886. In his earlier years in the Frémy laboratory, he participated in research on ruby crystal growth by a melting technique using porous alumina crucibles. He also became friends with Henri Moisson (1852–1902) who worked on diamond crystallization in Frémy's laboratory.

In 1886, an unknown group from Geneva started selling larger synthetic ruby crystals than were available elsewhere. It is now believed that these so-called "Geneva Rubies" were actually grown by an early version of the flame fusion process [63]. Verneuil was intrigued by these samples, and it stimulated him to develop the method for which he became famous. The mysterious group from Geneva ceased operation in 1905, not long after the Verneuil Process had gone into commercial production. Such groups have appeared from time to time trying to pass off synthetic crystals for natural stones that garner much greater value.

The flame fusion method was first developed to produce large, high-quality ruby for the gemstone market and also for watch bearings. The process, which is still in use today, involves passing a powder of the compound through a vertically aligned oxy-hydrogen flame. Molten droplets descend by gravity onto a rotating alumina pedestal containing the growing crystal and the crystal grows upward on the pedestal. The basic apparatus used by Verneuil is shown in [Figure 1.5\(B\)](#). Temperature gradients are steep, boules are prone to cracking and the early powder delivery systems were often unreliable. Important processing refinements were made by Verneuil over his lifetime to improve the process reliability and crystal quality. The first problem he solved was the severe cracking problem. He accomplished this by reducing the contact area of the boule with the pedestal. While preventing cracking, the boules after growth were still highly strained. This strain was relieved naturally when the boules split in half or were split by hand. Powder delivery was done by mechanical tapping mechanism mounted on a hopper containing the charge powder. For ruby growth, the powder Verneuil used was a mixture of ammonium and chrome alums. The chromium oxide concentration in the boules was ~2.5%. The oxygen content in the ambient gas phase was critical for achieving the appropriate oxidation state in the crystal. A flame rich in hydrogen and carbon was necessary to prevent introduction of gas bubbles in the molten ruby melts.

In 1909, Verneuil worked with L. Heller & Son of New York and Paris on developing his process for making blue sapphire. Instead of chromium additions, the sapphire was doped with a mixture of iron and titanium oxides, two impurities found in natural minerals. He suggested that the titanium in the crystal gave the deep blue color by converting the ferrous ions created by the flame back to ferric ions. Another pioneer of the flame fusion growth method was Leon Merker (1917–2007). He also worked with the Heller Co. starting during the early days of World War II, after he escaped fascism in Europe and came to the U.S. to study at the University of Michigan. Based on a friend's recommendation, he met Mr Heller from France. After some fruitful discussions, Heller assigned Merker the task of setting up the Verneuil Process for ruby and sapphire in New Jersey. The venture was successful and the General Synthetics Corporation was formed

in 1941 to provide ruby to the military and for the gem industry [64]. Merker also worked on barium, calcium and strontium titanates; the latter two with greater success.

Since Verneuil dedicated much of his career to the successful development of a commercial process for growing sizable crystals with controllable properties, he might be considered the father of the commercial crystal growth industry.

1.3.1.2 *The Twentieth Century*

Even while Verneuil was improving on his method, other researchers at the turn of the century were beginning to produce crystals in the laboratory to study both their solidification behavior and physical properties.

One of the earliest was Gustav Tammann (1861–1938). He was born in Russia of Baltic and German parents and spent most of his life in Germany. Among other notable achievements, he established the first Institute of Inorganic Chemistry in Germany at Göttingen University in 1903. Tammann's interests led him to study the solidification of metal alloys and their nucleation behavior. He made important contributions to the fields of heterogeneous equilibria, crystallization and metallurgy. One of his important contributions to crystal growth involved the solidification of metal alloys in long narrow tubes tapered to a point to both confine nucleation and supercooling to a small volume and thereby promoting the propagation of a single crystal along the tube [65]. He was probably one of the first to understand the relationship between grain selection and growth rate anisotropy and the concept of confining the melt to control the number of grains that form. His method would be classified today as the gradient freeze method. He also grew crystals of a number of organic compounds and studied their crystallization behavior.

Within the same time period, Obreimov and Schubnikov from Saint Petersburg, Russia, [66] published a paper describing the growth of metal crystals using a modification of Tammann's method, i.e., in a long glass tube with an imposed temperature gradient along its length. They also briefly discuss the easy to operate Czochralski process (to be discussed below) but rejected it in favor of the Tammann's method because the free-standing Czochralski crystals were not of uniform shape and some of the low-melting metals could deform during growth without being supported. In their experiments, they used a vertical cylindrical tube tapered at the bottom like Tammann. Nucleation was achieved by cooling the tapered tip with cold air and then, after crystallization in this region was accomplished, slowly cooled the furnace to propagate the crystal up the length of the tube. Both these methods distinguish themselves from the Bridgman and Stockbarger methods (also to be discussed later) in that growth is not achieved by moving either the ampoule or furnace to solidify the melt.

1.3.1.3 *The Czochralski Crystal Pulling Method*

1.3.1.3.1 **The Invention**

Following Verneuil's pioneering work, a number of other researchers began to grow metal and alkali halide crystals for property studies. In 1918, Jan Czochralski, a well-known young Polish metallurgist (head of AEG's metals laboratory in Berlin), published a

paper [67] that would describe a technique that quickly became one of the most powerful methods for growing crystals in use today. In a story related by Tomaszewski [68], Czochralski, while working late at night in his laboratory, discovered by accident the crystal pulling method for which he became famous. His studies concerned the crystallization rate of metals and while working on his experimental notes, instead of dipping his pen tip into the ink well, dipped it instead into a crucible of molten tin on his desk. When he pulled it out he found a long filament of solidified tin on the end. He subsequently found it to be a single crystal. He then realized the value of studying crystallization rates using such a device. His early apparatus (see Figure 1.6(A)) consisted of a clock-motor-driven lifting mechanism. Replacing the pen tip, a short tapered glass rod with a hook on the end was held on a silk thread connected to the pull mechanism. The rod could be raised or lowered in a continuous fashion. By dipping this rod into the surface of the melt, he was able to solidify metal onto it and pull out crystals of tin, lead and zinc in a continuous and controlled fashion. Czochralski later modified the glass rod, incorporating a capillary at the bottom to draw up the molten metal. This had the effect of restricting nucleation to the limited volume of melt in the capillary. With this apparatus he produced 1 mm thick single crystal wires at maximum crystallization velocities of up to 140 mm/min and in lengths up to 19 cm. Czochralski's life and research accomplishments can be found in Tomaszewski's monograph [68].

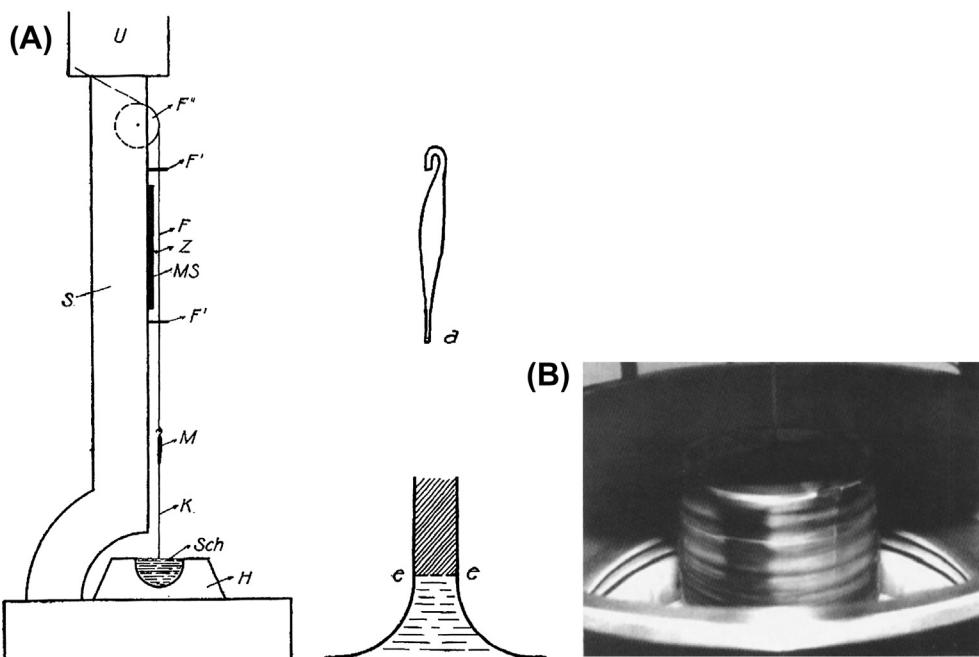


FIGURE 1.6 (A) Czochralski's original experimental setup [67], and (B) a photograph of a five-inch diameter commercial single crystal silicon boule growing by Czochralski's method. (*From the front cover of the AACG Newsletter 13 (1983)—photo courtesy of the Siltec Corp.*)

Czochralski's pulling method was almost immediately put to use by von Wartenberg [69] to grow zinc single crystal wires onto oriented seed crystals. Somewhat later, Von Gomperz [70] pulled single crystal fibers of metals through a hole in a mica plate floating on the surface of the melt. He also used a capillary for seeding. His work was the fore-runner of the edge-defined film-fed growth (EFG) and the laser heated pedestal fiber growth methods. In 1928 E.P.T. Tyndall [71] wrote a paper on the *Factors Governing the Growth of Zinc Crystals by the Czochralski-Gomperz Method*. In 1937, Henry Walther of Bell Laboratories published the first paper on the use of Czochralski's method for the growth of nonmetals [72]. He rejected other methods such as the Kyropoulos method because he was intent on growing long, uniform, cylindrical bars of NaCl single crystals for property measurements. He therefore was attracted to the pulling methods that Czochralski and von Gomperz used to grow low-melting metals. He used a quartz crucible to hold the melt and dipped a platinum rod or closed tube into its surface, sometimes with an oriented seed attached. In the beginning, he used Kyropoulos's method of pulling the tube up slightly after the first melt solidified on the rod to reduce melt contact with the crystalline solid that formed. He placed an air-cooled coil containing small holes above the melt to cool the growing crystal and pulled up at rate of 5 cm/hr while rotating the crystal at 10 rpm. He was the first to apply rotation to the Czochralski method and produced the first bulk crystals of a high melting point compound by this method. Walther successfully produced NaCl boules 2 cm in diameter and 30 cm long. It is rather amazing that this paper, although published in a prominent journal and referenced twice a few years after its publication, was only found very recently (by Reinhard Uecker [73]). Strangely, even many Bell Laboratories researchers from that period to the present time seem to have been unaware of Walther's work, and it was not mentioned in the rather extensive review of engineering and science research in the Bell system during the period 1925–1980 [30]. In 1940 Evans [74] used Walther's method to grow single crystals of NaCl, KCl and KBr.

1.3.1.3.2 Semiconductors

Bardeen and Brattain discovered the transistor in 1947 using large-grained Ge samples produced by unidirectional solidification [30]. Shortly afterward, it was demonstrated that single crystals were better, and this led to a dramatic expansion of the crystal growth field in general, and the Czochralski method in particular. This versatile technique has been applied to a wide variety of materials of commercial importance—particularly semiconductors and optical materials.

According to [30] (p. 422), “A single crystal growth technique, first used by J. Czochralski in 1917, was adapted and improved in 1950 by G.K. Teal and J. B. Little for the growth of single crystals of germanium” [75]. They dipped an oriented Ge seed crystal into the melt surface and, while rotating, pulled modest sized crystals (by today's standards) of 2.5 cm diameter and 10 cm in length. The minority carrier lifetimes were significantly better than in polycrystalline materials, and therefore the semiconductor researchers shifted their efforts to producing bigger and better crystals with control of

the dopant concentrations and uniformity. In addition, the single crystal technique allowed for the creation, during growth, of n-p-n junctions by perturbing the growth conditions [76]. While this junction technique was eventually superseded, it was an important step in transistor technology. The importance of homogeneity in semiconductor devices led many researchers to study the thermodynamic and kinetic aspects of impurity and dopant incorporation. One such seminal study, as mentioned earlier, was that of Burton, Prim and Slichter [28,29]. Shortly after the germanium research activities began, the focus shifted to silicon whose properties were deemed to be superior. In 1952, Teal and Buehler [77] reported on the Czochralski growth of silicon crystals—a much higher melting compound (1414 °C compared with 938 °C for Ge) and more difficult to grow due to its reactivity. Over the years, crystal sizes have constantly increased (see [Figure 1.6\(B\)](#) above), and today commercial systems are available to grow Si boules 12 in in diameter and 6 ft long from which substrates can be cut for the preparation of integrated circuits. In situ recharging to grow longer crystals and controlling melt flows using magnetic fields were added over the years to boost production rates and quality. One of the most important factors in producing high quality crystals was not only to control impurities and other point defects but their complex interactions with each other, as well as with dislocations. Removal of one defect can lead to the redistribution of other defects to lower the overall energy of the system.

It was recognized early on that purity of the starting material was critical to semiconductor performance. In 1951, William Pfann [78] invented the zone refining method for ultrapurifying Ge. This very important method, in wide use today, has been successfully adapted to the purification of all classes of materials. Shortly afterward, Theuerer [30] invented the crucible-free float zone process to grow O₂-free silicon. Oxygen incorporation during Czochralski growth was due to the use of SiO₂ crucibles. Theuerer's method is still in commercial use today to produce O₂-free Si for special device applications. It also has been used with other materials for which melt-crucible interactions are problematic. With the use of optical heating systems (such as lasers or xenon lamps), its simplicity makes it very useful for growing crystals of numerous materials for physical property studies. Pfann [79] also invented the zone leveling crystal growth method that is a combination of horizontal Bridgman growth coupled with zone refining. In this case a seed and a dopant are placed at one end of a horizontal tube and by moving a molten zone along the tube, the dopant could be uniformly distributed along the boule. This method was used early on to produce transistors and diodes.

It became apparent that dislocations were affecting the electrical properties of Si single crystals and the need for zero-dislocation material arose. In 1959, William Dash [80] developed a method for doing this during Czochralski growth. Since dislocations propagate mainly from the seed, he used high-quality seeds together with careful control of the initial growth conditions. He was able to produce dislocation-free crystals by “necking” down the growing boule to a very small diameter before widening it back out to the desired size.

Important advances in both purification and control of crystalline perfection has led to the improved performance of Si devices.

When compound semiconductor materials such as GaAs, InP and their alloys became important to the electro-optic field, special Czochralski techniques had to be developed because they have high vapor pressures at elevated temperatures. In 1962, Metz et al. [81] were the first to report the use of molten B_2O_3 as a melt encapsulant for the Czochralski growth of PbTe. Both Pb and Te are volatile at the compounds melting temperature, and they successfully sought to cap the melt to prevent losses. In 1965, Mullins et al. [82] demonstrated that molten B_2O_3 was also a useful encapsulant for the growth of GaAs and InAs. They were able to adapt a commercial low-pressure Czochralski system for the growth of these compounds. This method is now known as the liquid encapsulation Czochralski (LEC) method. A few years later, Mullins et al. [83] extended their work to include the growth of GaP and InP in high-pressure furnace systems. One problem with group V elements was that when the crystal emerges from the encapsulating layer, it starts to lose P or As from its surface. In 1983, Azuma [84] came up with an innovative approach to inhibit these losses. He used a pressure balancing system to control the partial pressure of P in the InP growth chamber. In the upper chamber was extra P_4 , maintained at a pressure such as to prevent evaporative losses at the crystal surface.

1.3.1.3.3 Oxide Growth

Following the success of the Czochralski method for growing elemental Si and Ge single crystal boules at Bell Laboratories, they and other laboratories started to use this method extensively for growing bulk single crystals of oxide compounds for laser, nonlinear optical, scintillator and numerous other applications.

The laser was predicted by Arthur L. Schawlow and Charles H. Townes in 1958 [30, 358, 359] but not actually demonstrated until the work of Maiman in 1960 [85] with a single crystal ruby rod prepared at the Union Carbide company. In the same year, Nassau and Van Uitert [86] were the first to use the Czochralski's method to grow a high-quality oxide crystal. They prepared laser crystals of Nd:CaWO₄. During the following decade, the Czochralski method was vigorously pursued in many research and industrial laboratories around the World. A wide variety of important optical materials were grown, including LiNbO₃ [87,88], LiTaO₃ [89], Bi₁₂Ge(or Si)O₂₀ and Sr_xBa_{1-x}Nb₂O₆ [90], YAG (Y₃Al₅O₁₂) [91], Nd:YAG [92], Sapphire [93,94], and Gd₃Ga₅O₁₂ (GGG) [95]. Many of these materials are still commercially important. A concise history of oxide crystal growth by the Czochralski method was given by C. D. Brandle [96].

Many improvements to the method were made over the succeeding decades. Compositional variations along the length and diameter were of major importance and stimulated the construction and analysis of related phase diagrams. It was found, for example, that the stoichiometric composition was not always the congruent composition [97] and to get uniformity one needed to shift the composition to the off-stoichiometric congruent composition to achieve homogeneity. Another problem often

encountered was that the shape of the phase field boundary of the compound might be curved instead of straight leading to precipitation of a second phase.

During the 1960s, very little was known about how the growth interface shape could influence crystal quality. This was very important in Si growth where zero-dislocation crystals rely on a particular interface shape. Cockayne et al. [98] were the first to show that interface shape could be modified and controlled by crystal rotation. Nominally, crystals growers find that a slightly convex interface toward the melt is most desirable. Another factor of major importance in melt and solution growth is fluid convection. It affects mass and heat transport and therefore interface shape, boundary layer and growth rate instabilities, etc. In Czochralski growth natural convection and crystal rotation can interact to modify both the interface shape and the composition in the melt near the growth interface (boundary layer). Various researchers have achieved significant improvements in crystal quality by controlling these parameters.

The application of computer modeling to help solve crystal growth problems was begun in the 1980s by Robert Brown and his group at MIT. One example is a paper written by Derby and Brown [99] on the dynamics of Czochralski growth. One of the major tasks of computer simulations is to model the flow regimes in a system in which the thermal configurations are adjustable. In recent years, facilitated by the dramatic increase in computing power, almost all types of crystal growth processes (Bridgman, float zone, etc.) have been modeled. Simulations performed have been very successful in helping design and guide refinements to laboratory and commercial crystal growth process.

During Czochralski growth, the melt level in the crucible drops as the crystal grows. This changes a number of factors including the thermal gradients and convection patterns. Often the temperature has to be changed during growth or some other parameters modified. Whiffin and Brice [100] have shown that melt height can affect thermal oscillations in the melt. These thermal fluctuations can lead to growth rate variations and crystalline imperfections such as striations. A striation is a compositional variation parallel to the growth interface, usually caused by poor temperature control and/or melt oscillations. In the 1960s most growth was carried out manually, i.e., the temperature was changed or the crucible position altered by analog temperature and motor controllers. With commercialization came the need for automated diameter control systems. These were based on either crucible or crystal weighing or by controlling the meniscus position optically.

1.3.1.4 Bridgman–Stockbarger/Gradient Freeze Methods

Little did Percy Bridgman (1882–1961) or Donald Stockbarger (1895–1952) know at the time of their respective discoveries that their names would become historically intertwined in describing one of the most popular techniques for growing crystals. Their versatile method(s) made possible the growth of many different types of materials including metals and their alloys, semiconductors, and both inorganic and organic compounds. It was also a method that allowed the preparation of some of the largest manmade crystals ever produced.

Percy Williams Bridgman was a Noble Prize-winning American physicist working at Harvard University, only a few miles away from MIT where Donald C. Stockbarger worked as an Associate Professor of Physics. His prize (1946) was for his work in the field of high pressure physics. The crystal growth method he developed and published in 1925 [101] departed from the work of Tammann [65] and Obreimov and L. Schubnikov [66] in that the vertical tube containing the melt was not stationary during growth. Growth was initiated in a capillary tube at the bottom end of a larger cylindrical ampoule and propagated upward along the tube by lowering it down through a single zone vertical tube furnace and out the bottom. The capillary was used for seed selection and was further enhanced by reducing the capillary diameter at the juncture between the capillary and the larger bore container. His first experiments were done using bismuth melts. Not long afterward, various other researchers used his method or variants of his method to grow other metal crystals, such as copper, and zinc.

In the late 1920s Stockbarger started his work on the growth of large, high-optical-quality crystals of LiF and later CaF. At first, he tried Bridgman's method [101] for CaF but it required more careful atmosphere control to prevent hydrolysis, better starting material purity and temperature stability to produce useful crystals. This led Stockbarger to modify Bridgman's method [102,103]. He used a so-called vertical "elevator furnace" that had two graphite heaters separated by a Mo baffle through which a covered crucible containing the melt could be passed from the upper higher temperature region into a lower temperature section by a motorized translation device. The use of a two-zone furnace led to better control of the thermal gradient at the growth interface. The crucible, support rod and pedestal were graphite. The V-shaped crucible bottom rested in the pedestal. There was no capillary region below the tapered region for seed selectivity, and the included angle was much larger than those used in the Bridgman and other earlier methods. So it is speculated that seed selection was controlled by the locally steep gradient at the tip created by the thermally conducting graphite support rod coupled with the baffle, thereby limiting the volume of super-cooled melt that can form.

The Bridgman–Stockbarger method (shown in Figure 1.7 below) has been widely used to grow crystals of varying sizes from its development in the 1920s until the present day. It has also been used extensively in a horizontal configuration. While initially used for metals and then shortly afterward for inorganic optical materials, it has since been used to grow hundreds of other compounds including semiconductors (GaAs, CdTe, HgCdTe, and chalcopyrite compounds such as CdGeAs₂, ZnGeP₂), organic materials, oxides such as Pb(Mg_{1/3}Nb_{2/3})O₃–PbTiO₃ (PMNT) and halides such as Tl:CsI and Tl:NaI, and Eu:SrI₂ etc. Process improvements include the use of the accelerated crucible rotation technique to improve melt homogeneity and interface boundary conditions [104], vibroconvective mixing [105], baffles in the melt near the interface, growth under high pressure, etc.

The gradient freeze (GF) method of Tammann [65] differs from the Bridgman–Stockbarger approach in that there are no moving parts. Neither the ampoule nor furnace

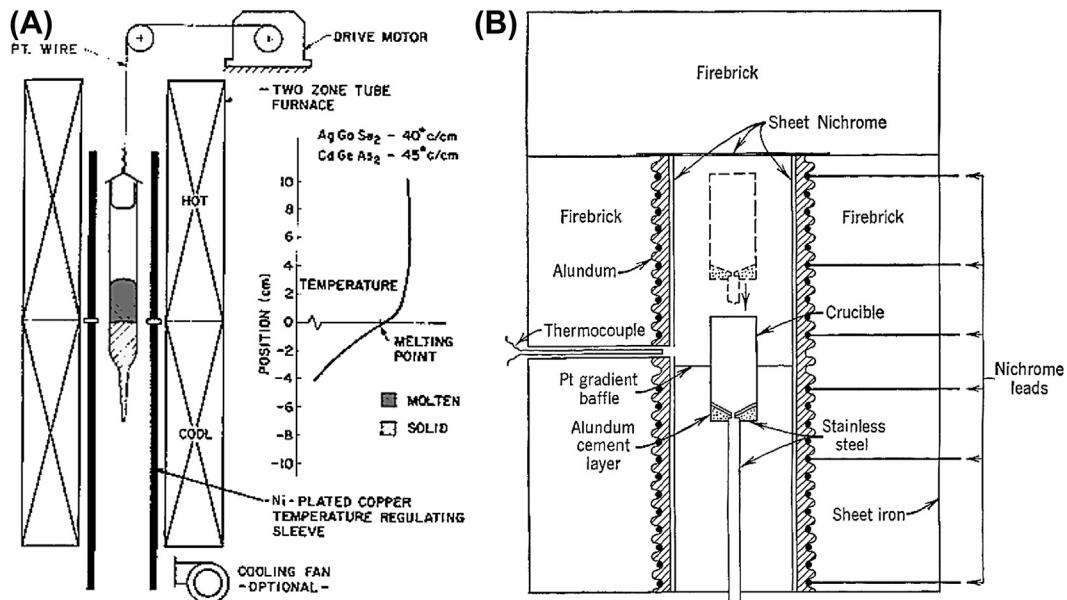


FIGURE 1.7 (A) Drawing of a Bridgman apparatus showing a tapered crucible being lowered through a stationary furnace having a steep gradient at the growth interface. In Bridgman's experiments the crucible is lowered out of the furnace. (B) A schematic diagram of Stockbarger's growth apparatus. Note the platinum baffle that separates the two furnace zones for gradient control and the crucible pedestal.

is translated with respect to the fixed thermal gradient in the furnace. Instead, a temperature gradient is maintained across the melt-containing crucible such that when the temperature of the furnace is lowered, the cool end of the melt solidifies first, and the rest of the melt solidifies layer by layer as the freezing point moves across the melt. This method is simple to implement and was used for the growth of a number of materials. Its big disadvantage was that as the furnace temperature decreased, so did the gradient across the remaining melt. Under constant cooling conditions this change in gradient could lead to changes in growth velocity and thereby variable crystal properties along its length due to component segregation and perhaps interface breakdown. One method used to solve this problem was by continuously changing the furnace-cooling rate to maintain constant freezing rate in the melt. In 1986, Gault et al. [106] successfully applied the vertical gradient freeze method (VGF) to the growth of large diameter GaP, InP, and GaAs crystals.

Attempts to grow some important III-V compounds by the vertical Bridgman and gradient freeze methods were complicated by the fact that these compounds expand on cooling and can aggressively stick to the walls of many crucible materials [107]. These methods both exist in horizontal versions that are applicable to certain important commercial crystals. While many different types of crystals have been grown by the horizontal Bridgman and gradient freeze techniques, their sizes are limited compared to their vertical counterparts, and the boules have noncircular cross-sections.

1.3.1.5 Nacken–Kyropoulos Methods

During the early decades of the twentieth century, many new developments in crystal growth technology came out of Germany. During the 1920s in particular, a burst of activity in the field led to numerous growth techniques being developed, many of which are being used today in either their original or modified form.

One of the most important crystal growth pioneers of this period was the German mineralogist Richard Nacken (1884–1971). A few years before Czochralski's discovery, he reported on a process for growing crystals from the surface of a melt using a cooled copper rod with a rounded end and a seed attached [108]. Nacken's apparatus is illustrated in Figure 1.8(B) below. The general idea was to locally supercool the melt adjacent to the rod and initiate growth under controlled conditions. After growth started, the furnace temperature could be lowered to keep the seed growing. No pulling was involved. As the crystal grows, the melt level drops due to the higher density of the crystal. The method was later used by J. M. Adams and W. Lewis [109] to grow very large ice crystals. Nacken also developed a viable hydrothermal process for growing quartz crystals. His unpublished work was found in secret WW II German reports. E. Buehler and A.C. Walker at Bell Laboratories [110] based their successful hydrothermal quartz growth technology on Nacken's process.

About 10 years later, Spyro Kyropoulos (1887–1967), a student of Tammann and professor of Applied Physics at the Gottingen University (later he taught at the California

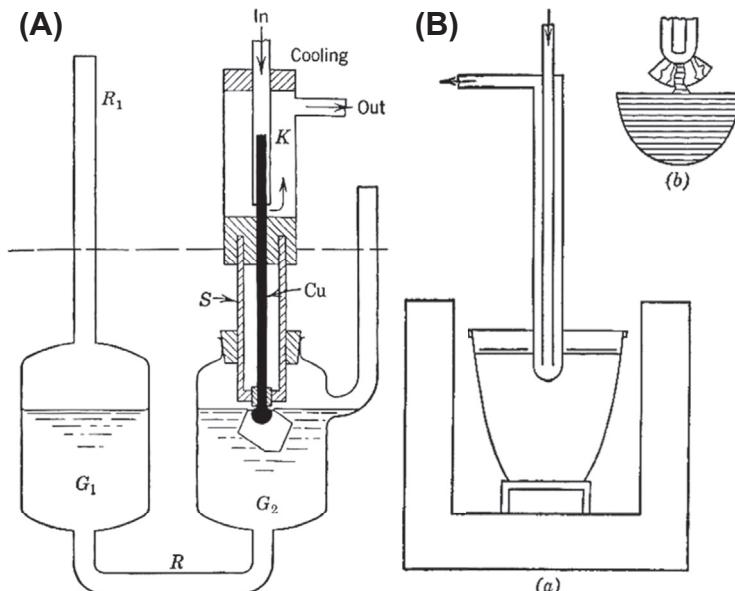


FIGURE 1.8 (A) A drawing of Nacken's apparatus illustrating the growth of a faceted crystal using a seeded cold "finger" inserted into the melt's surface. (B) A schematic diagram of Kyropoulos's experimental setup where, unlike Nacken, a cold rod is placed in the melt surface without a seed. The inset shows how seed selection can be accomplished using a rounded seed rod.

Institute of Technology) took up Nacken's melt growth method to grow crack-free alkali halide crystals for precision optics. The advantage of Nacken's method is that the crystal is grown within the melt rather than being confined to a container that can induce strain in the crystal during cooling. Instead of using a seed, Kyropoulos [111], using an air-cooled platinum tube, nucleated a few crystallites on the end of his tube and then lifted it up slightly so that the melt stayed in contact with only one grain. Kyropoulos's apparatus is shown in [Figure 1.8\(B\)](#) above. This seeding method had to be carefully controlled so that the tube did not break free from the melt surface. After the seeding stage, the furnace is slowly cooled to allow the crystallite with the fastest growing direction of heat flow to grow to cm-size crystals before being pulled out of the melt. The thermal gradients in the melt are generally quite small. As mentioned before, the melt level drops in systems where the density of the solid is greater than the melt density. Kyropoulos used this process for growing many alkali halide crystals [112]. The method is attractive because of its general simplicity, reliability and low operating costs. Two other advantages of the method are (1) the ability to see what was going on and to make adjustments to enhance the crystal quality and (2) its use of lower thermal gradients than in the Czochralski method. On the other hand, the lower gradients lead to faceting at the interface and thus chemical inhomogeneities in the crystals. Several years later, Korth [113] took up this method but used a seed attached to the cooled rod as did Nacken many years earlier. He grew crystals as large as 6×8 cm. A few years later, Katherine Chamberlain in the United States used this method to grow very large KBr crystals up to five inches in diameter and weighing up to seven pounds [114]. Typically Kyropoulos's method does not involve continuous pulling or rotation as in the Czochralski method. Growth rates are of the order of mm's/hr with cooling rates below 1 °C/hr. The crystal diameters usually are up to 90% of the crucible diameter. Bliss [115] gave a detailed review of Kyropoulos's life and method.

The Kyropoulos method has been in commercial use for over 75 years. From its inception until the present time, the method has been used to grow large alkali halide crystals for windows, prisms and scintillators (e.g., Tl:NaI and Tl:CsI) compounds. Due to the development of GaN-based light emitting diodes, there has sprung up a very large industry around the growth of large sapphire crystals for use as substrates. The Kyropoulos method is one of the most widely used methods today for this applications. Up to 12 inch-long crystals have been produced. It is also used in the commercial production of Ti:Sapphire laser crystals. A variety of other materials have been grown by the Kyropoulos method in laboratory settings, including organic materials, semiconductors such as Si, ZnSe, and InP and other types of laser crystals. For the growth of InP crystals [116], liquid encapsulation together with magnetic fields has been applied to the Kyropoulos configuration to improve crystalline perfection. This has been called the MLEK method. Over the years, furnaces have become much more complex. Heat shields are now used to control thermal profiles. Numerical analysis has helped to define the optimal conditions for growth of specific materials through proper baffling and positioning of the crucible in the heater. Other improved capabilities include the ability to weigh the crystal or crucible during growth to control the rate of mass increase with time.

1.3.1.6 Stöber/Heat Exchanger Methods

In 1925, F. Stöber [117] reported on the growth of large crystals of anisotropic materials such as sodium nitrate, zinc and bismuth by removing the latent heat of crystallization from the bottom of a stationary bowl-shaped crucible containing a melt (growth from the bottom upward). A heater plate was placed above the surface of the melt and a water-cooled plate at the bottom creating an axial temperature gradient. The radial heat flow, present in most other growth systems, was minimal. Stöber's method, along with one of Tamman's techniques, were perhaps the first gradient freeze methods (i.e., moving the gradient along the melt rather than by moving the crucible or furnace). Stöber also found that crystal singularity was enhanced when the thermal conductivity in one crystallographic orientation was significantly greater than in other directions. One attractive feature of Stöber's method was that you could produce very large crystals in near-net shape, i.e., in the exact shape of the container. In addition the method is very simple to implement since there are no moving parts, and lower thermal gradients employed help reduce stresses in the final boule. He grew crystals of NaNO_3 up to 10 pounds by his method. He also grew ice crystals by inverting the cooler and immersing it into the liquid surface.

In 1970, Frederick Schmid and Dennis Viechnicki [118] from the Army Research Laboratory at the Watertown Arsenal, reported on a new method to produce large-diameter sapphire crystals from the melt. This work was stimulated by the need by the military for very large transparent armor plates. They called their new technique the heat exchanger method (HEM). The method is similar to the Stöber process in that the crystal grows upward from the bottom filling the crucible and taking its shape. Neither the furnace, crucible nor crystal moves during growth. A He-cooled cold finger (similar to the water-cooled bottom plate used by Stöber) extracts heat from the crucible bottom in a controlled manner and independent of the heat input. A furnace that surrounds the crucible replaced the upper pancake heater. In addition, the technique allows for a small-diameter seed to be centered over the cold spot created by the He heat extraction tube. Heat can be removed from the crucible bottom by increasing the He flow rate. Since then (1975), a He recirculation system was developed along with the technology to grow large-diameter, flat-bottom crystals free of light scatter from the small seed centered over the heat exchanger. High-quality sapphire crystals have been grown commercially up to 44 cm in diameter and weighing 160 kg [119]. In situ annealing in shallow gradients is used to relieve stresses. The crystals produced are competitive with commercial Kyropoulos sapphire. The method has also being used to produce single crystal ingots of spinel, ruby, Ti:sapphire, Nd:Y₃Al₅O₁₂ and silicon. Commercial growth systems are available.

1.3.1.7 Kapitza's Method

Pyotr Kapitza (1894–1984) was an important Russian physicist who spent many years in England before returning to Stalinist Russia. He was awarded a Nobel Prize for his work in low-temperature physics. He used the Bridgman method to prepare metal single

crystals for his experiments, but when it came to preparing Bi rods of a specific orientation, he found that its expansion on cooling was sufficient to cause enough strain to prevent the seeded orientation from propagating down the rod. To solve this problem, he developed a method in which the crystal was not completely constrained [120]. He placed a bismuth rod on a copper plate and covered it with loose-fitting glass plates to reduce drafts and then melted the rod. At one end, an oriented seed was attached and by unidirectionally solidifying the rod by cooling he was able to produce an oriented Bi single crystal at rates up to 5 cm per hour. This method was taken up and modified by others, and today it might be considered the forerunner of the horizontal Bridgman method which is widely used today for growing materials like GaAs for LED's [121] and ZnGeP₂ and CdGeAs₂ [122] for nonlinear optical applications.

1.3.1.8 Zone Melting

Zone melting methods have played an important part in (1) purification of materials for crystal growth and other materials processing (zone refining), (2) for producing crystals with uniform composition (zone leveling) and (3) for growing crystals without crucibles (the float zone method). There are a number of variants to all these methods including different methods of heating, horizontal and vertical arrangements, traveling mechanisms, etc. The first reported use of zone melting was by Kapitza in 1928 [120]. In his experiments, he passed a short resistance heater along a Bi filled tube to produce a single crystal. In 1937, Andrade and Roscoe [123] used zone melting (also a traveling heater) to grow lead and cadmium single crystals having low strain. By far the most important and extensive work on zone melting for purification (zone refining) and zone leveling was that of William Pfann [78]. In 1952, Pfann conceived of the zone refining method when asked by the transistor researchers at Bell Laboratories (where he had worked since the late 1930s) to develop a method to produce higher purity Si and Ge for use in growing crystals with better electronic properties. Toward this end, it was used with great success in the early days of semiconductor processing. This very versatile method was found applicable to numerous other materials, including inorganic and organic compounds, metals and semiconductors. Many papers on its adaptation to different materials and operational improvements have been published since then, and it has become an important tool for both research laboratories and industry. Pfann's book on zone melting [124] is the seminal publication on the method, comprehensively covering both the theory and practice involved.

The method consists of moving a molten zone through a bar of material. Two solid interfaces are created. As the zone moves (by moving the heater or furnace), material from one interface dissolves in the zone and is recrystallized at the other interface. Purification occurs for those impurities whose solubility in the liquid is different than that in the solid (segregation coefficients, K , greater or less than one). Materials with $K < 1$ will be rejected at the growth interface and will build up in the last to freeze region. Those with $K > 1$ will tend to congregate at the start of the ingot. It is also a very useful method for growing crystals from materials that melt incongruently.

Various types of heaters have been used with the zone melting method, including resistance, RF, electron beam, plasmas, lasers and xenon lamps. Refining can be done with one zone moved through the ingot many times (passes) or by moving multiple zones simultaneously. The ends of a sample can be removed and the sample zone refined again as many times as needed. More passes are needed when K for a particularly detrimental impurity is close to 1. Volatile species can complicate the process but techniques to control or minimize melt losses have been developed.

Zone leveling is a way to produce material with uniform composition along its length. It has many of the features of zone refining. Once the zone has reached a steady-state composition, the species of interest will transfer from one interface to the other. The composition will be the same on both the melting interface and the solidifying interface. In both zone methods, crystal growth can be carried out during the purification or leveling procedures.

The floating zone technique is a very important variant of the zone melting method. It allows for crucible-free growth and eliminates possible contamination from the crucible material and also stresses due to differential expansion between the crystal and container. The method was invented and patented by H. Theuerer [125], a close colleague of Pfann, to grow ultra pure Si. For better uniformity, the rods can be rotated during growth. As mentioned before, the method is used commercially today for growing low or oxygen-free silicon. In recent years, automated commercial optical lamp heated float zone systems have become available and have permitted researchers from a variety of disciplines to grow crystals of a wide variety of materials for physical property studies [126].

The pedestal growth method is essentially a floating zone process. However, because the pull rate of the crystal (smaller diameter) is different from the push rate of the source rod (larger diameter) it has some characteristics of the Czochralski method. Parenthetically, one might classify the Verneuil method as a pedestal growth method since the crystal is grown on a pedestal and the molten zone is fed by molten powder rather than a solid rod. The first use of a pedestal growth technique was in 1958 by F. Horn [127] at the General Electric Corp. His method was a hybrid technique between the Czochralski and float zone methods. The charge in the crucible was only melted near the top surface and the crystal, of smaller diameter, pulled from this melt. As the crystal grew he changed the heater position to melt some more of the solid below. He grew boules of Sb-doped Ge having a more uniform composition than achievable by the Czochralski technique where the entire charge was melted. Dash [128], and Poplawski and Thomas [129] used this method to grow dislocation-free crystals of Si and Ge.

Two techniques that have been found particularly useful for producing small-diameter crystals for property studies are the *laser-heated* pedestal fiber growth (LHPG) [130] and micro pull-down (μ -PD) [131,132] methods. The LHPG method is a zone melting method in which, rather than a zone traversing a bar of material of uniform diameter, a fiber is grown from a source rod of larger diameter. The pedestal configuration was first used by Horn [127] and Poplawsky [129]. The source rod forms a pedestal

whose upper surface is melted with a small spatially fixed laser beam. A seed crystal is lowered into the melt and is withdrawn at a rate faster than the rate at which the source rod is pushed upward to maintain constant melt volume. It is a crucible-less method, minimizing contamination; the growth rates are much faster than bulk growth (mm/min) because the temperature gradients at the interface are very large ($>1000\text{ }^{\circ}\text{C/cm}$). These high-growth velocities can lead to greater dopant incorporation and to the growth of metastable phases. The method is useful for incongruently as well as congruently melting compounds, although it is limited to systems where the vapor pressures are modest and dissociation is not a problem. The small diameter fibers were often found to have better crystalline perfection than bulk materials. The LHPG method has been used to grow fibers of a vast array of materials including oxides, halides, borides, carbides, and metals. Haggerty [133] was the first to use the pedestal method with laser heating. He grew LaB_6 single crystal fibers. A few years later, it was used to grow single crystal Nd:YAG fiber lasers [134]. One of the big advances in LHPG growth was the replacement of individual laser beams (two or four) with reflaxicon optics [135] giving a circular beam and a much more uniformly heated molten zone. An interesting discovery came about during the growth of LiNbO_3 fibers. Lithium niobate is a ferroelectric material whose as-grown bulk crystals contain numerous parallel and antiparallel domains. To be useful in nonlinear and other device applications, these have to be aligned after growth in an electric field at elevated temperatures. During the growth of LiNbO_3 fibers using a two-beam laser system, however, the small diameters and steep gradients led to single domain fibers when grown along the c-axis and a bi-domain fiber of opposing 180° domains when grown along the a-axis [136]. The axial gradients were responsible for the single domain c-axis fibers and the radial gradient a-axis fibers. These observations later led to a method to produce fibers with periodically poled domain structures by periodically shuttering one of the laser beams during growth [137]. Later, other periodically poled structures for quasiphase matching applications were produced by other methods.

In 1980, Mimura et al. [131] published a paper on the growth of KRS-5 fiber crystals using an inverted pulling system (modified floating zone technique). They had a crucible filled with melt on the top with a feed rod continuously feeding the melt as the fiber grew. At the bottom of the crucible was a long heated capillary tube with a shaper at the end. The growth interface was below the shaper. The growing crystal was pulled downward. This method was taken up by D. Yoon et al. [132] and called the micro-pull down method. It has been used successfully for many materials, and growth systems are available commercially. This method was reviewed by V. Chani [138].

1.3.1.9 Shaped Growth

Shaped growth generally means a method for producing a crystal with a predetermined cross-sectional configuration. The quest to develop such methods is associated with a need to reduce product cost and/or improve crystal quality. Notable savings can be achieved in device fabrication, such as cutting and polishing, reducing the loss of expensive material and reducing mechanical damage. In addition, the method usually

allows significantly higher than normal growth velocities, thereby increasing production rates. In a very real sense, shaped growth is a hybrid method that borrows from other more established methods. For example, some are simple modifications of the crystal pulling or directional freezing methods.

One might consider the Bridgman–Stockbarger method to be one of the first shaped growth processes because the crystal retains the shape of the ampoule used. It is not quite so obvious since almost all Bridgman crystals are grown from cylindrical ampoules. One of several recent exceptions being a paper by Feigelson and Route [139] on the growth of square cross-section crystals of AgGaSe₂ in vacuum-formed quartz crucibles. Using oriented seeds, they grew crystals not only aligned along the c-axis, but also so that the flat crystal side faces would be normal to the [110] planes in which light propagates during type 1 phase-matched nonlinear interactions. A comprehensive review of the various shaped crystal growth methods is given in Ref. [140] and elsewhere.

Perhaps the earliest attempt at shaped crystal growth is attributed to the 1921 work of von Gomperz [70] at the Institute of Fiber Chemistry in Berlin-Dahlem. He worked in Michael Polyani's group. Polyani [141], reminiscing some 40 years later, recalled "Some metallurgists, interested in my work on the hardening of single crystals, told me of a method invented by Czochralski for producing metal crystals in the form of wires. It consisted in pulling out a thread from a pool of molten metal, so that the thread continued to solidify at the rate at which you were pulling it out. Erwin von Gomperz, who was doing his thesis with me, was put to growing single crystals of tin and zinc in this way. Unfortunately, the metal tended to come out in lumps, and the project was saved only by the intervention of Hermann Mark who covered the liquid metal by a sheet of mica with a hole in the middle, through which the thread came out as a smooth cylindrical wire. But for this ingenious intervention, our subsequent investigations of the plastic flow of metals might not have come about" [142].

In 1938, Stepanov at the Ioffe Institute in St. Petersburg began his extensive studies on shaping crystals during growth using wetted and nonwetted dies [143,144]. These dies have one or more capillaries or slots to transport melt from the crucible to the growth interface. The shape and height of the melt column is dependent on capillary properties such as surface tension, density, melt viscosity, impurities and wetting angle. Over many years, Stepanov's group produced a wide variety of shaped crystals including single and multibore tubes, rectangular bars, sheets, discs, etc. Shaped crystals of a number of different types of materials were grown, including oxides, metals and compound semiconductors.

Shaped growth in the United States began in the late 1960s with the preparation of sapphire filaments (later sapphire tubes for Na-vapor lights) by the edge-defined film-fed growth method (EFG) and single crystal superalloy turbine blades by directional solidification in complex molds [145,146]. The EFG process is in effect one of Stepanov's techniques, but it specifically focused on the advantages of wetted dies. It was discovered independently by LaBelle [147] who made a significant observation during his early attempts to pull sapphire fibers from a die placed in the melt surface. He noticed that the

melt wet the die and instead of being the diameter of the capillary within the die was the shape of the outer rim of the die. This was recognized by Mlavsky [148] as being of significant benefit and thus began extensive work on the EFG method. A sketch of the EFG method is shown in Figure 1.9. In a relatively short time after its discovery, it became a commercially viable technology. This was due to the early recognition that concurrent with experimental work, theoretical studies were needed to thoroughly understand the mechanisms involved in the process and ways to maintain better shape stability and rapid growth rates [149,150]. In 1980, an entire volume of the *Journal of Crystal Growth* was devoted to the subject of shaped growth methods. The EFG method has been successfully used in the commercial production of sapphire single fibers, tubes and ribbons and other materials. Today, the EFG method has gained an increasingly greater market share in the production of sapphire ribbons for GaN substrates used in lighting applications. Automated commercial EFG equipment can now be readily obtained, permitting companies to produce such wafers themselves.

The Stepanov and EFG methods are a meniscus-controlled process like Czochralski growth, and like it, growth is driven by crystal pulling. However, instead of pulling directly off the melt surface, the crystal is pulled from a suitable die face located above the melt surface. It can either float on the surface, like in von Gomperz's early experiments [70], held in a fixed position with respect to the crucible or moved during growth. The die position leaves the growth interface some distance above the hot melt surface and the thermal gradients are much steeper permitting enhanced growth velocities. The die material is chosen on the basis of its wettability with the melt and its reactivity. For sapphire, Mo dies have been used. In commercial systems the die can be moved during growth to maintain constant conditions and be equipped with an automatic monitoring system based on crystal weighing.

During the 1970s, the oil energy crisis led to serious efforts to produce silicon solar cells at a much lower cost than using cut wafers from Czochralski boules. This led to a robust effort to produce Si sheet at high growth rates. One of the most promising methods at the time was the EFG process. Extensive efforts went into adapting it to produce low-cost Si solar cells, but with limited success. Other innovative Si shaped crystal growth methods were studied during this time period, including the dendritic web process [151] in which a silicon dendrite is used a seed. It grows out laterally

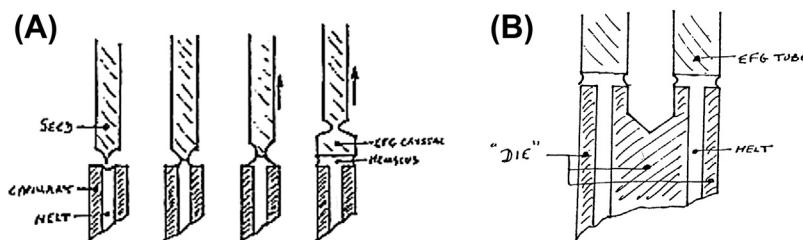


FIGURE 1.9 Illustration of the EFG shaped growth process. (A) the sequential steps involved in seeding and growing a crystal from a cylindrical die. (B) a die used to grow a hollow tubular crystal [148].

forming a thin sheet of silicon bounded by two new dendrites that define the width of the sheet. Some other methods include the ribbon against drop (RAD) method [152], where silicon is deposited as aligned grains on a carbon substrate, and the silicon on ceramic process [153], which is similar to the RAD process except that the substrate is a ceramic material. Two other methods of note are the ribbon to ribbon (RTR) [154] and horizontal ribbon (HRG) [155] growth methods. The former is a laser heated float-zone technique using a poly ribbon as the source and the latter involves pulling a ribbon (cooled from the top) horizontally from a free melt surface. The growth rates achievable in these processes are in the 5–10 cm/min range except for the HRG method where controlled cooling of the upper surface permitted growth rates of 10–40 cm/min. These methods are reviewed in Ref. [140].

The unidirectional casting method used for making single crystal jet engine turbine blades, as mentioned above, has had an important influence on aircraft performance. These blades, made from nickel-based superalloys, were found to have superior creep resistance if they have aligned grains [140] or better yet be one single crystal [156]. The method is like a Bridgeman technique with the mold having the shape of the blade and extending down below is a zig-zag-shaped capillary tube mounted on a hollow pedestal that sits on a chill plate (see Figure 1.10). Growth is upward, initiated first from the melt in the pedestal by cooling the chill plate. This produces elongated grains along the mold's vertical axis, one of which will be in line with the capillary to provide seed selection. If by chance more than one grain makes it into the capillary from the pedestal, the crooked capillary will aid in seed selection.

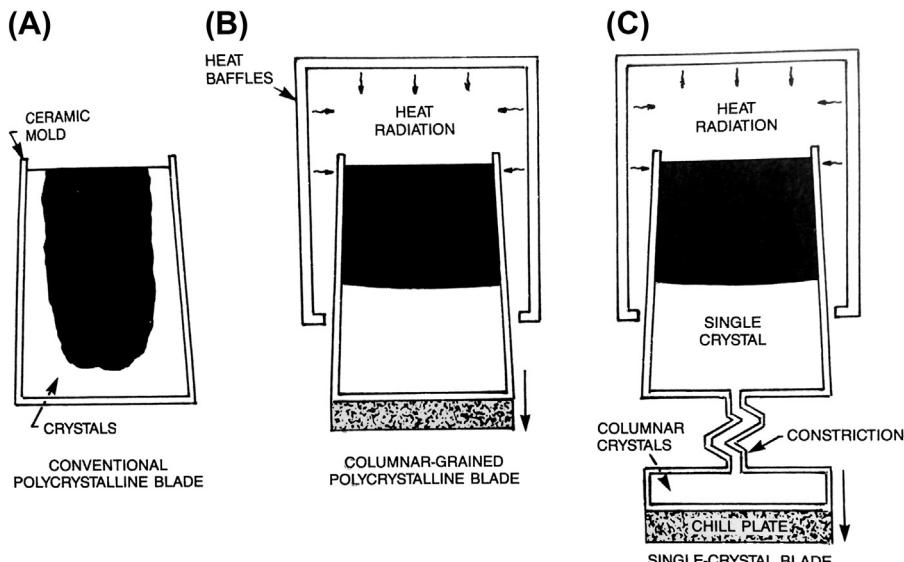


FIGURE 1.10 Schematic diagrams showing various methods for making jet engine turbine blades. (A) original casting method (polycrystalline), (B) single crystal growth by unidirectional solidification and (C) unidirectional growth with grain selection [146].

1.3.1.10 *Skull Melting*

The skull melting method is a quasi-crucible-less crystal growth method that was developed in the late 1960s in Russia, especially for growing large, high-purity oxide crystals for laser and gemstone production [157]. Since the 1970s it has become an important method for manufacturing cubic zirconia gemstones in a variety of colors (J.F. Wenckus et al. at the Arthur D. Little Company [158]). The method is adaptable to Czochralski and Bridgman growth methods using seed crystals and also in centrifugal casting.

In skull melting, a relatively large powder charge is contained within a water-cooled cylindrical Cu crucible surrounded by an RF heating coil. The RF field generates a magnetic field that in turn generates eddy currents due to ohmic losses in the material within the crucible. The process works for materials whose electrical conductivity increases with temperature, even through the melting stage. Due to the cold crucible wall, a skin (skull) of unmelted materials surrounds the melt and keeps it from coming into direct contact with the crucible, thus preventing contamination. Temperatures of over 3000 °C can be achieved and a wide selection of gas atmospheres are possible. Unless coupled with seeding, it is impossible to grow one single crystal due to the seeding effect of grains in the skull. For the gem industry, large slabs of crystals are retrieved from large-grained poly masses. The nature of the heat flow encourages the grains to grow along the vertical direction.

Cubic zirconia (ZrO_2) is used in the gem industry as a substitute for diamond since its optical properties, hardness, and fracture toughness are similar. Pure zirconia, however, undergoes a number of destructive phase transformations upon cooling. In order to grow single crystals from the melt, therefore, its composition has to be modified (stabilized) by doping to allow the high temperature cubic phase to persist to room temperature. The most common stabilizer is yttrium (Y CZ), but CaO and MgO are also used. Concentrations of dopants vary from 10 to 40 mol%. These stabilizers work by creating many vacancies on the oxygen sublattice that prevent the cubic phase from transforming to phases of lower symmetry. Partially stabilized zirconia (PSZ) can be produced by reducing the dopant concentrations to less than 6 mol%. In these materials, part of the material transforms into the tetragonal phase creating a composite structure with excellent mechanical properties, making them attractive for applications such as drilling, threading, medical instruments such as scalpels, etc. [157]. The wide range of colors possible in zirconia gemstones are created using rare earth or transition metal element dopants.

Recently a Ukrainian group [159] developed a technique for growing large Tl:NaI scintillator crystals by a method similar to skull melting. Since the melting temperatures are quite low (~661 °C), they did not need RF heating and reconfigured the system from horizontal heating to vertical resistance heating. Basically, they hold a heater plate about 1 cm over the charge, which is held in a rectangular aluminum tray sitting on the bottom of water-cooled vacuum chamber. Since the heater is smaller in area than the container, only the center part of the charge is melted leaving a skull 5–10 mm thick surrounding

the melt and keeping it out of contact with the aluminum. Growth is achieved by slow cooling from the bottom up by lowering the temperature of the upper heater. It is not clear what the grain structure of the resulting slab is like, since seeding is not used and the plates produced are quite large. However, the scintillator properties are in line with those of single crystals produced by other methods and in a more cost-effective manner.

1.3.2 Solution Growth

1.3.2.1 *Introduction*

Solution growth methods involve dissolving material in a liquid (or gel) medium and then recrystallizing it under controlled conditions to produce a crystal of a desired size, shape and perfection for a specific application. The control of crystal shape and size can extend from very large crystals for optical applications down to fine powders for pharmaceutical, agricultural, or specialty chemical uses. The solvent media may be a low-temperature solvent like water or a high-temperature flux like PbO. Pressure-enhanced solution growth (the hybrid hydrothermal growth method) has also been a commercial success for the preparation of large crystals of quartz. The most common solvent used is water, and an impressive number of inorganic salts have been converted into single crystals using this technique, some weighing over 50 pounds. Other solvents include organic liquids (for the growth of organic crystals) and liquid ammonia.

Growing crystals from water solutions was undoubtedly the earliest effort by early man to replicate what he observed in nature. Natural salt ponds drying up in the hot summer months and then redissolving during winter rains assuredly piqued his interest and led him to experiment. Since salt became such an important commercial product, it is not surprising that this material and method became one of the first industrial crystal growth activities. Sugar was another material of early commercial interest. Through trial and error, a rudimentary understanding of saturation and supersaturation began to develop and, along with techniques such as seeding and solution homogenization (via stirring), better control of nucleation, crystal size and purity was achieved. Later, the role of additives to enhance growth behavior and tailor crystal properties was incorporated into the growth procedures. The eventual use of solubility diagrams greatly aided crystal growers in choosing appropriate growth conditions, i.e., temperature and composition regions. In these early days, as today, control of purity and size were of great commercial significance. Several basic methodologies are employed in solution growth: (1) controlled evaporation, (2) temperature programming, (3) mass transport in a concentration gradient at constant T and (4) changing the composition of the solution (salting out method).

1.3.2.2 *Aqueous Solution Growth*

Like all other crystal growth methods, a variety of modifications have been made over the years to facilitate the growth of a specific type of material, and to achieve an appropriate dimension and degree of crystalline perfection (purity, homogeneity, strain,

etc.) required for the application intended. Materials vary so widely in their thermodynamic and kinetic properties that even the growth of related materials of similar composition and structure can require changes in growth procedure or even in overall methodology.

In 1901, G. Wulff [160] published his famous theorem on the influence of surface energy on equilibrium shape of a crystal (morphology). It established a relationship between the crystal habit and the structure of crystals. It was derived from studies on the growth rates on different faces of crystals grown in water solutions. He used a rotating cylindrical crystallizer, in which a seed crystal was placed along the axis of the cylinder at its center-point. This allowed the crystal to grow out of contact with the vessel walls and be exposed to nutrient equally on all faces. Other early pioneers advancing the development of water solution methods during the first half of the twentieth century included Kruger and Finke [161], and Valeton [162]. Kruger and Finke were the first to investigate growth under constant temperature and supersaturation conditions. Their apparatus, shown in Figure 1.11, had in common two vertical chambers connected by upper and lower tubes through which solution passed in a specific way. One chamber contained source material and the other a stirring paddle (growth chamber) to move nutrient and depleted solution from one to the other. After equilibration of the growth chamber in a slightly undersaturated state, a seed crystal was added. Valeton's apparatus had a more precise way to control temperature in each bath. These methods utilized mass transported from the source chamber to the growth chamber to control the growth process. Crystals of potash alum and potassium sulfate were grown in these early experiments. In 1916, Nacken [163] developed a similar but more sophisticated apparatus using a vertical configuration for solute transport. Some 30 years later, Walker and Kohman [164] at Bell Laboratories developed a large-scale commercial crystallizer similar to these earlier methods known as the constant temperature process. Together with Holden's contributions on seed mounting [165], this apparatus was capable of growing four large EDP (ethylene diamine tartrate) piezoelectric crystals at a time. These crystals were used to replace natural quartz in telephone circuits. Crystals weighing up to 40 pounds could be

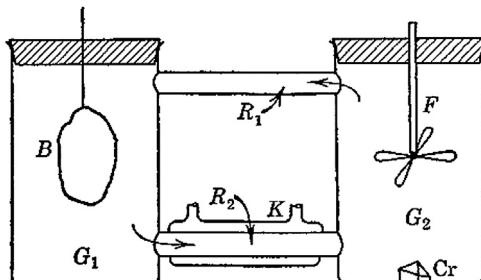


FIGURE 1.11 The aqueous solution crystallizer used by Kruger and Finke [161]. The nutrient was contained in a porous bag in heated beaker G_1 . The stirrer in beaker G_2 recirculates saturated from G_1 through a water-cooled tube K , where it becomes supersaturated, into beaker G_2 where the crystals grow. Large potassium sulfate crystals 2 cm in size were produced in this reactor.

grown by this method. The method involved several large chambers with solution in one chamber saturated at one temperature being continuously fed into the crystallizer chamber being held at a slightly lower temperature, thereby providing the supersaturation conditions necessary for growth.

In 1919, R.W. Moore [166] working at the General Electric Company needed large Rochelle salt crystals for electrical property studies. Since suitable material was not available commercially, he was forced to develop his own method. At first he started with the method of Kruger and Finke [161]. This proved unsuccessful. After thoroughly studying the available literature he came up with a new and simple approach based on the temperature lowering method. First, a saturated solution was formed 10–15 °C above room temperature, the solution decanted to separate it from the excess salt and then filtered. After heating the saturated solution 7–8° above its saturation point, it was poured into a vessel containing small seeds suspended on silk threads or metal wires, covered with a glass plate and then placed in water bath at 0.5 °C above the saturation temperature. From that point onward, the temperature was lowered to cause the seeds to grow. No means of stirring the solution was provided in these early experiments.

Moore's temperature lowering method was eventually modified to supply some fluid movement and distribute nutrient more uniformly to all the faces. The so-called rocking tank method was applied in 1947 by Walker [167] to the growth of large ammonium dihydrogen phosphate (ADP) crystals needed for submarine detection. The tanks were large rectangular trays that were gently rocked to replace depleted solution at the growth interfaces with fresh supersaturated material. Like EDP, crystals as large as $6 \times 6 \times 20$ in were produced by this method. Many crystals could be grown in each tray and for production (Western Electric Co.) rooms were filled with many rocking trays. Evaporation was inhibited and the room temperature had to be carefully controlled. One famous name associated with water solution growth was Alan Holden [165]. Aside from his research at Bell Laboratories, he also wrote a very popular book on the subject [168]. Numerous amateurs have used it to initiate crystal growth experiments. In 1949, he introduced the “rotary crystallizer” originally to grow EDP and then later for ADP crystals. It consisted of a large, one-foot-diameter cylindrical vessel holding the solution. It was heated from the bottom by two concentric heaters, an inner one to keep the bottom center somewhat under saturated. In this way, errant crystallites that have fallen to the bottom would dissolve. The outer heater controlled the overall solution temperature. The important feature introduced by Holden was the rotating seed holder (called a “spider”). The seed crystals were mounted on spokes emanating from the rotation shaft. Several sets of spokes holding the seeds were used along the vertical axis. The seeds were rotated first in one direction for a selected period of time and then in the other direction. The system was sealed and some water condensed on the upper lid forming droplets. When large enough, the droplets fell to the solution surface keeping it under saturated and thus preventing the nucleation of spurious grains.

Most of the growth methods mentioned above have inherently slow growth rates (0.5–1 mm/day) due to low solution supersaturation. The higher supersaturation

needed to yield increased growth rates were hard to achieve and control. In 1983, Loiacono et al. [169], using a three-stage crystallizer (modeled after Walker and Kohman's growth system from 1948 [164]), and under conditions of constant temperature and supersaturation were able to achieve 5 mm/day growth rates for large potassium dihydrogen phosphate (KDP) crystals. KDP is an important nonlinear optical material for modulating lasers. It has been grown commercially for many decades using aqueous methods similar to the ones described above. The need for even larger crystals of KDP for electro-optic switch and frequency converter plates in inertial confinement fusion research led to a big advance in solution growth methodology. It started in 1982 in Rashkovich's group at Moscow University. There they developed a rapid growth process for KDP from water solutions [170]. Over the next several decades, that work was taken up by Zaitseva and colleagues at the Lawrence Livermore National Laboratories in California [171]. They demonstrated that the standard Holden [165] crystallizer with temperature reduction could be used to grow large high-optical-quality KDP and deuterated KDP (DKDP) crystals up to 50 cm on a side at rates 10–100 times faster than older methods and without spontaneous nucleation and macroscopic defects. From their research on growing large crystals under fast growth conditions, they were able to develop a more thorough understanding of the mechanisms involved in solution growth. In addition to the influence of temperature, supersaturation and dislocations on growth rates, they realized the importance of impurities, mass transport (via high solution velocities) and in having a highly stable growth system. It was found imperative to control secondary nucleation. The most important feature of their rapid growth process was using highly supersaturated solutions (70–76 °C) coupled with elaborate techniques for preventing spontaneous nucleation. Toward that end a continuous filtration system and a seed protector were important modifications to the growth system.

1.3.2.3 Growth of Biological Macromolecules

Determining the crystal structure of complex biological molecules such as DNA, proteins, enzymes, etc., is important to both our understanding of animal and plant biology and functionality and our ability to develop pharmaceutical products to combat various illnesses that afflict these species. During the past century, protein crystallographers have slowly worked out the structures of a myriad of important species using X-ray diffraction methods. To accomplish this, researchers needed small, high-quality single crystals of controlled composition.

The first recorded protein crystallization experiments were done by German scientist F.L. Hunfeld in 1840. He prepared acicular crystals of earthworm hemoglobin by pressing blood between glass slides and allowing it to slowly evaporate. Since then, many techniques have been developed to prepare such crystals and the quality and size of the crystals produced were essential to the success of the structural detail obtained. The working out of the structures of myoglobin (1950) and hemoglobin (1955) using heavy metals covalently bonded to the protein led to the Nobel Prize for their researchers.

Another Nobel Prize winner who grew crystals in order to study their crystal structures was crystallographer Dorothy Crowfoot Hodgkin (1910–1994) [172]. As a child, Hodgkin was influenced by books that described how to grow crystals and on the interaction of X-rays with crystals. She won her prize in 1962 for her part in unraveling the crystal structure of the Vitamin B-12 molecule [173]. She also, together with Kathleen Lonsdale, grew crystals of penicillin and potassium and rubidium benzyl-penicillin. One of her major accomplishments was deciphering the structure of insulin.

While the crystal growth of biological macromolecules was primarily the domain of protein crystallographers and biologists during most of the century, in the 1980s the effort expanded to include experts more familiar with the theoretical and practical aspects of crystal growth (albeit small molecule materials). This came about in two ways. First, NASA had received requests from the crystallography community to fund protein crystal growth experiments in the low gravity environment of outer space. It was believed that the quality and size might be enhanced under these conditions. At the same time, NASA had been funding a variety of small molecule crystal growth experiments in low gravity with some promising results. NASA decided to try to engage some of the small molecule crystal growth community in the protein growth field. Several such programs were funded, one of which was my group at Stanford University. I immediately realized that we did not know enough about biological species to carry out his program successfully, and so when I found out that protein crystal growers did not have their own forum to discuss growth problems of mutual interest, I decided to bring them to Stanford basically to teach us about the field. Together with Alex McPherson [174], and with support from the American Association of Crystal Growth and NASA, we organized the first international conference on protein crystal growth at Stanford University in 1985. It not only brought together protein crystal growers for the first time, it also included well-known scientists and engineers from the small molecule crystal community. A total of 140 attendees were present. It was a somewhat contentious meeting at first, but as it proceeded, both sides, who spoke quite a different scientific language, came to understand more clearly the relevant issues, i.e., the physics behind the growth process and the influence of various processing parameters on the size and quality of the crystals produced. This international conference series has been held regularly every since.

Crystals of proteins and other biological species can be grown by a number of techniques including dialysis, sequential extraction, interface diffusion, vapor diffusion (plates, hanging or sitting drops), via pH and temperature changes, evaporation and in thermal (concentration) gradients. McPherson's original book, *Preparation and Analysis of Protein Crystals* [175], gives a comprehensive review of growth methods (see also Ref. [176]). Purification of starting materials and the composition of the growth solutions, like in most small molecule systems, are critically important to produce suitable crystals for X-ray structural analysis. Most of the growths are done in small batches. To establish the correct crystallizing conditions, a matrix approach is often used. Here, small samples with a systematically varied concentration of protein, salting agent,

solvent, etc., are placed within many cells and crystallized under the same conditions. Regions in the matrix that contain crystals are then regrown on a more refined compositional scale to enhance the results. In effect, this is the combinatorial chemistry approach and one that lends itself to automation using robotics to meter out the desired quantities into each cell. This latter approach was pioneered by Ward et al. [177] during the mid-1980s and is in wide use today.

One final comment worthy of mentioning again (see Scientific Study section) is that the large size of the growth units in biological macromolecules gave crystal growth scientists a unique opportunity to dynamically study the morphology and kinetics of step and ledge movement (including step bunching) during growth using the relatively new atomic force microscopy technique. The first such *in situ* studies were carried out in 1995 by Land et al. [178] and Malkin et al. [179].

1.3.2.4 Growth from Gels

In 1896, the German chemist Raphael E. Liesegang slowly put a drop of silver nitrate-water solution onto a thin gel layer containing potassium dichromate, and in doing so discovered the precipitation ring phenomena named after him [180]. This initial discovery stimulated a strong interest in understanding how the process worked. A gel is a semisolid containing small pores of angstrom dimensions in which a variety of salts can be dissolved. Early efforts on growing crystals in gels include the work of Hatschek [181] in 1911 and Dreaper [182] in 1913. The former grew small crystals of gypsum by letting sulfate ions diffuse in a gelatin containing a dilute solution of calcium chloride and the latter lead chloride crystals in a test-tube-shaped vessel. The idea for growing crystals in a gel media was stimulated by the research work of Fisher and Simons [183] in 1926. They were intrigued by some earlier work with gold and copper crystals produced by the reduction of their metal salts in a silica gel and the coincident occurrence of gold in quartz veins. From their early experiments, they predicted that this method would be “far-reaching” and this enthusiasm caught the attention of later researchers and became an area of vigorous research, particularly from the early 1960s onward. The work by Heinz Henisch’s group at Pennsylvania State University stimulated researchers around the world and was summarized in his book *Crystals in Gels* [184].

The gel growth method has been used to prepare an impressively wide range of inorganic and organic crystals, including proteins. Gels provide a medium where mass transport is by the slow diffusion of suitable ions to a region where they can react during crystallization. It is a convection-free method and the crystals, when nucleated under carefully controlled conditions, are suspended from one another. These factors, plus the near room-temperature growth conditions purportedly result in higher crystal quality. Crystal dimensions can vary from micron to centimeter sizes depending on the system under study, but typically they only reach mm sizes. Like other solution growth crystals, they exhibit growth rate anisotropy and faceting. Typical gels used are silica hydrogel (sodium metasilicate), agar (derived from seaweed) and gelatin; however, many other gel compositions have been used as well. Crystals can be grown within gels by a number of

techniques, including (1) chemical reaction, (2) complex dilution, (3) chemical reduction and (4) solubility reduction. An extensive list of crystals grown is given in Ref. [185]. During the last decade or so, interest in gel growth has diminished along with the number of publications.

1.3.2.5 Nonaqueous Solution Growth

Organic crystals are useful for a number of applications including semiconductors and scintillator devices. Organic materials, like other substances, vary widely with respect to their thermodynamic and physical properties. Therefore it is not surprising that a suitable crystal growth method will depend on the specific properties of the material in question. They can be grown by a variety of common crystal growth techniques including vapor, melt and solution methods. Organic materials that melt without dissociation are prime candidates for melt growth methods. Others have been grown in solution or by vapor phase techniques. Solution growth methods usually involve organic solvents such as ethyl alcohol, acetone, hexane, and carbon tetrachloride. The techniques used are similar to water solvent methods and include solvent evaporation, slow cooling or heating, vapor diffusion and liquid–liquid diffusion and are nicely summarized in Ref. [186]. One of the recent examples of solution growth using organic solvents is the work at the Lawrence Livermore Laboratories on the growth of large, high-quality crystals of trans-stilbene ($C_{14}H_{12}$) for fast neutron detectors [187]. The solvents used were toluene or anisole, the latter preferred due to its lower evaporation rate. Melt growth techniques did not yield large, high-quality crystals. Building crystallization systems to withstand the organic solvents and by using the temperature reduction method together with rotation, very high-quality crystals in dimensions up to four inches have been produced.

1.3.2.6 High Temperature Solution (Flux) Growth

1.3.2.6.1 Bulk Crystals

As with other solution growth methods, the high temperature flux growth method also relies on the careful control of the supersaturation and melt composition. Like the low temperature processes, there are three general methods for controlling supersaturation: (1) slow cooling, (2) evaporation and (3) transport in a concentration gradient. In its early incarnations, the method was unseeded and crystals grew on the surface of the melt where supersaturation is usually greatest (due to volatility) or on the crucible walls where heterogeneous nucleation is favored. Later, the use of seeds or cooled probes helps facilitate growth. Generally solvents are classified as common ion or noncommon ion fluxes. An example of the former is the growth of $(Ba,Sr)TiO_3$ from excess TiO_2 melt [188], and the latter, the growth of $Y_3Fe_5O_{12}$ from $BaO-B_2O_3$ based fluxes [189]. The $BaO-B_2O_3$ flux, while used early on, was not nearly as successful as $PbO-B_2O_3$ or $PbO-PbF_2-B_2O_3$ fluxes that form ionic solutions. The 1975 book *Crystal Growth from High Temperature Solutions* by Elwell and Scheel [190] still remains the most thorough, encyclopedic treatment on the history, theory and methodology of flux growth.

Crystal growth from high-temperature solutions probably began during the nineteenth century. One of the earliest documented studies (1823) was by Friedrich Wöhler (1800–1882), a famous German chemist who used a flux-reaction technique to grow sodium tungsten bronze (Na_xWO_3 , where x is ≤ 1) crystals by passing H_2 gas over a Na_2WO_4 flux [191]. He is also famous for his synthesis of urea and the codiscovery of Be, Si and silicon nitride. By mid-century, early experiments were of a similar nature and a variety of materials were produced including CdS (using a CdCl_2 solvent and H_2S reactant), alkaline earth and transition metal oxides, silicates and sapphire [190]. Later in the century, more traditional flux methods were used to grow a variety of binary, ternary and higher order compounds using chemically compatible solvents. Some examples include Doepter [192], who in 1886 grew Ag_2S by dissolving and recrystallizing it from AgCl or SbCl_3 melts. AlB_{12} crystals were grown from B_2O_3 melts by Wöhler and Deville in 1857 [193], and ruby was grown by Fremy and Feil in 1877 [194] using PbO as the flux (which from the 1950s onward became a popular flux for growing oxide crystals for optical applications). The results varied from laboratory to laboratory, and generally the crystal sizes were on the small side. Over 100 flux-grown compounds and their solvent phases are listed in Ref. [190]. In this time period this was probably the most important method used for preparing crystals of non water-soluble materials.

Solvent requirements include (1) a suitable melting temperature and solubility in the temperature range of interest, (2) a temperature coefficient of solubility, (3) low volatilization (an issue with PbO and halide fluxes), (4) compatibility with available crucible materials (reactivity and wettability) and (5) a relatively low viscosity. In the 1950s, the flux growth method again became an important adjunct to other developing crystal growth methods such as the Czochralski and Bridgman methods. It was particularly important for compounds that melt incongruently, have high vapor pressures at their melting temperatures, are refractory with excessive melting temperatures or have destructive phase transformations, etc.

After World War II, the flux growth method gained interest commensurate with device researchers' interests in finding new and better materials for optical, electronic and magnetic applications. The use of this method was very extensive during the 1950s through about 1980 and took place in many laboratories around the world. As a result, it is only possible to cite a few illustrative examples in this brief historical review to give a sense of what growth activities were like during this period. In 1964, Edward Giess [195] successfully prepared $\text{Cr:Al}_2\text{O}_3$ (ruby) using a PbF_2 flux. Lead fluoride is quite volatile, and so it was often combined with PbO with some added B_2O_3 to stabilize it. At about the same time, Stanley Austerman [196] used the flux growth method to grow BeO crystals. BeO substrates were of interest because of its very high thermal conductivity and therefore its ability to remove heat from electronic devices. This would permit higher power operation. Austerman grew BeO from a Li_2MoO_4 -based flux. Later, Newkirk and Smith [197] grew BeO from PbO -based fluxes. In Russia, V.A. Timofeeva's group was very active during this time period, studying the flux growth of many different oxide compounds including Al_2O_3 , Cr_2O_3 , Fe_2O_3 , rare earth oxides and the garnets $\text{Y}_3\text{Fe}_5\text{O}_{12}$, (YIG)

and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG). In the latter case, she investigated how growth defects formed as a function of the flux growth conditions and solvent composition [198].

Single crystal garnets ($\text{A}_3\text{B}_5\text{O}_{12}$) were of great interest for laser, microwave and ultrasonic applications. In 1958, Nielsen and Dearborn at Bell Laboratories were the first to report on the flux growth of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG) [199]. Major improvements in size and quality were achieved by adding impurities such as CaO to a $\text{PbF}_2\text{--PbO--B}_2\text{O}_3$ flux. Van Uitert et al. [200] worked on the growth of large, optical-quality $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) crystals in very large platinum crucibles. Remeika, whose extensive crystal growth activities also included the flux growth of YIG, found that pure YIG crystals contained small amounts of Fe^{4+} , which resulted in reduced optical quality [201]. By adding small additions of tetravalent ions such as Si, Sn and Ge to the flux, the problem was eliminated. Some examples of flux grown crystals are shown in Figure 1.12.

Flux growth methods vary from simply slow cooling a melt without seeding (self-nucleation) to more complicated seeded growth techniques. The bottom cooling method helps control nucleation in unseeded melts. A small supersaturated region is created in the melt to limit the volume in which nucleation can take place. This can also be used to prevent a seed from dissolving before it starts to grow (like in the heat exchanger method). In 1955 and 1956, Reisman and Holtzberg were the first to prepare single crystals of potassium niobate KNbO_3 (KN) and potassium tantalate KTaO_3 (KT). These compounds were of interest for ferroelectric and piezoelectric applications [203]. A K_2O flux was found suitable for this purpose. KN in particular became a very important material for efficient direct diode doubling and other NLO frequency conversion processes, such as generating blue light from a Ti:Sapphire laser via critical phase matching. Over the years, large-scale

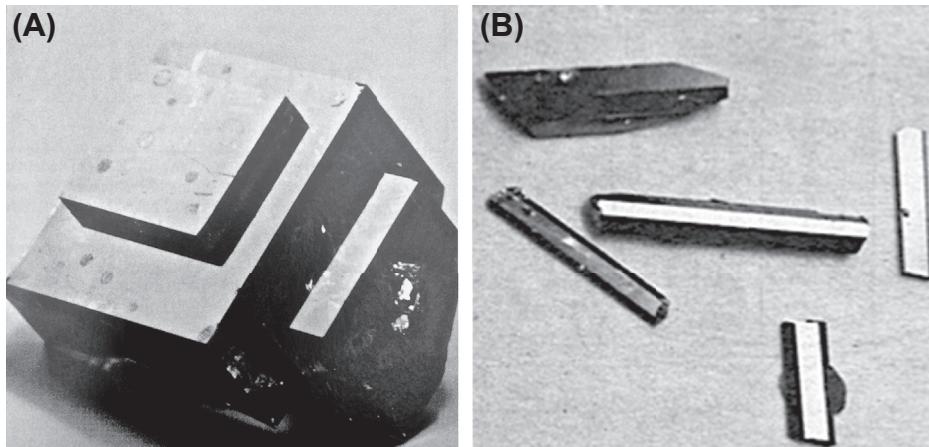


FIGURE 1.12 (A) A photograph of a large ($3.5 \times 3 \times 2.5$ cm), flux-grown crystal of GdAlO_3 . It contained large inclusion-free regions. A $\text{PbO-PbF}_2\text{--B}_2\text{O}_3$ flux containing some other minor additives was used. The large size and quality is attributed to ACRT stirring method [202]. (B) Photograph of some highly faceted acicular crystals of CdGeAs_2 grown from a Bi flux (author). Some are solid, others contain a core of solidified Bi solvent. Strong growth rate anisotropy is evident.

crystal growth methods capable of producing 100 gm crystals were developed [204,205]. While the K₂O flux was still used, top seeding was added later to control nucleation and growth conditions. This seeding technique, now known as the top-seeded solution growth method (TSSG), became a very important flux growth method. The first description of this method was in a 1958 paper by Miller [206]. He used a seed crystal mounted on a rod that rotated in a reciprocating fashion. Without pulling, he grew KN crystals up to 15 gm from a charge containing K₂CO₃ and Nb₂O₅. He also used an electrical circuit between the crucible and seed to determine the exact moment when the seed touched the melt. The method was used later by Linares for YIG growth [207] and at MIT by Belruss et al. [208] for the growth of SrTiO₃ and BaTiO₃ crystals from melts containing excess TiO₂ and GeO₂. More recently, the method has been used for growing beta barium borate crystals (β -BaB₂O₄, BBO) from melts containing some Na₂O [209] or other solvents to lower the η_e viscosity and to permit growth at temperatures below the α - β phase transformation temperature. BBO and other similar compounds like LiB₃O₅ (LBO) and CsLiB₆O₁₀ (CLBO) are very useful for optical applications in the visible and ultraviolet regions.

As seen with aqueous solution growth, stirring during growth is very beneficial to the enhancement of crystal quality and growth rates. In addition to top seeding with rotation that provides some fluid flow, other methods have been devised. One useful approach is the accelerated crucible rotation technique (ACRT). It was first used by Nelson and Remeika [210] in 1964 for pregrowth stirring. Scheel and Schultz-Dubois first demonstrated its usefulness during growth in 1971 [104]. The method is very helpful with growth from volatile melts that need to be grown in sealed crucibles. No moving parts, like stirring rods, need to be placed in the melt. The method relies on acceleration and deceleration of the crucible, thereby decoupling the fluids movement from the crucible's trajectory in a periodic fashion. Two major flow mechanisms, spiral shearing distortion and Ekman-layer flow, are operative during acceleration and deceleration. It has been found to limit nucleation and to help produce large, inclusion-free crystals. It was first applied to the growth of GdAlO₃ crystals from a PbO-PbF₂-B₂O₃ flux and yielded the largest such crystal to date [202].

One other method worth mentioning was that devised by Tolksdorf [211] at the Phillips Central Laboratories in Hamburg. In the past, one of the problems with growing YIG crystals from the volatile PbO-PbF₂ flux was that it redissolves below 950 °C. To prevent this, Nielsen [212] poured off the flux at 1040 °C outside the furnace. Unfortunately, the crystals cracked due to thermal shock. An improvement on this method was by Grodkiewicz, Dearborn and Van Uitert [213]. They punctured the bottom of their large platinum crucibles draining off the melt. This was expensive, as the flux material could not be reused. In Tolksdorf's method he used a sealed crucible that could be rotated on its axis. It was half filled with a PbO/PbF₂/YIG melt and, after the crystals were grown by slow cooling, the crucible was spun 180° separating the crystals from the melt. In a similar way, he could mount a seed on the empty side, and when the melt was saturated, could rotate the seed into the melt, slow cool to initiate growth onto the seed, and when done, rotate the crucible back to its original position to remove the flux from

the crystal. Toldsdorf's method and apparatus was later used to grow KTiOPO₄ (KTP) crystals (an important nonlinear optical material) using the flux method.

1.3.2.6.2 Thin Film Liquid Phase Epitaxy

In addition to bulk crystal growth, high-temperature solutions have also been used to grow thin films of semiconductors, oxides (magnetic and electro-optic) and various other compounds. The method is known as liquid phase epitaxy (LPE). The LPE method involves the crystallization of a single crystal or crystallographically oriented layer on a substrate in contact with a liquid phase. The substrate (usually a single crystal wafer) may be either of the same base composition (homoepitaxy) or a different composition (heteroepitaxy). The field of epitaxial growth extends well beyond the LPE method to include numerous vapor phase depositions techniques to be discussed later. While these other methods are very important, the LPE has certain advantages including (1) greater crystalline perfection due to the near equilibrium growth conditions and use of a near perfect substrate template, (2) better stoichiometry control, (3) higher growth rates due to higher solutes concentrations and (4) lower cost compared to other methods. A comprehensive review of LPE field is given in Ref. [214].

Epitaxial deposits have been found in various natural mineral formations. One example is rutile crystals growing on hematite facets [215]. In 1836, Moritz Frankenheim (1801–1869), a German physicist, was the first of many researchers to observe epitaxial growth in the laboratory when he produced oriented crystals of sodium nitrate on a cleaved surface of calcite crystals [216]. In 1906 Baker did some experiments on the orientation of crystals growing from droplets crystallizing on cleaved surfaces [217]. In 1928, Royer followed this line of research [218] and using X-ray diffraction analysis, was the first to describe the requirements for lattice matching between the film and substrate to achieve epitaxy (an orientation relationship between the layer and the substrate).

In the 1960s, attention turned to thin film semiconductor devices. At the RCA Laboratories, H. Nelson [219] was the first to develop an effective LPE method for growing epilayers of GaAs on GaAs substrates (homoepitaxy). He used a horizontal graphite boat system with a GaAs + Sn melt at one end. When the substrate, located at the other end was at 640 °C, the boat was tilted and the melt flowed over the substrate. After cooling for a period of time the melt was poured back off, leaving the substrate covered by a single crystal layer of GaAs. Other LPE techniques involved dipping substrates (either vertically or horizontally) into an appropriate solution and then, after deposition, withdrawing them back out. Substrate rotation has also been used to achieve better uniformity. By using these various methods p-n junctions could be produced using doped layers. These epilayers were used in a number of important device applications including GaAs [220] and Al_xGa_(1-x)As [221] lasers and the extensive commercial production of light emitting diodes (LED's). The LPE method has also been used to prepare thin film structures from silicon, germanium and their solid solutions, II-VI compounds such as ZnSe, CdTe, Hg_{1-x}Cd_xTe (MCT), SiC, the III-V nitrides (AlN and GaN) and many other alloy compositions [214]. As with any flux growth method, the solvents have to be tailored to the specific film

composition to be grown and the substrate and its orientation carefully chosen. The requirement for high-quality substrates for both LPE and vapor phase epitaxy have kept the bulk crystal growth industry very active.

In addition to semiconductor research, various applications for magnetic garnet crystals (e.g., $\text{Y}_3\text{Fe}_5\text{O}_{12}$ and $\text{Ca}_{2x}\text{Bi}_{3-2x}\text{Fe}_{5-x}\text{V}_x\text{O}_{12}$) were developing during this same time period. LPE became an important method for the preparation of various types of microwave, magneto-optic and bubble memory thin film devices. One of the first attempts to use the LPE method for YIG film deposition on garnet substrates was in 1965 by Linares et al. [222]. In 1968 Linares [223] grew high quality YIG films on GGG using the tilting boat method and a lead borate flux. Magnetic bubble memory thin film devices became an important research activity during the 1970s [224]. These thin film structures were once expected to replace Si-based memory chips and various groups extensively studied both their preparation and properties. Magnetic garnet single crystal LPE films were typically grown from $\text{PbO}-\text{B}_2\text{O}_3$ fluxes. The substrates used were nonmagnetic $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG). It is a very good lattice match with YIG. Various techniques such as substrate dipping and rotation during growth were studied. Withdrawal after growth could be problematic due to cracking and film peeling. The process gave high growth rates and crystalline perfection, film thickness uniformity, and compositional homogeneity. Over time, ever more complex film compositions evolved to enhance their properties [225,226]. The technology reached its zenith with the growth of bismuth-doped rare earth iron garnet thick films up to one-half mm thick from $\text{Bi}_2\text{O}_3-\text{PbO}-\text{B}_2\text{O}_3$ fluxes onto large lattice parameter-matched Ca–Mg–Zr substituted GGG substrates.

In 1986, Bednorz and Müller discovered Hi-Tc superconductivity while working at the IBM research laboratories near Zurich [227]. The ceramic material they produced was an oxygen-deficient Ba-doped Lanthanum cuprate ($\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$), a perovskite-like compound that exhibited zero electrical resistance at 35 K, twice the highest transition temperature achieved to date. This set off a whirlwind of research activities to find other cuprates with even higher T_c 's including $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (92 K) followed by $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n+x}$ ($n = 1, 2$ and 3) with a T_c between 85 and 110 K. Thallium- and mercury-based cuprates had even high T_c 's, the latter a record at 134 K. At this point a great effort was made to grow single crystals of these compounds for physical property studies and to enhance their properties. Due to the complex nature of the phase equilibria in these systems, crystal growth was very complicated, making difficult the preparation of large, high-quality single crystals. All manner of bulk and film deposition methods were tried with varying success. In Scheel et al. [228], the LPE method was used to prepare very flat, high quality epitaxial layers of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ on NdGaO_3 substrates. Step heights were between 1.2 and 7.2 nm and did not exhibit the spiral islands found using vapor phase deposition techniques.

1.3.2.7 Hydrothermal Growth

Hydrothermal growth is a solution growth method operated at modest temperatures and elevated pressures. Byrappa and Yoshimura [229] authored an exhaustive treatise on the

history and technology behind the hydrothermal growth process. The subject has also been discussed to a lesser extent in numerous other books and journal articles, for example [230]. The process involves the controlled growth of crystals in an autoclave (see **Figure 1.13(A)**) onto seeds immersed in a water solution containing the nutrient and usually a mineralizing agent. The driving force for growth is the solubility difference generated by a temperature gradient. The method has several advantages. Growth takes place below the material's melting temperature and often below a destructive phase transformation (e.g., α -quartz, the low-temperature polymorph of SiO_2). Since the growth process takes place in a sealed system, the atmosphere can be modified to suit the material being grown (i.e., maintaining an oxidizing or reducing environment). In addition, the method generally produces less stress on the crystal and can lead to an increased crystalline perfection. Another attractive feature of hydrothermal growth is that the growth rates are relatively fast compared to other solution growth methods. High-pressure vessels can be made of various materials depending on the temperature and pressures required.

Hydrothermal growth's principal use has been for the commercial growth of large, highly perfect (dislocation-free) α -quartz crystals for piezoelectric applications. A rack of crystals produced from one large-scale commercial autoclave is shown in **Figure 1.13(B)**. Piezoelectric materials such as quartz generate an electrical polarization when subjected

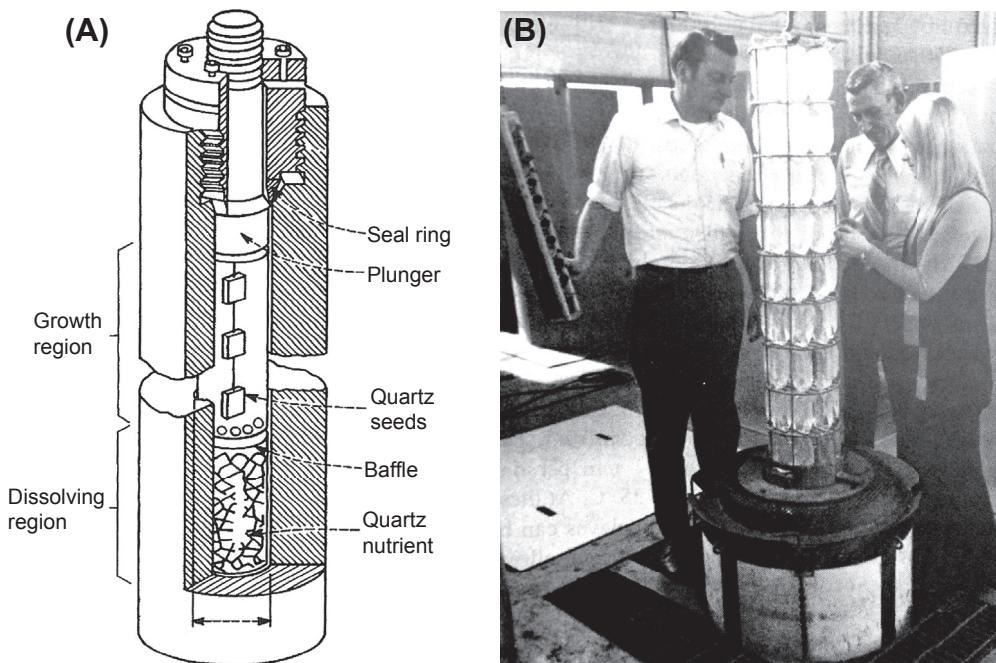


FIGURE 1.13 (A) A schematic diagram of a hydrothermal quartz autoclave. (B) The commercial harvesting of quartz crystals at AT&T's factory in Massachusetts [30].

to a mechanical stress. The hydrothermal method has also been used to successfully grow a variety of crystals of many different classes of compounds from simple binary compounds, such as ZnO, ZnS and GaN, to more complex compounds, such as the phosphates (AlPO_4 , and KTiOPO_4), calcite, hydroxyapatite, zeolites, silicates, metal borates, vanadates, tungstates, and rare earth garnets (e.g., YIG and YAG).

Geologists trying to understand how crystals grew in nature (in an aqueous media under high pressures and temperatures) were the first to carry out hydrothermal phase equilibria studies. Experiments have been traced back to the twelfth century. Their main interest was in phase relationships rather than the growth of large crystals. One of the first published papers on hydrothermal crystallization was by Karl Emil von Schafhäutl in 1845. He prepared microcrystals of quartz. A short time later, in 1848, Robert Bunsen prepared some of the alkaline earth carbonates. The first attempt to grow large crystals hydrothermally was by Henri De Séarnmont in 1851 [231]. He introduced the use of seed plates. It was one of his many studies on the hydrothermal crystallization of minerals. Fifty years later, Giorgi Spezia (1905) published one of the seminal papers on the seeded growth of α -quartz [232]. These early research efforts in Europe eventually formed the basis of the commercial quartz crystal industry.

The modern synthetic quartz crystal growth industry arose during World War II. Supplies of natural Brazilian quartz were not getting to the U.S. due to German submarine attacks on allied shipping. Ironically, one of the applications for quartz crystals was for submarine detection. Piezoelectric materials are needed in single crystal form to take advantage of their anisotropic properties. In oscillators for example, the frequency depends on crystal orientation and devices require precisely oriented parts. Quartz is also used for watches and clocks for precision time management and in signal processing applications.

Major developments in the hydrothermal growth technology were centered on the growth of quartz crystals at the Bell Telephone Laboratories and the Western Electric Company during the 1950s. Walker and Buehler [233] developed a hydrothermal growth method capable of producing very large crystals. They used a welded steel autoclave that was capable of temperatures of 450°C and pressures up to 3000 atm. Improvements in autoclave designs were based on some early high pressure studies by Bridgman. Over the following years, improvements were made by the Western Electric Company that led to its successful commercialization. It was in large part due to the efforts of Laudise and Sullivan [234]. Systematic kinetic studies by Laudise [235] led to significant improvements in crystal growth rates. An effort to improve the resonance of quartz oscillators was undertaken by Bell Laboratory scientists and other researchers. Lithium and nitrite ions added to the growth solutions led to improved mechanical Q values [30].

Important hydrothermal growth parameters include (1) operating temperature, (2) temperature gradient, (3) pressure, (4) percent fill, (5) impurity and mineralizer concentration, and (6) seed orientation and surface area. Using quartz as an example, the autoclave is placed in a two-zone furnace with the upper section, containing the oriented seed plates, being cooler than the bottom in which the nutrient, SiO_2 , is placed.

A perforated metal disc serves as a baffle between the two zones. The vessel is then filled with solvent to a desired level. The nutrient dissolves in the hot region of the furnace and the upper becomes supersaturated and deposits crystal layers on the seed plates. Convective currents generated by the temperature gradients help move saturated solutions to the seed chamber. For commercial quartz production (see [Figure 1.13\(B\)](#) above), a typical set of conditions might include a hot zone temperature of 400 °C, a seed zone temperature of 360 °C, a fill factor of 80% and a solution containing 1.0 M NaOH, a baffle opening of 5% and a pressure of 21 kpsi (144 MPa) [230].

An important more recent application of hydrothermal growth has been in the preparation of ZnO crystals. ZnO is a transparent, wide bandgap semiconductor (n- or p-type when doped) with a range of useful properties. It is piezoelectric, ferroelectric, exhibits room temperature ferromagnetism, has a large magneto-optic response, etc. It is useful for chemical sensors, catalysis and optoelectronic applications. When doped, its conductivity can vary from insulating to metallic. Bulk crystals, thin films and various nanostructures can be produced using this method. Nanostructures, in the form of platelets, rods, columns, and complex bilayer (column-to-rod), have recently been prepared using hydrothermal methods [236–239].

1.3.2.8 Electrochemical Crystal Growth

Another useful solution growth technology is electrodeposition. It can be carried out in both aqueous and molten salts solutions, and both bulk and thin film single crystals can be grown in this way. The process involves introducing an anode and cathode into either type of solution (of appropriate composition) and applying a suitable voltage across the cell. The driving force for crystallization is the passage of current between the electrodes. The electrode can be a single crystal substrate (wafer or seed), a wire or a more complex structure. Electrodeposition has recently become an attractive method for use in preparing nano-, bio- and micro-structures. It can be used to make functional materials with the aid of three-dimensional masks and scaled up from the deposition of a few atoms to thick deposits.

The first use of electrolysis in chemical processing is attributed to the famous English chemist Sir Humphry Davy (1778–1829). Davy, who was responsible for the discovery of several alkali and alkaline earth metals, separated K from KOH in 1807, the first metal isolated by electrolysis. It has been used since then for the synthesis of a variety of materials. The Hall process, developed in the 1930s for separating Al metal from bauxite (dissolved in a molten salt), is one of its most important industrial applications of electrodeposition. It has also been used to produce many refractory compounds such as borides, phosphides, silicides and carbides. The application of this technology to crystal growth had a late start, surprising since Kunmann [240] observed that “materials electrochemically precipitated from fused melts can almost always be obtained in the form of reasonably large crystal when sufficiently low current densities are employed.”

The potential advantages of electrocrystallization for crystal growth include (1) growth can be accurately controlled solely by electrochemical parameters (current

density and electric potential), (2) the process is isothermal (thermal gradients and temperature ramps are unnecessary), (3) its insensitivity to temperature fluctuations, (4) low growth temperatures minimize thermal decomposition and stresses, as well as vapor losses, (5) purification can be achieved electrochemically and (6) growth features can be studied quantitatively by varying electrochemical parameters [241]. On the other hand, the material to be grown and substrate have to be electrically conducting, and the growth rates are typically slow due to the generally low solute concentrations in the solution. An interesting hybrid method, developed by DeMattei et al. [242], combined molten salt electrodeposition with the Czochralski pulling technique. They demonstrated the method by growing long [110] oriented crystals of sodium tungsten bronze from [110] oriented seed crystals.

Silicon was first electrodeposited in 1854 by Claire-Deville [243]. He used a $\text{NaAlCl}_4\text{-Si}$ molten salt solution. This work was followed a decade later by Ullik [244] who used a $\text{K}_2\text{SiF}_6\text{-KF}$ flux. Cohen and Huggins [245], using a similar flux, were the first to produce coherent epitaxial layers of Si on Si substrates. Metal substrates yielded polycrystalline films. Other semiconductors electrodeposited from molten salt fluxes include the III-V compounds GaP, GaAs and InP. A review of molten salt electrochemical crystal growth was given by Feigelson in 1980 [246].

In the 1990s, an active research area developed around the growth of heteroepitaxial thin films of chalcogenide semiconductors using the low temperature aqueous solution electrodeposition method [247]. Large-scale solar cells were made from electrodeposited polycrystalline CdTe films [248]. Epitaxial films of CdTe can be electroplated from solutions containing cadmium sulfate and TeO_2 onto an InP substrate [249]. In addition, epitaxial films of PbS [250], CdS [251], ZnSe [252] and other related compounds have been electrodeposited. Schlesinger et al. [253] presented a comprehensive review on the subject of semiconductor electrodeposition.

As mentioned above, ZnO is an important and versatile material of great interest to the research and industrial communities. The electrodeposition of ZnO was first demonstrated by Izaki et al. [254] and later Peulon et al. [255]. The growth of oriented rods and flat, disc-shaped crystals were described in Refs. [256–258]. Xu et al. [259] electrodeposited well-defined nano- and micro-structures onto to indium-doped tin oxide substrates using low molecular weight salts in the solutions to control crystal shape. They produced hexagonally shaped tapered ZnO rods and platelets and rhombohedral rods by using amine and other inorganic ions in their solutions.

1.3.3 Vapor Growth

1.3.3.1 Introduction

Vapor phase crystal growth methods have been used extensively for the preparation of both bulk crystals and single crystal thin films. The latter, called vapor-phase epitaxy, are usually deposited on single crystal substrates and have found their greatest utility in the preparation of films and patterned nanostructures for electronic and electro-optic devices.

Important film deposition techniques include OMVPE, MBE, sputtering, etc. In most of these techniques the crystalline lattice of the film needs to be tailored to the substrate upon which it is deposited. Their properties depend not only on their composition, but also on lattice matching between the film and substrate and the crystalline defects that might arise from any misorientation. The substrates are typically thin, crystallographically oriented wafers cut from bulk crystals usually grown by melt growth techniques. The process can be homoepitaxial (growth on a substrate of the same material) or heteroepitaxial (growth on a different substrate material). Some common examples being Si integrated circuits, GaAs LED devices and more recently GaN on sapphire for lighting applications. Artificial epitaxy, to be discussed later, involves the creation of a geometric pattern (containing some orientational relationship with the film lattice) on a substrate by etching or deposition. The base substrate can be an amorphous material like glass.

Vapor growth technology does not have as long a history as other crystal growth methods. Most research and development work began mainly from 1960 onward. However, it has been traced back a bit further to the German chemist Robert Bunsen (1811–1899) [260]. In 1852, Bunsen observed that Fe_2O_3 crystals formed together with HCl in volcanic gases through a reaction between ferric chloride and water vapor, i.e., a chemical vapor deposition (CVD) process [261]. Not long afterward, in 1861, French chemist Henri Claire-Deville (1818–1881) became the first person to put a CVD process to use preparing artificial oxide minerals of magnesium, titanium and tin [262].

The first commercial CVD process was inaugurated in 1880 for the fabrication of filaments for the new incandescent lamp industry [263]. In 1914, F.C. Brown, studied the crystal habits of Se crystals deposited by sublimation of its vapor in a closed tube under either vacuum or atmospheric pressure [264]. He held the Se at 270 °C for up to a week and the crystals formed along the tube where the temperature was lower. The largest crystals always formed at the higher condensation temperatures (~210 °C). During the 1920s, Fritz Koref and immediately afterward Anton Eduard Van Arkel used WCl_4 to deposit W on single crystal tungsten wires. Koref [265] used a hydrogen reduction method to dissociate WCl_4 gas near the wire, which was heated to between 110 and 1000 °C. This led to a W deposit containing oriented grains. In Van Arkel's process [266], H_2 was not needed as the process was operated at much higher temperatures (1600–1700 °C). In 1921, research began on growing metal crystals by sublimation. Gross [267] and Gross and Volmer [268] grew leaflet crystals of Zn and Cd by directing vapors onto cool glass plates. This work led Volmer to his adsorption-layer theory discussed earlier. In 1932 Straumanis [269] grew Mg, Zn, and Cd crystals by a similar technique. The metals were held at temperatures somewhat below their melting points.

Three basic techniques have been used to grow crystals from the vapor phase: (1) direct sublimation or evaporation of material followed by condensation, (2) chemical transport reaction and (3) chemical vapor deposition. Chemical thermodynamics (shifts in vapor–solid equilibrium) and mass transport are some basic differentiating features between these methods. The process relies on mass transport of species from the source through the gas phase to its incorporation onto the crystal surface. The sublimation and

chemical vapor deposition methods have been operated in either an open system, using an inert carrier gas, or in a closed growth chamber containing vacuum or higher gas pressures. The chemical vapor deposition method, most often used in thin film epitaxy, involves the decomposition of molecular species (precursors). The chemical transport reaction method, a reversible process, converts nonvolatile species into volatile ones prior to crystallization in closed systems.

Crystals can usually be grown by vapor growth techniques at lower temperatures than from melts of the same composition. Vapor phase methods are especially useful when a compound is difficult to grow because of a high vapor pressure, dissociation prior to melting, etc., or where a thin film is required. While these methods are used more extensively to grow epitaxial thin films, bulk crystals of a wide variety of elements and compounds (inorganic and organic) have also been prepared in useful sizes. Seeds are often used but many studies have involved heterogeneous nucleation on the walls of an ampoule. Vapor grown bulk crystals have been particularly useful for the preparation of small crystals for physical property studies, and in a few cases larger crystals, such as SiC and CdS, have found commercial markets. Crystals prepared by vapor techniques include halides, chalcogenides, oxides, pnictides and organic compounds. Growth rates vary for different materials systems and process details, but generally tend to be slower than melt growth methods. Comprehensive reviews of vapor growth theory and methods have been given by Kaldis [270], Faktor and Garrett [271], and Wilke [272].

1.3.3.2 Bulk Growth

1.3.3.2.1 Physical Vapor Transport

A volatile compound that congruently sublimes (or evaporates from the liquid state) can form crystals when it condenses in a cooler region of a furnace. In its simplest form, a closed glass ampoule containing the source at one end is placed in a temperature gradient. The source sublimes at a selected temperature and condenses at the cooler end either as self-nucleated crystallites or on a seed crystal. When no seed is used, many nuclei usually form and some may outgrow the others due their temperature of deposition or their orientation with respect to the heat flow in the system. In 1954, Pizzarello [273] made an important modification to the method that helped improve crystal size and quality. It involved translating the ampoule in the furnace gradient and has some similarities to zone melting with the source and crystal separated by the gas phase rather than the melt. The amount of vaporization at the source end is balanced by amount deposited on the crystal [274]. This “zonal sublimation method” has been used to grow doped crystals of Cd and Zn chalcogenides (see Ref. [275]). Both vertical and horizontal methods have evolved. By controlling the nutrient flux toward the growth interface, seeded growth is possible. This was demonstrated both by Fuchs in 1960 with CdS [276] and by Prior in 1961 with PbSe [277].

Some refractory materials such as SiC and ZnO require high temperatures to achieve useful vapor pressures. SiC and ZnO are important wide bandgap, high-temperature/high-voltage semiconductors. Large crystals are sought-after for the

fabrication of substrates. Since melt growth would require pressures of 100,000 atm and 3200 °C, other growth methods were sought. Various novel growth chambers and heating methods were developed for the vapor growth of these crystals. One of the earliest was by Frisch [278] in 1935. He grew ZnO needles by sublimation of a ZnO pellet heated to very high temperatures. In 1955, Jan Anthony Lely [279] developed a sublimation process for growing SiC single crystals that forms the basis of all commercial processes today. In his method, silicon carbide was placed in a graphite crucible and heated to 2500 °C in an argon atmosphere. Large hexagonal platelets of 6H-SiC formed. The crystals were of different sizes up to $2 \times 2 \text{ cm}^2$ and were of very high quality. In 1978, Tairov and Tsverkov [280] modified the process to include seeding. They placed the source at the bottom of the reactor and the seed at the top. Growth rates of 0.5–1 mm/h were achieved. Further modifications have been made since then, and now crystals greater than 50 cm in diameter can be produced. The formation of defects in these crystals, in particular micro-pipes has been a challenging problem [281]. Much effort has gone into their reduction or elimination.

Large crystals of organic compounds such as urea have also been grown by sublimation techniques [282]. However, the formation of gaseous byproducts such as ammonia during growth were problematic. To remove these unwanted species, which either slowed down or stopped the growth process, a vacuum pumped effusion hole was incorporated into the ampoule. Large cm-size high-optical-quality boules of urea were grown on [001] seeds at rates of 2.5 mm/day (by comparison growth from methanol solutions was 0.3 mm/day). The reactor used for the PVT growth of large urea crystals is shown in Figure 1.14.

1.3.3.2.2 Chemical Transport Reaction

When a material is nonvolatile under convenient processing conditions, it can often be chemically converted into a volatile species. Crystal growth can then proceed in a reversible process. This method is called the chemical transport reaction method (CRT). For example, ZnSe crystals can be grown in a sealed ampoule in the presence of a small amount of I₂ vapor (the transport medium). The ZnSe charge at the hotter end will react to form ZnI₂ (v) + Se (v). These gaseous species will then be transported to the cooler end reforming ZnSe on the growing crystal and thereby releasing I₂. The freed iodine can then react with more ZnSe source material and return to the growth zone. In this case, for deposition at the cold end, the required conditions are that the enthalpy (ΔH) and entropy (ΔS) are <0. For materials where ΔH and ΔS are >0 deposition takes place in the hot zone.

The chemical transport method is based upon the pioneering work of Van Arkel and de Boer [283]. In 1925, they prepared the refractory metals titanium, hafnium and thorium using this iodine transport technique with deposition taking place on a heated wire. By 1963, the field had expanded to encompass many different materials using a variety of transporting agents. Harold Schafer's book entitled *Chemical Transport*

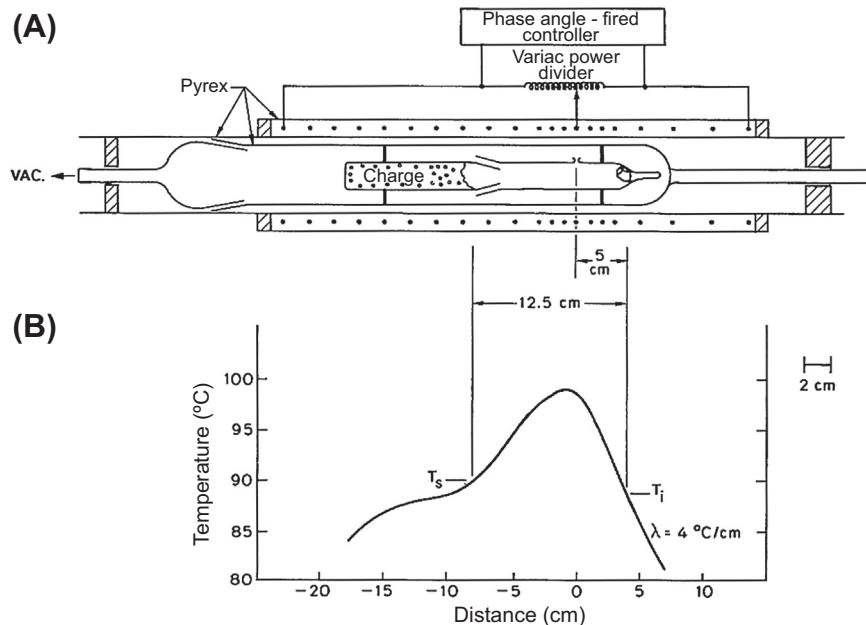
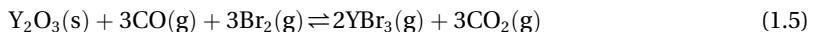


FIGURE 1.14 An example of a physical vapor transport bulk crystal growth apparatus. This growth system was used for growing urea crystals [282].

Reactions [284] has been an invaluable reference source for workers in the field since 1964.

Some important process requirements include (1) a chemical reaction that produces only one stable phase, (2) a free energy close to zero to facilitate reversibility, (3) a non-zero ΔH° and (4) the ability to control nucleation and the growth kinetics via crystallization zone temperature, temperature gradients, etc. Dopants have been added by incorporating volatile species of the desired element(s) into the growth ampoule. The choice of transporting agent is based on the thermodynamic propensity for the volatile species to form and dissociate in a useful temperature range. Sometimes additional species such as CO are added to the ampoule to facilitate the desired reaction. Sagal showed in 1966 that the growth of Y_2O_3 crystals solely by halogen transport was not favored due to relatively high values of ΔG° (near 60 kcal/mol for the Cl_2 gas and higher for Br_2 and I_2) [285]. However, by adding CO to Br the ΔG° value could be shifted closer to zero. The reaction therefore would be:



During the 1950s and 1960s, considerable research work was in progress using the CTR method. Metals such as iron, cobalt, copper and nickel crystals were produced, as well as classical semiconductors such as silicon, gallium arsenide and gallium phosphide. In addition, various oxide crystals such as alumina, beryllia and silica were grown.

1.3.3.2.3 Chemical Vapor Deposition

The same basic chemical transport process can be used in open systems; however, the process is not reversible. This method is typically known as chemical vapor deposition (CVD). Its most important application by far is the growth of epitaxial thin films to be discussed later. Bulk crystals or thin oriented films are grown by reacting and/or decomposing one or more volatile precursors in the vapor state and depositing them onto the crystal or substrate. These sources can be in many forms; gases, liquids, solutions and aerosols. Any unwanted reaction byproducts can exit the system in the gas stream. Very pure crystals can be produced by this method depending on the type of precursor used. Perhaps the earliest example of this technique was reported by Lorenz in 1891 [286]. He reacted Cd vapor with H₂S gas to form fairly large crystals of CdS. In 1947, Frerichs [287] modified the technique by using a slow stream of H₂ gas to drive the H₂S over Cd metal that was heated to 800–1000 °C. His open tube system produced crystals up to 2 cm². An extensive discussion of bulk crystal growth from the vapor phase is given by Schönherr [288]. He provides many useful and practical details including the various methods used, ampoule designs and furnace systems, etc. Bulk growths can be grown in vertical or horizontal configurations or any angle inbetween. Translating the growth chamber or ampoule in a temperature gradient is an often-used procedure. The reactors can be operated at pressures ranging from atmospheric to ultra-high vacuum. Materials produced by the CVD method include refractory metals (such as tungsten), semiconductors (such as silicon and III-V compounds), oxides (such as SiO₂), silicon carbide, nitride and oxynitride, and various carbon structures, including diamond as discussed later. Since the late 1990s, it has found use in the preparation of nanocrystals, one important example being carbon nanotubes and fibers. The nanotubes can be produced by a number of methods including the catalytic decomposition method [289], a CVD technique using metal catalysts together with hydrocarbon precursors. Depending on the details of the process, i.e., the metal catalysts used, etc., aligned single- or multi-walled nanotubes can be produced.

1.3.3.3 Vapor Phase Epitaxy

1.3.3.3.1 Organometallic Vapor Phase Epitaxy

Organometallic vapor phase epitaxy (OMVPE aka MOCVD) is a subset of the more general Chemical Vapor Deposition (CVD) method. It uses at least one organometallic precursor (OM) but may also be combined with other types of volatile species to produce films of many different II-VI and III-V semiconductor compounds and their solid solutions. Like other methods, there are lots of variations in technique. One of the earliest recorded descriptions of the OMVPE process was in Scott et al.'s little known 1957 United Kingdom patent [290]. In it, he describes the deposition of InSb in a cold wall reactor by the pyrolysis of a Group III alkyl (i.e., triethylindium) and a Group V hydride (i.e., stibine-SbH₃). The second, in a 1965 U.S. patent, described the pyrolysis of a Group III alkyl (i.e., triethylindium or trimethylgallium) and a Group V reactant such as arsine to produce a III-V semiconductor [291]. However, the first published work in the

scientific literature was in 1969 in a paper by Harold Manasevit and W. Simpson [292]. They grew single crystal Ga-group V compounds on insulating, GaAs, GaP or Ge single crystal substrates. Either trimethylgallium or triethylgallium in the presence of arsine, phosphine and arsine-phosphine or arsine-stibine gas phases was used in these experiments. In 2004, Manasevit, now considered one of the founders of OMVPE technology, published his recollections on how the OMVPE field developed [293]. A schematic drawing of his apparatus is shown in Figure 1.15. Along with his colleagues at the Autonetics Division of North American Rockwell, Manasevit published numerous other papers on this topic. In 1975, Seki et al. [294] produced the first important device quality (i.e., very high mobility) GaAs layers. This advancement was due to the enhanced purity and crystalline perfection of the films. Other major technological advancements followed soon afterward.

One of the important virtues of the OMVPE method is that it can be used to grow epitaxial semiconductor alloy films. In 1977, Dupuis and Dapkus [295] grew low oxygen and carbon films of AlGaAs by the OMVPE method. This material had excellent minority carrier lifetimes making them useful for light-emitting diode devices. In 1978, Gerald Stringfellow, from the Hewlet-Packard Laboratories, both proposed [296] and demonstrated [297] that with OMVPE one could grow very bright LEDs from AlInP and AlGaInP epitaxial films.

In the 1960s, Isamu Akasaki's group at Nagoya University started working on GaN-based LED's devices. In 1989, his work culminated in the invention of a bright gallium nitride p-n junction by using the low temperature OMVPE method with an AlN buffer layer on sapphire [298]. A major step was in creating p-type GaN using magnesium as the dopant and n-type with silicon. In 1994, Nakamura et al. [299] grew the first very bright InGaN/AlGaN double-heterostructure blue-light-emitting diodes also on

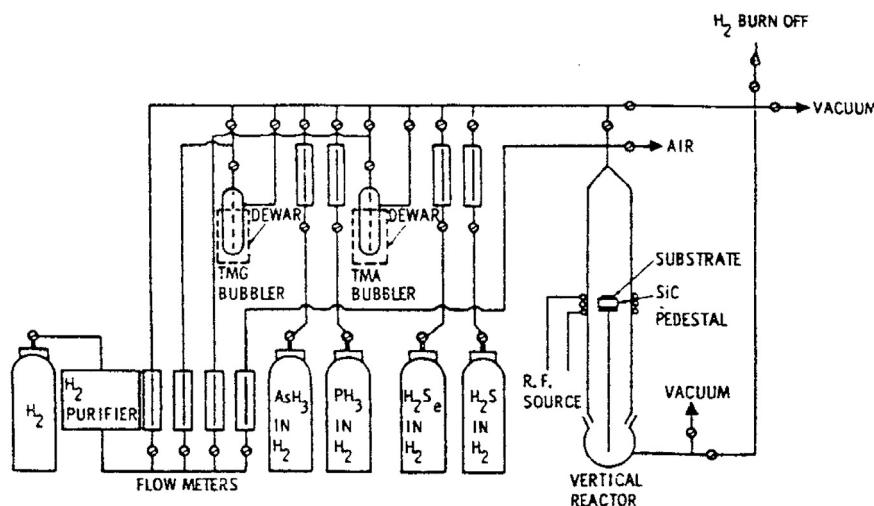


FIGURE 1.15 Schematic drawing of Manasevit's MOCVD deposition system [293].

sapphire substrates using a two-flow OMVPE method. The work of Nakamura's group at the Nichea Chemical Company, as summarized in Ref. [300], was a pivotal step in the development of the now multibillion dollar industry centered on the fabrication of highly efficient GaN-based/sapphire epitaxial films for optoelectronic devices. OMVPE development since then has been continuous with emphasis not only on improving the quality and properties of the epilayers, but also the quality and cost of the sapphire substrates. In an example of a more recent work (2002), Liu et al. [301] grew GaN single crystal epitaxial layers on sapphire in a three-step process using the low-pressure OMVPE method together with an AlN buffer layer and via atomic layer epitaxy (to be discussed later).

Stringfellow reviewed the development and status of the OMVPE method several times (e.g., Refs [297,302]). In the latter, he commented "One reason that OMVPE is so widely used today is that it is the most versatile technique for the growth of materials and structures for a wide range of devices."

1.3.3.3.2 Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy (MBE) is a process in which a thin single crystal layer is deposited on a single crystal substrate using atomic or molecular beams generated in Knudsen cells contained in an ultra-high vacuum chamber. The source beams can be created in a number of ways, including (1) melting and evaporation of solids or liquids contained in crucibles (2) solid sublimation from a crucible, (3) ion beam bombardment, and (4) cracking various chemical species, etc. Its greatest use is for making multilayer semiconductor device structures. Details of the MBE method, as well as other bulk and thin film growth techniques used to prepare compound semiconductors, are given in Ref. [303].

One of the earliest published studies on the use of the MBE method for single crystal film growth was that of Joyce and Bradley [304]. In the mid-1960s they grew homoepitaxial layers of Si from SiH₄. The growth rates were very low comparative to other Si film methods and therefore not competitive in a market that needed 10 um-thick films. A few years later, J. Davey and T. Pankey [305] from the Naval Research Laboratory, and J. Arthur [306] and A. Cho et al. [307] from Bell Laboratories expanded the MBE method for the deposition of GaAs. Arthur focused on surface kinetic studies, Davey and Pankey grew large-area GaAs epitaxial films on GaAs and Ge substrates using the three temperature technique, while Cho focused on device applications. The MBE technique is a powerful method both for film deposition and in situ analysis. It has yielded, in addition to device structures, a wealth of data on the surface atomistic phenomena such as surface reconstruction. It has also been applied to other semiconductor material systems such as the nitrides and has facilitated the construction of novel structures such as periodically poled GaAs for IR nonlinear applications and quantum dots. Today, it is a very important research tool and is used extensively in commercial optoelectronic device processing. A historical review of the MBE method was given by Joyce and Joyce in Ref. [308].

1.3.3.3.3 Sputtering

In 1852, Sir William Robert Grove (1811–1896), a noted Welsh judge, physical scientist and inventor of the fuel cell, was the first to discover the deposition process now known as sputtering [309]. He was able to deposit material from the tip of a wire in a chamber at a pressure of 0.5 Torr onto a polished silver surface when the latter was the positive electrode in an electrical circuit. An interesting factoid is that the first commercial application of the sputtering method may be attributable to Thomas Edison who early in the development of his wax phonograph cylinders using a sputtering methodology for plating them.

The sputtering method, as used to prepare thin films, became popular and of commercial importance from the mid-1960s onward. It has the advantage of not requiring high temperatures to deposit materials, even very refractory ones. The films have compositions similar to the target material and large areas can be deposited. While this physical vapor deposition method is more often used to deposit polycrystalline and amorphous films, single crystal films have been produced by carefully controlling the processing parameters. The method is used for fabricating integrated circuits, antireflection coatings, solar cells and optical waveguides, etc. Typical materials sputtered include metals, semiconductors, oxides, and nitrides, etc.

The simplest sputtering process involves just a temperature-controlled cathode and anode, a source of energetic particles, i.e., ions or atoms, and a vacuum chamber. A DC potential of several thousand volts is usually maintained across the electrodes. Radio frequency sputtering, where the sign of the electrodes is varied at a high rate, has also been found beneficial. The material to be deposited is ejected from the target (at the cathode) by bombarding it with ions or atoms, and the ejected material is transported in the plasma formed to the substrate (at the anode). In addition to the ions released from the target, electrons are also produced and they play an important role in maintaining the plasma. However at the same time they can cause excessive heating of the substrate. The transport mechanism within the gap between the two electrodes is complicated and depends to a great extent on the background gas pressure. For efficient ejection, the sputtering gas should have a similar atomic weight as the target elements. Nonreactive gases such as argon, krypton and neon are often used to eject atoms from the target, but reactive sputtering, using oxygen or nitrogen gas, has been employed to deposit oxide and nitride films (e.g., ZnO and TaN). In the latter process a chemical reaction takes place between the gas and the sputtered ions near the cathode before being transported to the substrate. Higher substrate temperatures encourage the deposition of single crystal films. Williams has given an extensive overview of the sputtering field and sputtered ion emission [310].

Conventional sputtering has some disadvantages including low deposition rates, low ionization efficiencies and substrate heating. One major improvement to this technology was the introduction of magnetron sputtering [311]. In this process a magnetic field is incorporated into the sputtering apparatus with the magnetic field positioned parallel to the target and confining the secondary electron movement close to the target. This

maximizes the probability of electron–atom interactions, increasing ionization efficiency. The result is higher sputtering and deposition rates. It also permits the use of lower operating pressures and voltages. The magnetron was originally conceived by P.M. Penning in 1936 [312]. In 1980, Naoe et al. [313] were the first to use it in a sputtering application. Over the years magnetron sputtering configurations have been modified, and these developments have led to improved film quality and device performance [311].

1.3.3.3.4 Atomic Layer Deposition

In 1977, Dr Tuomo Suntola from Helsinki University in Finland patented a novel technique to prepare highly oriented compound thin films [314]. The method was called atomic layer epitaxy (ALE). More recently, the nomenclature atomic layer deposition (ALD) has been favored. The ALD technique provides precise control of the film thickness and composition and with the proper substrate composition, orientation and temperature, can produce single crystal thin films. It involves the periodic (alternating) pulse deposition of a film's components in a vacuum chamber. In between pulses there is an equilibration period during which the excess components can desorb from the surface and exit the growth chamber. This leaves just one atomic layer on the substrate surface. The next atomic species is then deposited, and a controlled chemical reaction at the surface between these two layers creates the desired film composition or composite structure. By way of example, to produce an epitaxial ZnS film by this technique, a single Zn atomic layer is first deposited on the substrate surface. This layer is then exposed to $S_2(g)$ or $H_2S(g)$, either of which react with the Zn layer to form the compound ZnS. Following equilibration, another Zn layer is deposited and then reacted again with the sulfur-containing gas. The thickness is determined by the number of cycles employed.

Historically, the idea for a sequential layering film deposition process was first mentioned in the 1952 thesis of Professor V. B. Aleskovskii as molecular layering. And years later, (during the 1970s) his group in Russia worked on the developing this concept further [315]. The efficacy and implementation of the method into a commercially viable process derived from the work of Suntola's group during the years prior to their patent application. For a definitive review of all aspects of the methodology, see Suntola [316].

The ALD technique can produce atomically flat films with almost perfect stoichiometry and surface conformity through the self-limiting reaction mechanism. It can be used with many of the chemical vapor deposition methods described above that normally deposit the requisite phases simultaneously. It can be used to produce layered films with abrupt interfaces (e.g., TiO_2/Al_2O_3 films [317]), and M. Ritala and M. Leskela [318] reviewed the method's features and its potential role in nanotechnology. One of the drawbacks of the ALD method is the slow deposition rates. This has been somewhat overcome by increasing the substrate areas during deposition. The use of bias sputtering has given the best stoichiometry to date. Besides oxides and chalcogenides, as mentioned above, the method has also been used for the preparation of various semiconductors, nitrides, and metal films.

1.3.3.4 The VLS Method

Another interesting and useful growth method is the vapor-liquid-solid (VLS) technique. This hybrid method combines chemical vapor deposition with solution growth. Deposition takes place at localized positions on a single crystal substrate to yield a nanostructure, particularly whiskers, rods and nanowires. It starts with a single crystal substrate patterned with an array of small dots made from a solid metal solvent phase (the “catalyst”). The patterning can be done using lithography or by converting a solvent film deposited on the substrate surface to droplets. The growth procedure is simple. When the substrate is heated, the solvent phase melts. The liquid phase rapidly supersaturates by adsorption of nutrient species from the gas phase. Growth subsequently takes place at the substrate–liquid interface and not on the bare substrate surface. The solvent region rises up, as a mass is deposited below it, thus propagating the growth feature. The molten zone remains on the fiber tip during growth. As an example, silicon nanowires have been produced from a Au–Si alloy droplet and with a gas phase containing SiCl_4 and H_2 (see Figure 1.16 below). The VLS method has been used in conjunction with CVD, MBE, laser ablation and carbothermic reduction.

The VLS method was first described in 1964 in the pioneering work of Bell Laboratories scientists R. Wagner and W. Ellis [319] (see Figure 1.16). The VLS

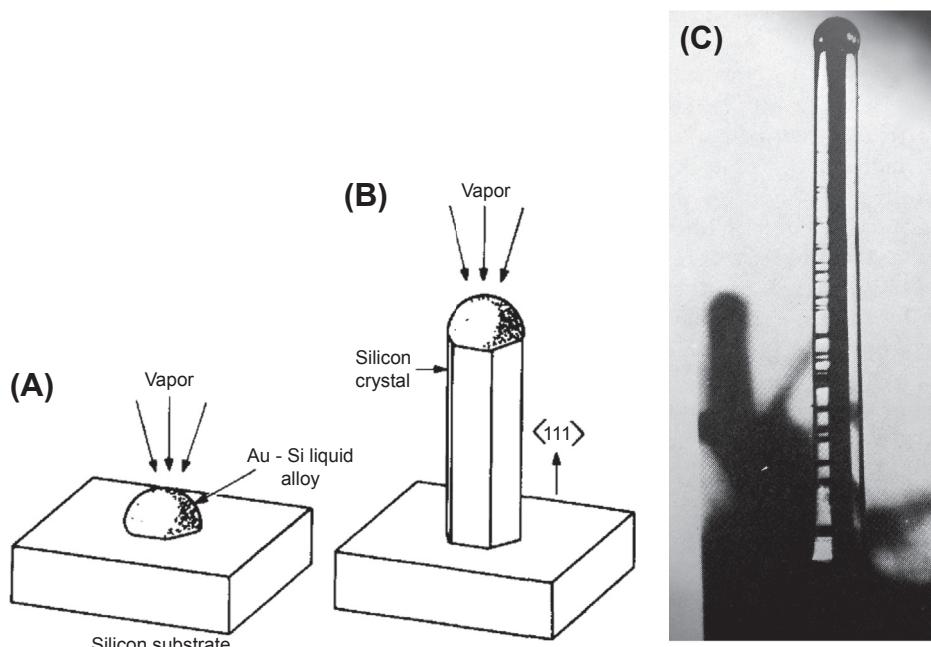


FIGURE 1.16 Original schematic diagram of the VLS process for Si whisker growth on a silicon substrate, (A) Au–Si alloy catalyst droplet on substrate surface before growth. (B) A growing whisker. A photograph of an actual Si whisker (0.5 mm diameter) grown on a {111} Si substrate is shown in (C). It has 12 side facets alternating between the {211} and {110} [318].

mechanism they proposed explained the growth of silicon whiskers on silicon substrates in the absence of the axial screw dislocation growth model described by Frank [22]. Some advantages to the VLS growth process include a lower reaction energy than with regular vapor growth techniques, the structures only grow where the solvent is located, and anisotropic-shaped columns can be produced. Important process parameters include (1) the wettability of the liquid droplet and its reactivity with the substrate, (2) the substrate orientation and surface roughness, (3) the processing temperature, etc. It is also very important and obvious that the solvent phase has to have a low equilibrium vapor pressure.

Some of the popular semiconductor materials grown by VLS include Si, Ge, GaAs, GaN, SiC and ZnO. Gold is most often used as the solvent phase, but other materials such as Ni, Pt have been successfully used. The substrates may be of the same or similar composition as the growth pillars (homoepitaxy) or on different material (heteroepitaxy). One example of the latter is the growth of densely aligned GaN wires grown on sapphire, LiAlO₂ or MgO substrates [320]. Schmidt et al. discussed various aspects of the growth of silicon nanowires and their electrical properties, including use of the VLS method [321].

The VLS method has been easily adapted to the growth of nanostructures. This has become a very important active area of research and should lead to exciting new commercial applications in the foreseeable future. One of the leading groups in this area is Lars Samuelson's group at Lund University. They have reviewed the fundamental mechanisms involved in the VLS processing of nanowires and the prognosis for further development of this technology [322]. Many new and unique structures have been created using the VLS process. One example being a decade old study that showed that certain material systems can phase separate into cored nanofibers. In a one-step VLS process, Choi et al. [323] grew GaN cored nanowires with a thick AlGaN skin. Other techniques have also been used to coat the nanowires. An excellent review of the VLS method was given by Choi [324].

1.3.3.5 Artificial Epitaxy (*Graphoepitaxy*)

Up to now, we have discussed the epitaxial growth of single crystal thin films on substrates made from materials of related composition and/or structure. The usefulness of high-quality single crystal or highly oriented films is well-known and crystalline perfection of the film depends on various attributes of the substrate and its quality. However, it would be highly desirable to be able to grow oriented films on inexpensive amorphous substrates or on substrate layers important to device function. In the early 1970s, Prof. N.N. Sheftal from the Russian Institute of Crystallography first described the concept of growing films on an artificial lattice. The paper, which described the technique as "artificial epitaxy," was translated into English three years later [325]. In 1982, the technique was renamed "graphoepitaxy" [326], and this more catchy term has gained favor in much of the subsequent literature.

Graphoepitaxy involves inscribing a micro-relief pattern onto a flat amorphous substrate surface. The surface patterns consist of only four symmetries, two-, three- four- and

six-fold (i.e., arrays of stripes, triangles, squares and hexagons). The walls of the relief pattern simulate the kinks and ledges associated with a crystal growth surface as described by the Kossel-Stranski model. Rather than atoms or molecules, however, the growth units that attach to these relatively large steps are microcrystallites of nanometer or micron sizes. The pattern chosen is determined by the crystal structure of the material to be deposited. For example, the three-fold relief would be used for the growth of the diamond lattices of Si and Ge. The reliefs can be achieved by a number of techniques including photolithography and etching, etc.

Graphoepitaxy can be accomplished using a variety of gas phase, melt or solution growth techniques, including the VLS method mentioned above. Like other methods described in this chapter many different materials have been prepared by graphoepitaxy, including very large-molecule biological materials [327]. By way of illustration, Figure 1.17 shows two crystals of catalase (an enzyme) that were deposited from an aqueous solution onto a silicon substrate that contained a striated micro-relief [327]. The pattern used here had a 5 μm periodicity and a groove depth of 1–2 μm . The crystals are clearly aligned with the micro-relief. Deposited on an unpatterned substrate, the crystals would have no orientational relationship with one another.

Graphoepitaxy has also been used to prepare oriented single crystal nanowires of semiconductor oxides such as ZnO, SnO₂, In₂O₃. The method has been exhaustively covered in a book by Givargizov [328]. Since this book was written, the technique has become very popular, particularly in the semiconductor field. For example, so-called nano-graphoepitaxy has been used to prepare semiconductors for three-dimensional integration devices [329].

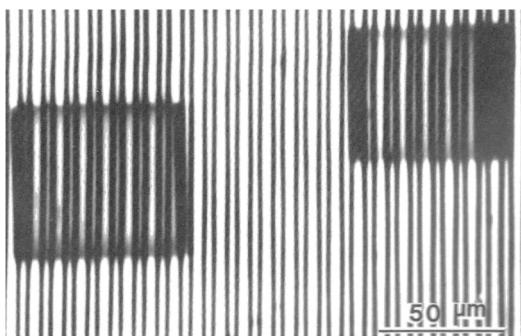


FIGURE 1.17 Two catalase crystals grown from solution onto an oriented Si substrate having an etched micro-relief pattern. The crystals, which are aligned with the pattern, grew by artificial or graphoepitaxy [327].

1.3.4 Synthetic Diamond Crystals

Diamond, while highly sought after as a gemstone, also has a unique combination of properties that make it very useful in industrial applications. Diamond not only has the highest known hardness, it also has a very high thermal conductivity and electron mobility, low thermal expansion coefficient and excellent optical transmission over a

broad spectral range. In addition to its major commercial market, i.e., cutting tools and polishing powders, diamond has a myriad of other uses. Diamond-based devices include high-power electronic devices, high-frequency field effect transistors, LED's, ultraviolet and high-energy particle detectors, substrates and optical windows. The two principal methods used to grow synthetic diamonds are (1) crystallization of bulk crystals from solution at high pressures and temperatures (HPHT) and (2) deposition at low pressures and relatively low temperatures using the chemical vapor deposition (CVD) method. Both were developed during the early 1950s within a few years of each other and are still in use today to manufacture synthetic diamond products.

The earliest known reference to diamond can be found in the Old Testament [330]. It was not until near the end of eighteenth century that it was realized that diamond, while transparent and colorless, was made up solely of carbon atoms like graphite. The discovery came from the French chemist Antoine Lavoiser (1743–1794), who shortly before his death, decomposed a diamond by heating it in oxygen and found CO₂ as the only byproduct. Thereafter, a number of credible researchers tried to synthesize diamond, one of the first being Scottish chemist James Hannay (1855–1931). His attempts in 1879 [331], later questioned, were followed in 1895 by the French Noble Prize-winning chemist Henri Moissan (1852–1907). He tried to synthesize diamond in the laboratory [332] starting with charcoal and iron heated to temperatures as high as 3500 °C using an electric arc furnace. The heated mixture was then quenched in water to hopefully create the high pressures under which diamond formed in nature. Other researchers who tried to duplicate these studies either failed or had their various claims discredited. Sir Charles Algernon Parsons (1882–1922), the inventor of the steam turbine, spent considerable time and energy over many years trying to duplicate the work of Hannay and Moissan. He also tried to develop his own method to produce diamond. In 1928, as reported by Desch [333], Parsons concluded that synthetic diamonds had not been produced. Kathleen Lonsdale used X-ray diffraction methods to study some of Hannay's "diamonds" held at the British Museum. She concluded in a 1962 paper [334] that they were natural diamonds and doubted that "... neither Hannay, Moisson or Parsons ever, in fact, made diamonds by their respective methods." Percy Bridgman, who as mentioned before won a Nobel Prize for his high pressure work, spent the better part of 50 years (from 1905 to 1955) trying to synthesize diamond. His efforts were apparently unsuccessful as well [330]. In addition to the researchers mentioned above, the nineteenth century was littered with numerous unsuccessful attempts to synthesize diamonds by various means. One particularly engaging and well-researched book on the history and growth of diamond crystals is *The Diamond Makers* by Robert Hazen [335].

In 1941, the General Electric Research Laboratories, in conjunction with the Norton and Carborundum companies, set about to develop a process to synthesize industrial diamonds. The effort was suspended during WW II but started up again in 1951. While GE put together a large staff charged with designing a furnace that could go to both high pressures and high temperatures, it was not until H. Tracy Hall, came

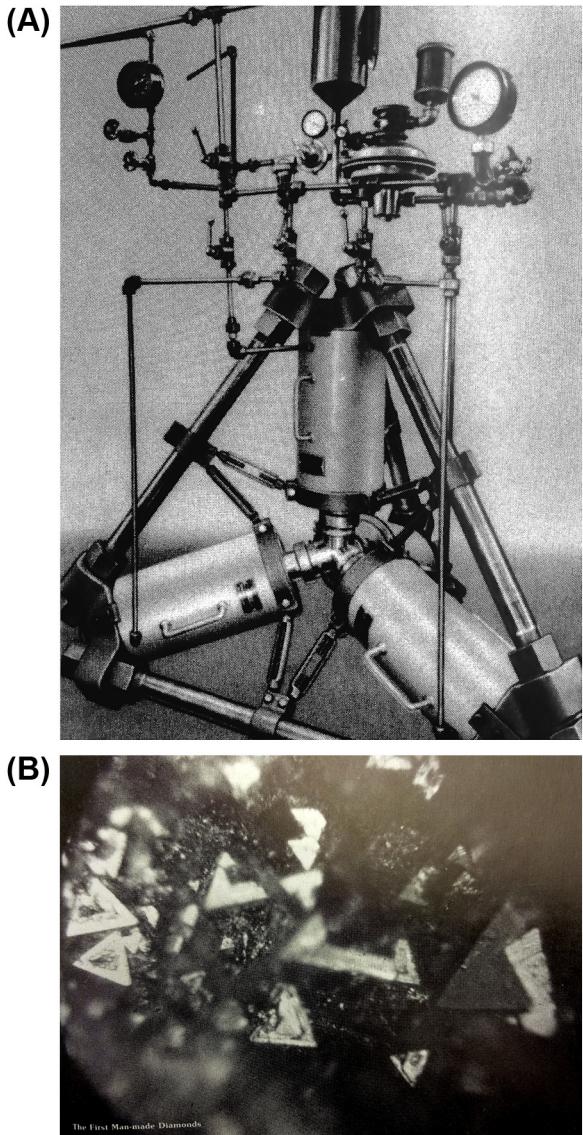


FIGURE 1.18 Early diamond crystal growth
(A) Schematic of the belt high-pressure, high-temperature apparatus built at the General Electric Corp., and (B) the first synthetic diamonds produced using this apparatus [330].

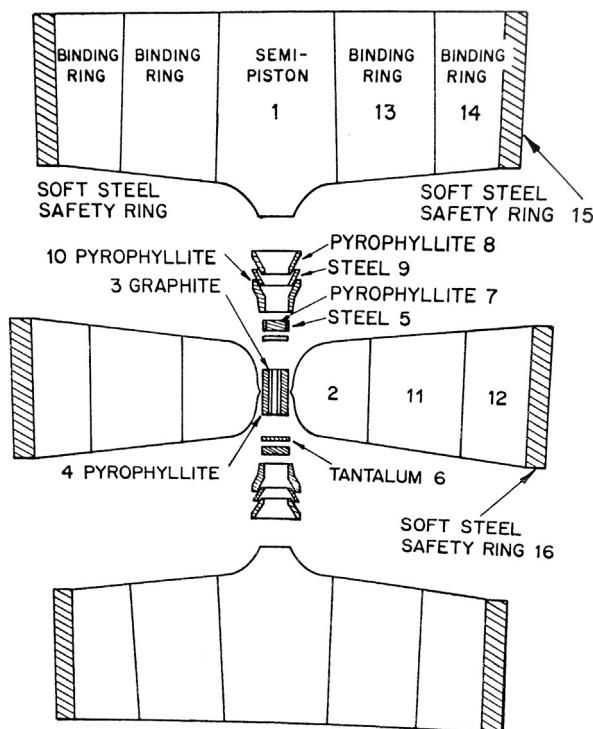
up with the “Belt” press (see Figure 1.18(A)) that a breakthrough was imminent. This device exceeded the original specifications of 35,000 atm and 1000 °C to achieve 250,000 atm and 1800 °C [336]. The growth chamber consisted of a graphite tube surrounded by a pyrophyllite container. Inside were placed Ni, Fe, or Co to act as a solvent-catalyst in which the graphite dissolved. The bottom was in contact with a Ta disc. However, even with this capability, diamond was not readily produced. It was

not until the end of 1954, after much experimentation and frustration, that the first small, micron-sized faceted diamond crystals were produced (see [Figure 1.18\(B\)](#)). The addition of FeS to the container did the trick. These were not gem-quality stones but appropriate for abrasive applications. Hall's personal reminiscences, given in Ref. [330], describe how the process was invented and the subsequent events that led to his other important invention—the tetrahedral anvil press shown in [Figure 1.19](#). Oddly, just before the GE success, the Swedish company ASEA, also managed to produce small diamonds in a top-secret project that only went public in 1980 [337].

The first successful preparation of gem-quality diamonds by HPHT was in 1970, again accomplished by GE. The process was similar to that described above with the addition of thin diamond seeds. The first crystals were 5 mm (1 carat) in size and took a week to grow. Longer growth times were required to produce larger crystals. These early crystals were yellow or brown in color due to nitrogen contamination and contained inclusions. By adding nitrogen getters such as Al and Ti, clear colorless crystals could be produced. On the other hand, other dopants have been used to modify the color of synthetic diamonds (e.g., boron gives it a blue color). A variety of colored stones have been produced.

The inherent technological difficulty in preparing diamonds or other materials at high pressures and temperatures and the high cost of equipment led many researchers,

FIGURE 1.19 The original tetrahedral press for producing synthetic diamond [330].



particularly in the U.S. and the Soviet Union, to try to find a low-pressure method. Not many scientists, however, thought this would be possible. Nevertheless, in 1952–1953, William Eversole, at the Union Carbide Corporation, became the first person ever to prepare synthetic diamonds [338] by the chemical vapor deposition technique. It involved slowly depositing carbon atoms on clean diamond particle surfaces (i.e., substrates) in a vacuum at temperatures in the 800 °C range. Carbon monoxide (CO) or methane (CH₄) was used as the source of carbon. Due to the propensity for graphite formation under these conditions, the residual graphite had to be removed after a period of time. This involved removing the crystals from the deposition chamber and cleaning them in an autoclave at 1000 °C and 50 atm of H₂ gas. Numerous such cycles were required. While he accomplished this feat about two years before General Electric and just a few months before ASEA in Sweden [337], his work (described in a patent only) was not published until 1962. In 1968, John Angus [339] independently verified Eversole's work, as did Deryagin and Fedoseev in 1970 [340]. While Angus also deposited diamond on single-crystal diamonds, Deryagin and Fedoseev made epitaxial films on other substrate materials such as Si and metals. From this point onward this very versatile method was aggressively pursued and refined by a number of groups in the USSR (Russia), the U.S. and Japan for the growth of both bulk crystals and homoepitaxial films on diamond substrates and by heteroepitaxial growth on suitably oriented materials like Si. A useful review of diamond growth by the chemical vapor deposition method was written by Garcia et al. [341].

One of the initial problems with the commercialization of CVD bulk diamond was the slow growth rates. In 1969, the former USSR scientists Spitsyn and Dervagin, who had been working on this problem since 1956, were finally able to increase the growth rates reported by Eversole by an order of magnitude. The improvement over their own previous work was due to the use of methane at higher pressures (13–40 Pa), together with an increased deposition temperature (950–1050 °C). Just a year later, a significant breakthrough was made independently by J. Angus (USA) and V. Varnin (USSR) [342]. They found that the use of atomic hydrogen in the growth chamber would remove the graphite co-deposits that form along with diamond due to a large difference in etching rates. A decade later, a group of researchers at Japan's National Institute for Research in Inorganic Materials made a series of important process improvements. They developed the microwave plasma, hot filament, and RF-Plasma CVD methods, new ways to dissociate the carbon-containing gases into reactive species [343–345]. Growth rates up to several $\mu\text{m}/\text{hr}$ were achieved. This in turn led to the development of a variety of other processes and process refinements by this and other groups, leading the commercial success of the CVD method for a variety of diamond products including gemstones and coatings for various types of electronic and optical devices.

Two other methods have been employed for growing small-size diamonds. One is the explosive detonation method in which a carbon-based explosive is detonated inside a metal tube containing graphite [346]. The procedure, an HPHT process, produces

nanoscale diamonds. The diamonds are prevented from reconverting to the more stable graphite form due to the quenching effect of a surrounding water-filled chamber. However, they have to be separated from the remaining carbon by dissolution in acid. The second method is the ultrasonic cavitation technique [347]. This more recent process is carried out at room temperature and atmospheric pressure. It involves the application of ultrasonic energy to a suspension of graphite particles in an organic liquid and results in micron-sized diamond crystals.

1.3.5 Solid State Recrystallization

The next to last topic to be covered in this chapter is the growth of sizable single crystals from the solid phase. This technology has a much smaller impact on the crystal growth field than the other methods described above. First, it is mainly limited to metals, and second, there are various processing difficulties associated with controlling nucleation and growth over extended length scales. The mechanisms involved are related to ceramic and powder metallurgy processing, where control of crystallite (grain) size and morphology in polycrystalline structures is a major concern. There are a myriad of important industrial applications for these polycrystalline materials (piezoelectric elements, magnets, etc.) and all aspects from theory to sample preparation are covered in various books on ceramics and powder metallurgy. The use of solid-state methods for crystal growth is covered in the book by R. Laudise [285].

At the heart of solid-state crystal growth (recrystallization) is grain growth. As mentioned before, the method is mainly used with metals such as aluminum, tungsten and iron. The material from which the crystal is grown contains grains of varying sizes and morphologies, plus grain boundaries and dislocations. Single crystals can be formed by controlling the growth of preexisting grains or by nucleating new grains with lower free energies. Wilhelm Ostwald's pioneering work in 1896–1897 explained how crystallites behave at elevated temperatures [348]. He showed that smaller particles adjacent to larger ones would decrease in diameter while the larger grains increased in size (an effect now known as Ostwald ripening). When the more energetic surface atoms on the smaller crystallites redeposit on the larger grains, the total energy of the system decreases. The driving force for grain growth can also be related to orientation differences between grains.

The principal method used to grow large metal crystals involves strain annealing techniques. A suitable polycrystalline sample, a bar, rod, plate, etc., is strained by one of a number of techniques such as rolling, drawing and extrusion. It then may be fabricated into a suitable shape to facilitate growth. The amount of strain induced is usually between 1 and 10% and the amount is critical in controlling the nucleation of strain-free grains. Growth is most often done in a temperature gradient and nucleation control is similar to other growth methods. In some respects, it is related to the Bridgman–Stockbarger method where the sample can be a rod with a tapered

end that is translated through the gradient. The gradients, however, are reversed from melt growth. The polycrystalline charge is heated until the tapered end reaches the recrystallization temperature and strain free grains are created in a localized region at the tip. Further movement propagates the strain-free grain(s) along the axis of the sample consuming the strained grains. If nucleation creates several strain-free grains, the sample can be notched somewhere along the length to permit only one grain to propagate through into the main part of the charge. Seeds can also be used. Suppressing nucleation ahead of the growth front has been a concern, and generally slow translation rates and sharp gradients minimize this problem (e.g., Ref. [348]).

The concept for strain-annealed crystal growth can be traced to Robert Anderson in 1918 [349]. This led, in 1921, to Carpenter and Elam's demonstration of the growth of large aluminum crystals by the strain-anneal method [350]. Over the ensuing years, various other metals have been grown by this method. One technique used to prevent random nucleation ahead of the growth interface during the strain-annealed growth of alpha iron crystals was the incorporation of pulsed heating [351]. Large, 25cm-long oriented single crystal rods and strips could be produced in a few hours using this method.

The solid-state recrystallization method has also been applied to semiconductor fabrication (e.g., Si and Ge). One technique of note is the solid phase epitaxial growth method. In 1968, L. Kulper at IBM, patented a process for the growth of aluminum-doped silicon films by the migration of silicon through an aluminum thin film during a heat treatment process [352]. The solid-state growth process provided doped layers with a maximum amount of aluminum in silicon. Later Mayer et al. [353], from the California Institute of Technology, patented a similar but more general process for doping with other species. In this process, a single crystal substrate is coated with a thin metal film having such properties that it will permit the migration of material through it to form an epitaxial layer without acting as an active dopant itself. Upon this film a dopant layer is deposited followed by an amorphous or polycrystalline layer of the material that will make up the doped epilayer. This sandwich structure is first heated to a temperature that permits the metal layer to dissolve some of the dopant, amorphous film and part of the substrate. After a time, the temperature is raised to allow the transport and epitaxial deposition of the doped layer onto the substrate. For the solid-state epitaxial growth of silicon, for example, the substrate and amorphous or polycrystalline layers would be silicon, the dopant layer might be phosphorous, aluminum, or boron, and the metal film palladium, vanadium, or nickel. A review of this technology is included in the book by Mayer and Lau [354].

Another application for solid-state crystal growth was in the preparation of piezoelectric single crystals, such as lead magnesium niobium-titanate (PMNT) [355]. The principal motivations were its potential cost advantage and enhanced

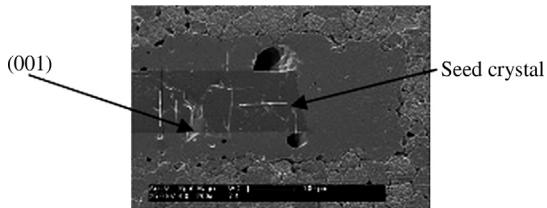


FIGURE 1.20 An example of template growth. Shown is a micrograph of a polished and thermally etched (1080°C for 30 min) sample of $\text{BiScO}_3\text{-PbTiO}_3$ (BS-PT) that was heat-treated with an embedded barium titanate (BT) seed crystal ($5\text{ mm}^2 \times 100\text{ }\mu\text{m}$ thick). A 5% excess of PbO was used in the mixture to enhance diffusion. An overgrowth of a BS-PT crystal onto the surrounding BT seed can be clearly seen [355].

manufacturing throughput over conventional crystal growth methodologies. Two techniques were explored, conventional grain growth and templated growth in which seed crystals were embedded into a powdered matrix and processed at elevated temperatures. An example of the templated growth of $\text{BiScO}_3\text{-PbTiO}_3$ is shown in Figure 1.20.

1.4 Epilogue

Crystal growth is a field that has had a major impact on modern society. The devices we have come to rely on today were made possible through the contributions of numerous scientists and engineers from a variety of disciplines. These devices are based on single crystals prepared in various ways and in forms and compositions reflecting the application intended. The foundations upon which our understanding of a crystal's structure, thermochemistry, growth mechanisms and methods is based on work from earlier centuries and dramatically expanded on all fronts (theory, growth and characterization) just after World War II. The book by Buckley in 1950 was the first comprehensive treatment (in English) of the prior art and science of crystal growth. Today, there are well over 100 books covering the topic, from surveys of the entire field to various specialized topics. This historical review of the crystal growth field is not comprehensive but was designed to highlight the major achievements. While I have tried to be as inclusive as possible, I apologize in advance if I have left out any major contributors to this field or important theories and growth methods. As a final comment, I must mention that a selection of some pioneering crystal growth papers were collected and reprinted in their original languages by D. Hurle [356].

Acknowledgments

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