Theoretical and technological solutions of the striation problem

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Abstract

With the increasing demand for solid solutions for numerous applications in micro- and optoelectronics, magneto-optics, and Lasers, the yield in producing extremely homogeneous crystals becomes more and more important. Growth-induced inhomogeneities called striations hamper the applications of solid solutions and doped crystals. Thermal striations have widely been regarded as inherent problem of crystal growth. They are commonly assumed to be caused by convective instabilities so that reduced convection by microgravity or by damping magnetic fields was and is widely employed to reduce thermal striations. Here it will be shown theoretically that temperature fluctuations at the growth interface cause striations, and that hydrodynamic fluctuations in a quasi-isothermal growth system do not cause striations. The conditions derived from the phase diagram were experimentally established and allowed the growth of striation-free crystals of KTa1-xNbxO3 "KTN" solid solutions for the first time. Hydrodynamic variations from the accelerated crucible rotation technique ACRT did not cause striations as long as the growth temperature around 1200°C was controlled within 0.03°. In the growth of facetted crystals the surface, consisting of regions with different local growth velocities, i.e. macrosteps, may cause the macrostep-induced striations. These can be suppressed by controlling the growth mode, by preventing or eliminating macrosteps by the faceting transition.

In specific solid-solution systems the striation problem can be circumvented by approaching the effective distribution coefficient \( k_{\text{eff}} \to 1 \) in growth from melts and from solutions.

The various theoretical aspects and technological solutions of the striation problem will be reviewed and discussed in this paper. © 2005 Elsevier B.V. All rights reserved.


1. Introduction

Solid solutions or mixed crystals are special crystals or alloys in which one or more lattice sites of the structure are occupied by two or more types of atoms, ions, or molecules. The statistical distribution of the species occupying the same site is in many cases random. However, it was theoretically shown by Laves [1] that the distribution can deviate from random in the direction of ordering, leading at full ordering to a superlattice or superstructure, or it can deviate in the direction of clustering leading in the extreme case to unmixing or phase separation. This aspect of site distribution and ways to control or modify it by annealing will not be discussed here, although it has an impact on the physical properties of metallic alloys and of magnetic bubble-domain devices, for example.

In solid solutions the concentration of the constituents can be varied and thus the properties optimized for specific applications, so that mixed crystals play an increasing role in research and technology. One example is III–V semiconductors where the bandgap can be adjusted, along with the lattice constant, to match the available substrates for epitaxial growth for optoelectronic applications. The misfit between substrate and layer is a decisive factor for controlling the epitaxial growth mode and thus the epilayer (device) performance [2]. Another example are III–V compounds for photovoltaic devices where the composition can be adjusted to optimize successive solar-light absorption and thus to maximize solar-cell efficiency as well as radiation and temperature resistance [3]. In certain cases, properties and effects may be obtained in solid solutions which are not observed in the constituents: The

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phase transition temperature and the related anomaly of the dielectric constant may be shifted near to the application temperature for electro-optic, nonlinear-optic and acousto-optic applications and thus allows development of highest-efficiency devices [4,5]. The hardening effect of solid solutions is often used to improve the mechanical properties of alloys [6].

In this paper the bulk fluctuations of concentration of the constituents of solid solutions and of dopants will be treated with respect to the application-dependent homogeneity requirements which are shown for the major material classes in Table 1, where the estimated tolerable composition (x) variations (Δx) are listed. Corresponding to these tolerance limits, analytical methods are to be applied or developed in order to assist in the achievement of "striation-free" crystals. In addition to the well-established methods to indicate striations, a colorful optical diffraction method has been developed [7] to visualize striations, and demonstrated with oxide, doped InP, and Si₁₋ₓGeₓ crystals. The types of inhomogeneities and their origin, and how inhomogeneities can be reduced or suppressed completely, will also be discussed. Here we define "striation-free" as the degree of homogeneity where the inhomogeneity cannot be detected by analytical methods or where it is less than required for the specific application. An absolute striation-free crystal may neither be achieved nor proven.

There is a strong tendency for fluctuations of the growth conditions causing concentration fluctuations vertical to the growth direction known as growth bands or striations. The suppression of striations is an old problem in crystal growth technology, so that several authors have described striations as an "intrinsic" or "unavoidable" phenomenon in crystal growth [5,8].

Based on the segregation analyses for growth from melts by Burton, Prim and Slichter (BPS 1953 [9]) and for growth from diluted solutions by Van Erk 1982 [10] the role of hydrodynamics and temperature as the relevant growth parameters will be discussed in Section 3, so that the experimental conditions for growth of crystals free of thermal striations can be derived. This theoretical result will be confirmed in Section 4 by the growth of quasi striation-free crystals of solid solutions.

The macrostep-induced striations are caused by locally different growth velocities and can be prevented by control of the growth mode [2] which requires the adjustment of several growth parameters as briefly discussed in Section 2. Alternative approaches to reduce or eliminate the striation problem are discussed in Section 5. They are based on achieving an effective distribution coefficient of unity which was shown for growth from melts by Mateika [11] and for growth from high-temperature solutions by Scheel and Swendsen [12]. Finally, in Section 6 novel approaches will be discussed which require further testing.

### 2. Origin and definitions of striations

Nearly all crystals have inhomogeneities and striations except for line compounds prepared from ultra-pure chemicals. Early observations of striations have been reported for CaF₂ [13] and in semiconductor crystals [14]. Hurle [15] has shown for metal and semiconductor crystals and Cockayne and Gates [16] for Czochralski-grown oxide and fluoride crystals, that striations are caused by temperature fluctuations correlated with convective oscillations when a critical Raleigh number for natural convection is surpassed, or when there is a lack of symmetry in crystal pulling.

Many compounds like GaAs and LiNbO₃ are not line compounds, but have an existence range, that is they have a certain degree of solid solubility with one or both of the constituents. This causes a difference between the congruent-melting composition and the stoichiometric composition. Therefore these crystals show composition variations along the growth direction and as striations, depending on the exact growth conditions (melt composition, growth temperature) and their fluctuations. For GaAs and compound semiconductors this is discussed by Wenzl et al. [17].

Melt-grown elements like silicon and line compounds like Al₂O₃ show striations due to impurities or dopants, in the case of silicon oxygen striations from partial dissolution of the SiO₂ crucible. Very pronounced striations are often found in doped crystals (semiconductors, lasers) and especially in crystals of solid solutions.

Various definitions for striations had been suggested. In the following, functional terms are proposed which relate to the origin of the specific striations (instead of type-I, type-II, etc.). Striations are defined as growth-induced inhomogeneities in the crystal which are aligned along the faceted or non-faceted growth surface, or which in the case of faceted growth are caused by step-bunching and thus are related to the traces of macrosteps. These, often periodic, inhomogeneities are caused in the first case by growth rates which fluctuate with time due to temperature fluctuations and are schematically shown in Fig. 1(a). Therefore they could be called thermal striations. In Czochralski crystal pulling these striations are frequently linked to the crystal rotation rate, since the crystal feels any lack of symmetry in the crucible-heater-insulation.

### Table 1

<table>
<thead>
<tr>
<th>Crystals, substrates, epilayers</th>
<th>Δx/x</th>
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</thead>
<tbody>
<tr>
<td>Doped crystals, dependent on function</td>
<td>10⁻²⁻¹₀⁻³</td>
</tr>
<tr>
<td>Metals and alloys</td>
<td>10⁻²⁻¹₀⁻³</td>
</tr>
<tr>
<td>Magnetic and magneto-optic crystals and layers</td>
<td>10⁻⁴⁻¹₀⁻⁵</td>
</tr>
<tr>
<td>Semiconductor substrates and layers</td>
<td>10⁻⁴⁻¹₀⁻⁵</td>
</tr>
<tr>
<td>Ga(As,P), (Ga,In)As, (Ga,In)Sb, (Cd,Hg)Te</td>
<td>10⁻⁵⁻¹₀⁻⁷</td>
</tr>
<tr>
<td>Dielectrics: Piezo- and pyroelectrics; electro-optic, nonlinear-optic and photo refractive crystals; Laser crystals</td>
<td></td>
</tr>
</tbody>
</table>
configuration [18]: these specific thermal striations are called rotational striations or in short rotations. It was shown by Witt et al. [19] by using time markers and etching of crystal cross sections, that re-melting may occur followed by fast growth, so that they defined microscopic (instantaneous) and macroscopic (average) growth rates and thus could explain complex striation patterns. The fluctuating temperatures at the growth interface, leading to growth-rate fluctuations in Czochralski growth, are related to convective instabilities [20], due to interactions of several different kinds of flows which will be discussed further below.

The second class of striations is caused by lateral growth rate differences \( v_1 \) and \( v_2 \) as shown in Fig. 1(b) and are named macrostep-induced striations or kinetic striations [21]. Facetted growth may be observed in growth from melts in low temperature gradients, and it is practically always observed in growth from aqueous or high-temperature solutions [22].

At high densities of growth steps, i.e. at high supersaturation, the bunching of steps occurs and leads to macrosteps with large multiples of the height of the monostep. Frank [23] and Cabrera and Vermilyea [24] in 1958 applied the kinematic wave theory, which was developed before for the general traffic-flow problem by Lighthill and Whitham [25], for the explanation of step bunching. As shown in Fig. 1(b) growth surfaces with macrosteps (also called terrace-riser structure) exhibit different local growth mechanisms and growth rates. The terrace grows by lateral propagation of mono- or double-steps with the facet growth rate \( v_1 \), whereas the macrostep with a rough or multistepped surface has the velocity \( v_2 \). These growth-rate differences cause corresponding differences in dopant or impurity incorporation and thus lead to striations which mark the traces of the macrosteps. These macrostep-induced striations are shown in Fig. 2 with LPE-grown multilayers, where the correspondence of the kinetic striations (visible in the angle-lapped and etched p-GaAs layers) with the marked macrosteps is clearly recognized [26]. In that work the transition of the misoriented macrostep-surface to the facet with continuous step propagation by the Frank-Van der Merwe growth mode is described, a transition which leads to layers (and crystals) with excellent homogeneity, i.e. without striations. Chernov and Scheel [27] analyzed the conditions for achieving such atomically flat surfaces. The flatness was experimentally shown in 1982 by STM by Scheel et al. [28].

Macrosteps can be regarded as a first step towards growth instability and are formed not only at high supersaturation, but also in the presence of certain impurities and on misoriented surfaces [29]. When the thermodynamic driving force is further increased, the impurity built up in front of the growing crystal may reach a critical level and is suddenly incorporated. Crystal growth continues until once again the impurity is incorporated, and so on. This oscillation of growth rate and impurity concentration leading to striations was
theoretically analyzed and experimentally proven by Landau [30] and could be named instability-induced striations.

3. Segregation phenomena and thermal striations

The concentration of the constituents of a crystallized solid solution generally differs from that in the liquid from which the mixed crystal is grown, a phenomenon known as segregation. In equilibrium or at very low growth rates, the ratio of the concentration of component A in the solid to that in the liquid is defined as equilibrium segregation (or distribution) coefficient

$$k_0 = C(A)_S/C(A)_L,$$

(1)

where $g$ is the fraction of crystallized material and $C_0$ the initial concentration. Here it is assumed that $k_{\text{eff}}$ does not vary with concentration or temperature changes. This inherent concentration gradient can be made zero by keeping the fluid concentration constant, which can be achieved by growth at constant temperature in combination with transporting feed material from a higher temperature in the gradient-transport technique [32]. Several groups have attempted to grow solid-solution crystals by material transport in temperature gradients [33-35]. However, the large temperature gradients for acceptable growth rates lead to temperature fluctuations so that thermal striations could not be prevented.

In Fig. 3 the phase diagram KNbO$_3$–KTaO$_3$ of Reisman et al. [36] is presented where the gradient–transport technique, using the temperature difference $T_3$ to $T_4$, is shown which was used by many groups listed in Ref. [8]. For electro-optic and other optical applications the variation of $x$ must be smaller than 0.00003 [8], see also Table 1, and this requires temperature fluctuations smaller than 0.01 °C as is indicated in Fig. 3. Also shown is the slow-cooling method where a quasi-isothermal solution is slowly cooled from $T_1$ to $T_2$. This allows the growth of striation-free crystals. The inherent temperature gradient can be kept within tolerated limits when a single crystal is grown from a large melt. For the KTN system Rytz and Scheel [8] have calculated the mass of melt $M$ which is needed to grow a crystal of volume $V$ with a tolerated inherent concentration difference $x_1 - x_2$. These data and also the temperature cooling range can be read from the nomogram shown in Fig. 4. For example a KTN crystal of 1 cm$^3$ with $\Delta x < 0.02$ requires a melt of 1000 g which is cooled by 12 °C. The results of growth experiments will be discussed further below.

In normal growth we have neither the case of very low growth rates near equilibrium with $k_{\text{eff}} = k_0$, nor the case with very fast growth rate where $k_{\text{eff}} \rightarrow 1$. Fig. 5 shows the situation at the crystal–liquid interface for the cases of equilibrium (which could also be achieved by “complete mixing”), for the case of steady-state normal crystal growth, and for very fast diffusion-less solidification. Also shown are the concentrations in the solid and in the liquid with the diffusion boundary layers. In steady-state crystal growth the effective distribution coefficient $k_{\text{eff}}$ lies between the equilibrium distribution coefficient $k_0$ and 1 and is dependent on the diffusion boundary layer $\delta$ and the growth rate $v$ as shown in Fig. 5.
Fig. 5. The concentration relations at the crystal-liquid interface and the effective distribution coefficients for three growth situations: \( k_{\text{eff}} \) approaches \( k_0 \) near equilibrium, that is at very low growth rate or complete mixing; in typical growth situations \( k_{\text{eff}} \) is between \( k_0 \) and 1; and at very fast growth rate \( k_{\text{eff}} \) approaches unity. The diffusion boundary layer thickness \( \delta \) depends on the growth rate \( v \) and the flow rate \( u \) (of melt or solution) according to Eq. (6).

Czochralski growth, the flow analysis of Cochran [37] invoking an infinite rotating disc was applied by Burton et al. [9] in order to derive \( k_{\text{eff}} \). It was considered that the solute concentration profile is virtually uniform in the radial direction, i.e. the diffusion boundary layer \( \delta \) can be regarded as having a constant thickness across the idealized flat growth surface. For moderate growth rates, \( \delta \) depends essentially on the crystal rotation rate \( \omega \) (except for the rim which is neglected), the kinematic viscosity \( \nu \), and on a bulk diffusion coefficient \( D \) (which includes solute diffusion and solvent counter-diffusion):

\[
\delta = 1.6 D^{1/3} \omega^{1/6} \nu^{1/2}.
\]  

BPS derived for the steady-state case the equilibrium distribution coefficient

\[
k_{\text{eff}} = k_0/[k_0 + (1 - k_0)^{-(v\delta/D)}]
\]

with \( v \) the growth rate. This approximation can be utilized since the growth-rate dependence of \( k_0 \) is small due to minor variations of the growth rates for growing striation-free crystals. Burton et al. [38] experimentally measured the distribution coefficients of several elements between solid/liquid germanium and correlated them with the tetrahedral covalent radii: the larger the element, the smaller the distribution coefficient. They also measured striations by radioactive tracers and photographic film and pointed out the importance of forced convection for growth of homogeneous crystals.

For growth of solid solutions from dilute solutions, Van Erk [10] has considered the complex solute—solvent interactions and has derived the effective distribution coefficient for diffusion-limited growth as

\[
\ln k_{\text{eff}} = \ln k_0 - (k_{\text{eff}} - 1)(v\delta/D).
\]

A further discussion of these segregation aspects and a comparison between BPS and van Erk can be found in Scheel and Swendsen [12]. Growth from solutions is normally limited by volume diffusion, and the relatively fast interface kinetics can be neglected. Based on the diffusion-boundary layer concept, Nernst in 1904 [39] derived the growth rate as

\[
v = D(n_{\infty} - n_\omega)/\rho_s \delta,
\]

where \( n_\omega \) and \( n_{\infty} \) are the equilibrium and the effective bulk concentrations of the solute in the solution, and \( \rho_s \) is the solute density. The time constant for the effects of temperature fluctuations (and thus on the growth rate \( v \)) is on the order of seconds, while that for hydrodynamic fluctuations on \( \delta \) and \( v \) is on the order of minutes. In steady-state growth, within a given range of temperature and time, the \( D \) and \( k_0 \) in Eqs. (4) and (5) can be taken as constants. Therefore, changes in the effective distribution coefficient \( k_{\text{eff}} \) are essentially determined by the product \((v\delta)\) of the exponent. As a first approximation, this product is constant due to the inverse relation between \( v \) and \( \delta \) in the Nernst equation (6). This means that hydrodynamic variations, which lead to changes of \( \delta \), are compensated by growth-rate changes. On the other hand are growth-rate changes caused by temperature fluctuations not compensated and thus lead to changes of \( k_{\text{eff}} \) and to thermal striations.

It follows from this discussion that for growth of striation-free crystals the temperature fluctuations should be suppressed to less than about 0.01 °C (and thus temperature gradients to less than \( 1 \) °C/cm). A compromising requirement is the need to impose a temperature gradient to remove the latent heat at practical growth rates, and to control nucleation.

Homogenizing the melts and solutions facilitates the achievement of above temperature conditions, and it reduces the diffusion problems leading to growth instability and inclusions as discussed in Ch. 6 of Elwell and Scheel [22]. Stirring may be achieved by a continuous flow along the growth interface, by Ekman or Cochran flow towards the rotating growth surface, by periodic flow changes as in reciprocating stirring in growth from aqueous solutions or by accelerated crucible rotation technique ACRT [40] in
Table 2
The role of hydrodynamics

<table>
<thead>
<tr>
<th>Starting point</th>
<th>General approach</th>
<th>Alternative approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Striations connected with convective instabilities [15,20]</td>
<td>Reduction of Convection by</td>
<td>Forced convection</td>
</tr>
<tr>
<td>- Baffle (Brice)</td>
<td>- Simple technical realization</td>
<td>- Flat interface in Vertical Bridgman/VGF/ACRT</td>
</tr>
<tr>
<td>- Microgravity/Skylab/Space experiments</td>
<td>- Rotating substrate/crystal plate [32]</td>
<td>- CdTe &amp; solid solutions [41]</td>
</tr>
<tr>
<td>- Magnetic fields ([15], SONY, Fukuda)</td>
<td>- Accelerated crucible rotation technique ACRT [40,45]</td>
<td>- GaInSb solid solutions [42]</td>
</tr>
<tr>
<td>- Sufficient suppression of convection not achieved</td>
<td>- Slashing [43]</td>
<td>- Reduced diffusion/segregation problems</td>
</tr>
<tr>
<td>- Complexity; large effort</td>
<td>- Magnetic stirring</td>
<td>- High (maximum stable) growth rates (Scheel &amp; Elwell, Goernert, Horowitz et al.)</td>
</tr>
<tr>
<td>- Diffusion/segregation problems</td>
<td>- Flat interface in Vertical Bridgman/VGF/ACRT</td>
<td>- High axial crystal yield</td>
</tr>
<tr>
<td>- Unstable growth</td>
<td>- Reduced diffusion/segregation problems</td>
<td>- Requirement of optimized forced convection</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Theoretical/numerical simulation approach</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Selective growth experiments</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Intuition</td>
</tr>
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Disadvantages:
- Requirement of optimized forced convection
- Theoretical/numerical simulation approach
- Selective growth experiments
- Intuition

Optimum approach of combined reduced and forced convection: CRCZ [64]

Role of dimension-less numbers and of numerical simulation

4. Growth of striation-free KTN crystals

The solid-solution system KTa_{1-x}Nb_xO_3 (KTN) is of special interest due to its very large electro-optic coefficient which can be optimized for specific application temperatures by the choice of x [5]. However, for optical applications the inhomogeneity in refractive index should be less than 10^{-6}, requiring that the crystals and layers be striation-free to this level.

As discussed above, this homogeneity cannot be achieved by the gradient-transport technique, but only by slow-cooling of nearly isothermal solutions. The latter approach was used by Rytz and Scheel [8] and Scheel and Sommerauer [44] who combined ultra-precise temperature control with optimized thermal profile in the furnace and with ACRT [45] to achieve striation-free KTN crystals for the first time. A typical crucible arrangement with bottom cooling to provide a nucleation site is shown in Fig. 6 along with the applied ACRT cycle. In ACRT the crucible with the growth solution is periodically accelerated and decelerated so that by inertia the liquid is moving relative to the crucible wall and forms a spiral when seen from top. This spiral shear flow was analyzed and simulated by Schulz-DuBois [46]. He also analyzed the Ekman layer flow in which, under optimized conditions (flat crucible bottom, time constant), the liquid is always pumped through a thin Ekman layer at the bottom of the crucible. This Ekman layer flow may be even more effective for mixing than spiral shear flow, and can be seen in a glass of tea with tealeaves which collect in the center bottom when the rotation is stopped. Elwell and Scheel [32] described the derivation of optimized ACRT stirring based on kinematic viscosity of the liquid and on the crucible dimension.

Temperature control with a precision of 0.03 °C at around 1300 °C could be achieved by using a thermopile of 3 to 9 Pt-6%Rh versus Pt-30% Rh thermocouples in series ([47], see also[32] Ch.7 ).

Unseeded KTN crystals with x = 0.01 [8] and x = 0.25 [44] and up to 33 × 33 × 15 mm^3 in size were grown. ACRT stirring and localized cooling controlled nucleation of one to two crystals only. In the best crystals no striations were visible in a Zeiss polarizing microscope with specially selected strain-free lenses, although very faint striations could be revealed by using extremely sensitive methods [5].

5. Homogeneous crystals with k_{eff} → 1

The segregation and thus the striation problem could be solved when the effective distribution coefficient
Fig. 6. The typical ACRT cycle is shown at top, and the ACRT-crucible arrangement in the furnace is shown as side view/cross section. The 300 cm$^3$ platinum crucible with welded lid and slightly cooled spot for nucleation control was used in the experiments for growth of KTN crystals [8].

Fig. 7. The dependence of the effective distribution coefficient on the solvent composition in growth of Y- and La-doped gadolinium aluminate, after Scheel and Swendsen [12].

approaches unity. As discussed above this is possible for the case of very high growth rates which cannot be applied for bulk crystals, but for low-dimensional crystals like plates, surface layers, and fibers. Edge-defined film-fed growth EFG allows the approach of $k_{eff} = 1$ as was shown theoretically [48] and experimentally [49] and [50] for platelet growth of doped LiNbO$_3$ and LiTaO$_3$. Miyazawa [51] grew relatively homogeneous Te-doped GaSb platelets by “shaped melt lowering”, by pulling downwards. A capillary-controlled Czochralski/Stepanov method for growth of shaped crystals of Sr$_{x}$Ba$_{1-x}$Nb$_2$O$_6$ of improved homogeneity was applied by Ivleva et al. [52,53].

A quite different approach to achieve $k_{eff} = 1$ was demonstrated by Mateika [11] who prepared complex garnet compositions, by using ionic radii and optimized replacements on the tetrahedral, octahedral and dodecahedral sites in the complex garnet structure, which resulted in $k_{eff} = 1$. Two examples of preparing substrate crystals for liquid phase epitaxy LPE of magneto-optic layers, with specific lattice constants, are

1. Gd$_3$Sc$_x$Ga$_{5-x}$O$_{12}$ with $x = 1.6$ approaches $k_{eff}$(Sc)$~1$ with $a = 12.543$ Å,

2. Gd$_{3-x}$Ca$_{x}$Ga$_{5-x-2y}$Mg$_{y}$Zr$_x$O$_{12}$ with $0.31 < x < 0.45; 0 < y < 0.37; 0.45 < (x + y) < 0.68$ approaches $k_{eff}$(Ca, Mg, Zr)$~1$ with $a = 12.453–12.507$ Å.

An effective distribution coefficient of unity could also be achieved in crystal growth from high-temperature solutions by optimized solvent mixtures as shown by Scheel and Swendsen [12], since the distribution coefficient depends on solvent-solute interactions. Systematic experiments have shown that different solvents and solvent mixtures may cause $k_{eff} < 1$ and $k_{eff} > 1$. By proper mixing of the solvent composition it is then possible to obtain $k = 1$ and thus eliminate the segregation problem. Two examples for perovskite solid solutions (Gd$_{1-x}$Y$_x$AlO$_3$ and Gd$_{1-x}$La$_x$AlO$_3$) are shown in Fig. 7. A systematic investigation would help to understand these approaches to achieve $k_{eff} = 1$ and to establish rules for general applicability.

6. Alternative approaches to reduce thermal striations

In Table 2 a number of approaches to overcome the striation problem have been listed. In the following specific attempts, which got wider interest or found application in crystal production, will be briefly discussed. Ostrogorsky
and Mueller [54] proposed a submerged-heater method for vertical Bridgman growth, where the combined effect of thin melt layer and stabilizing temperature gradient should minimize striations, but the complexity has hampered technological application so far. This is in contrast to the application of ACRT in VGF and vertical Bridgman production of CdTe and GaInSb solid solution crystals by Capper et al. [41] and Dutta [42]. A modified Czochralski process has been described by Goriletsky et al. and by Eidelman et al. [55] for pulling huge halide scintillation crystals (up to 700 mm diameter and 550 kg weight) from small melt volumes. In this case there is a combined effect of small melt volume and forced convection due to counter-rotation of crystal and crucible. In practical fabrication of semiconductor crystals it was recognized that microgravity would not be applicable for various reasons, so that magnetic fields of various configuration were introduced to increase viscosity and damp convection, first by SONY 1980 for silicon followed by Terashima and Fukuda [56] for GaAs. The sloshing of Gunn [43] was mentioned earlier and was re-introduced as special vibration technique [57]. Kirgintsev and Avvakumov [58] compared several stirring techniques including vibrators and found the latter not very effective. Recently several authors [59-61] revived the interest in vibration stirring although it has not found application in commercial crystal production.

For growth from melts by Czochralski crystal pulling there are six or more different kinds of flows below the rim of the crystal as shown in Fig. 8. A special problem arises with Taylor–Proudman cells [62] and with Taylor vortices [63]. Double crucibles will help somewhat to simplify the flow pattern and to increase axial yield and therefore are used in certain production lines of GaAs and of stoichiometric LiNbO₃, but have practical disadvantages in the growth process.

A technologically simpler approach consists of a solid ring co-axial with the crystal and rotating with same direction and velocity with the crystal. This ring, introduced into the melt, separates the melt fraction inside the ring from the well-mixed bulk melt (see Fig. 9). In simulation experiments it was shown that at optimized setting of rotation rate of crystal and ring, and counter-rotation of the crucible, the melt fraction can be quasi stationary with only minor Ekman-layer flow. This co-rotating ring Czochralski (CRCZ) approach [64] has the positive double-crucible effects (for increased axial crystal yield and reduced striations) without the disadvantages of double crucibles. Numerical simulations have started, but the growth technology has yet to be developed.
7. Discussion and Summary

Several experimental and theoretical solutions were presented to overcome the intrinsic pervasive problem of striations:

1. \( k_0, D, \nu, \delta = \text{constant}: \) very difficult; chance with submerged heater or with CRCZ.

2. \( k_0, D, \nu = \text{constant}; \) \( \delta \) may vary: Rytz and Scheel [8], Scheel and Sommerauer [44], Scheel and Swendsen [12], Capper et al. [41], Dutta [42].

3. \( k_{\text{eff}} = 1 \) for growth from melts: Mateika [11], for growth from solutions: Scheel and Swendsen [12].

Further conditions are

(a) Continuous flat or smooth (isothermal) growth surface: Scheel [26–28], Capper et al. [41], Dutta [42].

(b) Homogeneous melt or solution with \( \Delta n/n < 10^{-5} \) and \( \Delta T/T < 10^{-5} \) by forced convection leading to constant growth rate with \( \Delta \nu/\nu < 10^{-5} \).

These indicated tolerances are typical values and depend on the individual system and on the tolerated inhomogeneity of the crystal. Therefore it is advisable to first analyze theoretically a new growth system and the phase relations so that the technological parameters can be established. With respect to optimized hydrodynamics, simulation experiments with a liquid of similar kinematic viscosity are very useful in the early phase and may be complemented by numerical simulation for process optimization. In certain cases, dimension-less numbers may be helpful to get a feeling for the convection regime.

In conclusion one can say that the striation problem is solvable (on earth) but requires a certain theoretical and technological effort. Hydrodynamic fluctuations are not harmful as long as the fluid is sufficiently isothermal, as long as the transport of fluid of different temperature to the growth interface is suppressed. Forced convection is essential for economic growth of solid-solution crystals as it increases yield and assists to establish the conditions for growth of inclusion-free and striation-free crystals.

References


