Using magnetic field gradients to control the directional solidification of alloys and the growth of single crystals

Baskar Ganapathysubramanian and Nicholas Zabaras

Materials Process Design and Control Laboratory, Sibley School of Mechanical and Aerospace Engineering, 188 Frank H. T. Rhodes Hall, Cornell University, Ithaca, NY 14853-3801, USA

Abstract

There are various magnetic field based approaches to melt flow control that are used commercially to improve the quality of a crystal grown from the melt. Most of them are based on either a uniform or a rotating magnetic field. In this work, the effect of applying a suitably positioned magnetic field gradient on the growth of single crystals, particularly the interface curvature, growth rate and dopant distribution is investigated. Comparison between crystal growth under the influence of a uniform magnetic field and a magnetic field gradient brings out the significant advantages of the developed method. The use of a magnetic gradient is shown to give a uniform dopant distribution and produce a planar interface. The ease of control as well as the commercial feasibility of such a technique is emphasized. Finally, its promising role in biological macromolecular growth is addressed.

Keywords: Solidification; Crystal growth; Marangoni convection; Microgravity; Kelvin force; Magnetic gradients

1 Introduction

With the rapid reduction in the feature size of devices in application areas such as optoelectronics, lasers and lithography and their increasingly longer life times, there is a huge demand for single crystals of high quality [1]. It is well known that the quality of single crystals is affected by certain growth parameters and conditions. For example, non axisymmetric isotherms lead to a melt-solid interface that is not normal to the seeding axis. Variations in growth rate result in corresponding fluctuations in impurity incorporation. These variations can be induced by factors such as vibration, convective instability and temperature fluctuations among others. The shape of the melt-solid interface at the intersection with the crucible wall influences edge faceting, twin initiation and the nucleation of secondary growth orientations [2]. Convection in the
melt, surface tension effects, temperature and concentration fluctuations during growth all have an adverse impact on the quality of the crystal. For a detailed study of segregation, convection and cooling effects on the growth refer to chapters 12-14 in [1]. In the context of the quality of the crystal, one would like to be able to grow a single crystal with a planar interface into a quiescent melt where solute transport is by diffusion alone. This would yield a radially uniform dopant distribution and axial segregation can be avoided.

Various techniques have been developed to improve the quality of the crystal. Notably, most of these techniques utilize the conducting (or partially conducting) nature of the melt to affect the crystal growth using a magnetic field. The use of a uniform magnetic field has been found to have an impact on the quality on the crystal [1,3,4]. Prescott and Incropera [5] state that though a uniform magnetic field significantly affects the thermo-solutal flow, interdendritic flows and macrosegregation patterns are not affected significantly by the field. As a consequence, the use of different types of magnetic fields during crystal growth was investigated. In particular, the use of a travelling magnetic field (TMF) has been shown to have some advantages in crystal growth. Patzold et al. [6] used a rotating magnetic field (RMF) during the growth of GaAs. The RMF was shown to affect the heat flux at the solid-melt interface and the curvature.

There are some drawbacks to the use of uniform magnetic fields. Any significant convection damping and quality improvement requires prohibitively large magnetic fields. Furthermore, the magnetic field must be oriented in a direction normal to the fluid velocity for the Lorentz force to take effect and most significantly, this technique cannot be used for an electrically non-conducting material. That is, the application of a uniform magnetic field would have negligible effect on the growth of biological macromolecules and other non-conducting and insulating media. With the increasing demand for protein and other macromolecular crystals and organic semiconductors, the methodology proposed here of using magnetic gradients can ensure high quality and uniformity of crystals - organic, inorganic or metallic. Further, the effect of the application of a magnetic field gradient is independent of the electrical conductivity of the melt. Hence, a magnetic gradient will have a similar effect on the growth of biological macromolecules, ferrofluids, metal alloys and semiconductor melts.

The prospect of convection-less, diffusion-dominated growth has motivated crystal growth experiments in space and microgravity environments. Microgravity leads to a reduction in thermo-solutal convection due to density differences. Numerical modeling of microgravity growth has shown that it is possible to obtain significantly higher quality crystals [7–9]. Though the quality of crystals grown in microgravity makes it a promising and attractive technique, commercial large scale production of crystals in space is at present not commercially feasible.

The application of a magnetic field produces a force on the moving fluid. This Lorentz force depends on the direction and the magnitude of the fluid velocity. On the other hand, the application of a magnetic field gradient produces an addi-
tional body force (magnetizing or the Kelvin force) on the fluid system [10]. Wakayama [11] experimentally showed the effect of an applied magnetic field gradient on the flow patterns. With the application of a magnetic gradient of 40 T/m at 1.5 T, they were able to reverse the effect of gravity on the flow of pressurized gas. Tagawa et al. show that much beyond the critical Rayleigh number, buoyancy driven convection can be neutralized resulting in conduction-based heat transfer forced through the application of a magnetic gradient [12,13]. Evans et al. have elegantly brought out the huge promise of the application of a magnetic gradient to solidification [14]. They manage to suppress and then reverse the direction of convection by the application of a suitable magnetic gradient. The strength of the magnetic gradient could be chosen such that the Kelvin force neutralizes the net buoyant force close to the interface. This suppression of buoyancy is similar to the condition of microgravity. In other words, through the use of a suitable magnetic gradient, a state of ‘terrestrial micro-gravity’ can be achieved. As will be seen in the subsequent sections, the effect of a magnetic gradient combines the effects of a microgravity environment and an imposed magnetic field.

In this work, we investigate the application of a magnetic field gradient on the directional solidification and the crystal growth of materials. The effect of this methodology on the quality of the crystal grown is analyzed. This technique produces a highly uniform dopant distribution, negligible fluctuations in the temperature and concentration and significant damping of the velocity in the melt. The organization of the paper is as follows: In Section 2, the governing equations are given and the model is validated. Section 3 is devoted to examples of directional solidification and crystal growth along with the discussion of the obtained results. We discuss the implications of the method and conclude in Section 4.

2 Governing equations and validation

Let $\Omega$ be a closed bounded region with piecewise smooth boundary $\Gamma$. The domain $\Omega$ is filled with a dilute, electrically conducting, incompressible liquid with initially uniform temperature and composition. Let us denote the solid region by $\Omega_s$ and the liquid region by $\Omega_l$. These regions share a common solid-liquid interface boundary $\Gamma_I$. As seen in Fig. 1 depicting two-dimensional directional solidification, the region $\Omega_l$ has a boundary $\Gamma_l$ which consists of $\Gamma_I$ (the solid-liquid interface), $\Gamma_{ol}$ (the mold wall on the liquid side), $\Gamma_{bl}$ (the bottom boundary of the liquid domain) and $\Gamma_{tl}$ (the top boundary of the liquid domain). Similarly $\Omega_s$ has boundary $\Gamma_s$, which consists of $\Gamma_I$, $\Gamma_{os}$, $\Gamma_{bs}$ and $\Gamma_{ts}$.

At time $t = 0^+$, the temperature of the left vertical boundary $\Gamma_{os}$ is instantaneously dropped and maintained below the freezing temperature corresponding to the bulk concentration of the melt, so that solidification of the alloy immediately commences at this cold boundary. The motion of the alloy melt is determined by the combined action of buoyancy, surface-tension and electro-magnetic forces. Our analysis is limited to solidification systems with dilute concentration levels, moderate temperature differences
and a Newtonian melt [8]. The melt free surface deformation is assumed negligible which is strictly valid only at low capillary numbers. This is generally true for metals and semiconductor melts [15]. The Gibbs-Thompson effect is neglected as it is usually important only on very small scales [16]. Finally, a sharp solid-liquid interface model allows a simpler treatment of the physical problem while providing a detailed and qualitative insight into the complex interaction of heat, mass and momentum transport in the solidification system. Furthermore, our aim is to investigate the effects of a magnetic gradient on the solidification and a simplified system will help us to provide insight of these effects without destruction from other complications.

The governing equations for the binary alloy solidification system are now introduced. Let $L$ be a characteristic length of the domain, $\rho$ the density, $k$ the thermal conductivity, $\alpha$ ($\alpha \equiv k/\rho c$) the thermal diffusivity, $D$ the solute diffusivity, $\sigma_e$ the electrical conductivity and $\nu$ the kinematic viscosity of the liquid melt. All fields and properties refer to the liquid domain unless denoted otherwise. The characteristic scale for time is taken as $L^2/\alpha$ and for velocity as $\alpha/L$. The dimensionless temperature $\theta$ is defined as $\theta \equiv (T - T_o)/\Delta T$ where $T$, $T_o$ and $\Delta T$ are the temperature, reference temperature and reference temperature drop, respectively. Likewise, the dimensionless concentration field $c$ is defined as $(c - c_o)/\Delta c$ where $c$, $c_o$ and $\Delta c$ are the concentration, reference concentration and reference concentration drop, respectively. The characteristic scale for the electric potential $\phi$ is taken as $\alpha B_o$. Since only dimensionless quantities will be used in the remaining of this paper (unless is mentioned otherwise), the symbol $\phi$ is used from now on to denote the dimensionless electric potential. In the applications considered in this work, the magnetic field varies spatially in the $z$ direction and the gradient of the magnetic field in the $z$ direction, $\frac{\partial B}{\partial z}$, is constant. This is achieved by applying a uniform magnetic field of magnitude $B_o$ superimposed on a magnetic gradient of magnitude $\frac{\partial B}{\partial z}$. The magnitude of the applied field is usually given as the value of $\nabla B^2$. 

Fig. 1. Schematic of the directional solidification system with uniform magnetic field $B_o$ and a constant magnetic field gradient $\frac{\partial B}{\partial z}$. In this paper, the magnetic field is applied in the $z$-axis.
or when considering the present case of $B$ varying only in the $z$ direction (Fig. 1), as $B_0 \frac{\partial B}{\partial z}$.

The application of a magnetic field ($B$) to conducting fluids in motion causes the formation of induced currents ($J$). The induced currents interact with the externally applied magnetic field resulting in the damping of the flow field by the Lorentz force $f_{Lorentz} = J \times B$. We assume that the induced magnetic field is too small to affect the external magnetic field. (i.e. the magnetic Reynolds number $Re_m = Pr_m Re_d$ is sufficiently small [1]). The electric current density for a moving medium is governed by Ohm’s law, $J = \rho_e \mathbf{v} + \sigma_e (-\nabla \phi + \mathbf{v} \times B)$, where $\sigma_e$ and $\rho_e$ are the electrical conductivity and the free charge density, respectively. The free charge density is usually very small. Hence, the terms involving the free charge density are usually neglected.

The application of a magnetic field gradient produces a force (Kelvin force) given as follows:

$$f_{Kelvin} = \frac{\chi_m}{2\mu_m} \nabla B^2 = \frac{\rho \chi}{2\mu_m} \nabla B^2 \quad (2.1)$$

where $\mu_m$ is the permeability of free space, $\chi_m$ the magnetic susceptibility and $\chi$ is the mass magnetic susceptibility. According to Curie’s law, the mass magnetic susceptibility ($\chi$) of a paramagnetic material is inversely proportional to its absolute temperature. Most materials found in nature are diamagnetic. For a diamagnetic fluid, the mass susceptibility is independent of temperature, but the magnetizing force appears due to the change in density in the above equation. Toshio et al. [12] have derived a Boussinesq approximation for this force term:

$$f_{Kelvin} = \frac{\beta_T \rho_0}{\mu_m} (T - T_0) \nabla B \cdot B \quad (2.2)$$

where $\beta_T$ is the thermal expansion coefficient.

The basic equations used in the simulation of the melt flow are the incompressible Navier-Stokes equations including the Lorentz force. The Boussinesq approximation is also used for defining buoyancy. The other main equations governing the fluid flow in the liquid domain are the energy equation, the solute transport equation and the electric potential equation. These equations are written in dimensionless form as follows:

$$\nabla \cdot \mathbf{v} = 0 \quad (2.3)$$

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + Pr \nabla^2 \mathbf{v} - [Ra_T Pr \theta_l - Ra_c Pr c - Ra_T Pr_\gamma \theta_l] e_g + Ha^2 Pr [-\nabla \phi + \mathbf{v} \times e_B] \times e_B \quad (2.4)$$

$$\frac{\partial \theta_l}{\partial t} + \mathbf{v} \cdot \nabla \theta_l = \nabla^2 \theta_l \quad (2.5)$$

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = Le^{-1} \nabla^2 c \quad (2.6)$$

$$\nabla^2 \phi = \nabla \cdot (\mathbf{v} \times e_B) \quad (2.7)$$

where the governing dimensionless groups are the Prandtl number ($Pr \equiv \nu/\alpha$), the Lewis number ($Le \equiv \alpha/D$), the thermal Rayleigh number ($Ra_T \equiv g \beta_T \Delta T L^3/\nu \alpha$), the solutal Rayleigh number ($Ra_c \equiv g \beta_c \Delta c L^3/\nu \alpha$), the Hartmann number ($Ha \equiv (\frac{\sigma}{\mu \nu})^{1/2} B_0 L$), and the Kelvin force contribution to buoyancy ($\gamma \equiv \frac{\chi B_0^2 \frac{\partial B}{\partial z}}{\mu_0 g}$). In these definitions, $g$ is the gravity constant and $\beta_c$
is the solutal expansion coefficient. In the equations above, $\mathbf{e}_g$ and $\mathbf{e}_B$ are unit vectors in the direction of gravity and magnetic field, respectively.

Heat transfer in the solid is by conduction and is written in dimensionless form as

$$\frac{\partial \theta_s}{\partial t} = R_s \nabla^2 \theta_s$$

(2.8)

where $R_s \equiv \alpha_s / \alpha_l$ is the ratio of the thermal diffusivities of the solid and the melt. The shape of the solid-liquid interface is set by the slope of the liquidus curve from the binary equilibrium phase diagram as

$$\theta = \theta_m + mc$$

(2.9)

where the curve is approximated by a straight line with dimensionless slope $m$ ($m = m_{\text{liq}} \Delta c / \Delta T$, where $m_{\text{liq}}$ is the dimensional slope of the liquidus) and $\theta_m$ is the dimensionless melting temperature corresponding to the reference concentration. The interfacial temperature and solute fields are related to the corresponding values in the bulk melt by the balances

$$R_k \frac{\partial \theta_s}{\partial n} - \frac{\partial \theta_l}{\partial n} = Ste^{-1} \mathbf{v}_f \cdot \mathbf{n}$$

(2.10)

$$\frac{\partial c}{\partial n} = Le (\kappa - 1) \mathbf{v}_f \cdot \mathbf{n} (c + \delta)$$

(2.11)

where $\mathbf{v}_f$ is the freezing interface velocity, $R_k \equiv k_s / k_l$ is the ratio of the thermal conductivities of the solid and liquid, $Ste \equiv (C_p \Delta T) / L_H$ is the Stefan number, $\kappa$ is the partition coefficient and $\delta \equiv c_o / \Delta c$ is the ratio of the reference concentration $c_o$ and reference concentration drop $\Delta c$. In the above definition, $C_p$ is the heat capacity of the liquid melt and $L_H$ is the latent heat of solidification.

A no-slip and no-penetration boundary condition on the velocity field is imposed on all the liquid boundaries other than the upper free surface (Fig. 1). The hydrodynamic boundary condition on the free surface $\Gamma_f$ is expressed as

$$\nabla (\mathbf{v} \cdot \mathbf{t}) \cdot \mathbf{n} = Ma (\nabla \theta \cdot \mathbf{t})$$

(2.12)

where $\mathbf{t}$ is a tangent vector to the free surface, $\sigma$ is the surface tension and $Ma \equiv (\partial \sigma / \partial T) \Delta T l / (\rho \nu \alpha)$ is the thermal Marangoni number. Equation (2.12) is used as a Neumann boundary condition in the solution of the flow equations once the temperature field has been computed. As mentioned earlier, the free-surface deformation is neglected and a no-penetration boundary condition is imposed on the free surface.

It is assumed that adiabatic conditions are maintained on $\Gamma_{\text{is}} \cup \Gamma_{\text{di}}$. The equilibrium condition (see Eq. (2.9)) imposes a Dirichlet boundary condition on $\Gamma_{\Omega}$. A problem dependent flux/temperature condition on the outer liquid boundary $\Gamma_{\text{ol}}$ completes the definition of the thermal problem defined on $\Omega_l$. The solutal boundary conditions are provided by the impermeable wall condition on the outer boundaries and a flux condition determined by the solute conservation condition (see Eq. (2.11)) on $\Gamma_f$. The electric potential function $\phi$ is governed by an insulating wall condition on the boundary $\Gamma_{\Omega}$. In the solid phase $\Omega_s$, the equilibrium condition (Eq. (2.9)) on $\Gamma_f$, the problem dependent flux/temperature condition on $\Gamma_{\text{os}}$, and the adiabatic conditions on $\Gamma_{\text{is}} \cup \Gamma_{\text{bs}}$ (Fig. 1) provide the required
boundary conditions for the solution of the heat transport problem. Note that the conditions discussed here are applied to the directional solidification process considered in section 3.1. For the horizontal Bridgeman crystal growth simulation reported in section 3.2, the boundary conditions on $\Gamma_b$ and $\Gamma_t$ are different from those defined here to account for the thermal furnace conditions as will be discussed later in more detail.

Finally, note that the shape and position of the solid-liquid interface is an integral part of the solution of the nonlinear solidification problem. A stabilized finite element formulation is used for the coupled system of equations discussed above. The computational model is similar to that used in [8]. The developed algorithms were verified with a number of examples from the literature including the results in Toshio et al. [12] where Rayleigh-Bénard convection of water in the presence of a spatially varying magnetic field was investigated.

3 Numerical investigations of the effects of magnetic field gradients in directional solidification and crystal growth

3.1 Directional solidification of Antimony doped Germanium in an open boat configuration

A rectangular cavity is considered with an open free surface of dimensions $2 \text{ cm} \times 1 \text{ cm}$ initially filled with molten Antimony-doped Germanium at $40^\circ C$ overheat. The right hand side vertical mold wall $\Gamma_{os}$ is maintained at the initial temperature, while the left vertical mold wall $\Gamma_{ol}$ is suddenly cooled to a temperature $40^\circ C$ below the melting temperature of pure germanium and maintained at that temperature for times $t > 0$ (see Fig. 1). The thermophysical properties used in this study for Antimony-doped Germanium growth were taken from [8]. All thermo-physical properties are assumed to be independent of temperature. It is also assumed that the small concentrations of antimony do not lead to solutal-driven convection.

3.1.1 Reference problem: Solidification without the application of a magnetic field

The results obtained for the reference case are the same as in [8]. For the sake of comparison they are briefly summarized below. At early times the thermal gradients in the originally quiescent melt cause surface tension gradients on the free surface as well as density gradients in the bulk liquid. This leads to combined buoyancy and thermocapillary convection in the fluid. The fluid velocities are maximum at the top free surface in regions close to the moving solid-liquid interface. Continuity (incompressibility) of the melt flow slowly leads to counter-clockwise circulation of the melt filling the entire cavity. As the solidification process proceeds further, the solid-liquid interface starts to curve, with more solid volume formed at the bottom compared to the top part of the cavity. At around dimensionless time $\tau = 1$, two distinct weak recirculating cells form near the hot end of the cavity ($1.7 < x < 2.0$), in addition to the main (strong) counter-clockwise recirculating cell filling most part of the cavity. With continued solid-
Fig. 2. Calculated contours of stream function, solute concentration and temperature fields at dimensionless times $\tau = 2$ and $\tau = 5$ for the solidification of SbGe without the application of a magnetic field.

Fig. 3. Predicted solid-liquid interface location at intermediate times for the simulation of SbGe solidification without the application of a magnetic field of the cavity.

Fig. 4 presents the history of the solid-liquid interface concentration during the entire solidification simulation. Since the interface concentra-
Fig. 4. Calculated history of the solid-liquid interface concentration during the entire simulation of SbGe solidification without the application of a magnetic field.

The concentration is directly proportional to the solid concentration \( \left( C_s = \kappa C_l \right) \), this plot effectively shows the pattern of the solute variation obtained in the final solid. Initially, the heavy solute descends along the solid-liquid interface and settles at the bottom of the cavity. This steady accumulation of solute at the base continues as more solid is formed. Simultaneously, the convection in the melt becomes stronger and this strong convection in the bulk liquid transports and redistributes the rejected solute throughout the entire cavity. This vigorous solute convection leads to the macroscopic variation of the rejected solute as shown in Fig. 4 and the consequent inhomogeneity in the final crystallized solid.

**3.1.2 Solidification with an applied magnetic field gradient**

Calculations were carried out under the action of a magnetic gradient in the direction \( \mathbf{e}_B = -\mathbf{e}_z \) (e.g. in the positive z-axis in Fig. 1). A constant magnetic field gradient of \( 1.6 \ T^2/cm \) was imposed on the solidifying system. This magnetic gradient resulted in a value of \( \gamma = 0.95 \). The mean magnetic field due to the imposed magnetic gradient acting on the system was \( Ha = 60 \). The driving mechanisms for the flow are the surface tension gradients on the free surface and the thermal gradients along the solid-melt interface. The application of the magnetic field results in two more opposing forces, namely the Kelvin force and the Lorentz force. The Kelvin force due to the magnetic field gradient neutralizes the buoyancy force at the interface. This eliminates convection in the melt due to buoyancy. Thermal gradients on the free surface lead to surface tension gradients and a thermocapillary flow slowly develops. However, the imposed magnetic field exerts a force (Lorentz force) to damp down the magnitude of the thermocapillary flow considerably. Thus, as a consequence of the Kelvin and Lorentz forces, there is negligibly small convection in the whole of the melt.

It is interesting to note that the maximum value of the stream function calculated in this case (see Fig. 5) is around 0.42 as compared to a corresponding maximum of 6.71 in the reference case. At around \( \tau = 2 \), the weak recirculating cell occupies the left half of the melt. After \( \tau = 4 \), the cell reaches its maximum strength of 0.42 and occupies a large portion of the melt. Noting the small magnitude of the stream function, one can conclude that the fluid in the melt is in an almost quiescent state (compare with the streamlines in Fig. 2).

The application of the magnetic gradient clearly results in convectionless solidification and heat transfer is diffusion (conduction) dominated. This is reflected by the uniformly spaced isotherms in Fig. 5. Since the interface is assumed to be at
Fig. 5. Calculated contours of streamlines, concentration and temperature at times $\tau = 2$ and $\tau = 4$ for the solidification of SbGe under the influence of a magnetic field gradient.

A constant temperature, it is clear that the isotherms are almost parallel to the solid-liquid interface. The conduction-dominated evolution of temperature suggests that the distribution of the solute would also be diffusion limited. This is in fact the case. As solidification proceeds, the solute is rejected at the interface into the melt. This causes a uniform build up of solute in front of the interface. The weak recirculating cell very slowly causes the motion of the rejected solute to the bottom of the melt. The ‘high concentration spot’ moves down to the bottom of the melt by around $\tau = 2$. Beyond this time, there is an almost uniform distribution of the solute in the solid (see Fig. 6). Similar observations are given in [8] for the case of solidification growth under microgravity conditions with an applied magnetic field.

Fig. 6. Calculated history of the solid-liquid interface concentration under the influence of a magnetic field gradient.

This observation has significant implications in the growth of crystals. The lifetime of any semiconductor device is restricted by the fluctuations of concentration at the interface. On one hand, the nonuniform concentration causes the formation
of large residual stresses during cooling of the crystal due to the non-uniform thermal properties along the crystal. This leads to increased dislocations, possible cracking and consequent deterioration in quality. On the other hand, the nonuniform concentration distribution leads to variations in the physical properties of the crystal which affect the quality of the semiconductor device. The application of a magnetic field gradient smoothes over the fluctuations in concentration leading to a higher quality crystal. The action of the magnetic field gradient on the shape of the solidifying interface is two fold. While the Lorentz force damps out the thermocapillary flow patterns, the Kelvin force acts against the net buoyancy forces. This leads to an almost planar interface as can be seen in Fig. 7 (compare with the reference case in Fig. 3).

3.1.3 Solidification with a uniform magnetic field

To emphasize the fact that the planar interface and uniformly distributed temperature contours are to a large extent due to the imposed magnetic field gradient, we conducted simulations for the same system under a uniform magnetic field (Figs. 8-11). The magnitude of the magnetic field is set to the maximum value of the field generated in the previous case ($H_a=60$). Thermal gradients on the free-surface lead to a surface-tension-driven flow and continuity leads to a ‘back flow’. Since the magnetic field is oriented in the vertical direction, velocity components in the horizontal direction are damped (Fig. 8). This causes a reduction in the strength of the thermocapillary convection. Due to the temperature and concentration gradients near the interface, there is a significant amount of buoyancy driven flow near the interface. The buoyancy driven convection results in a large vertical velocity near the interface (Fig. 8). The region of large vertical velocities is restricted to a small area near the interface on the left and the bounding vertical wall on the right. This fact has a very interesting effect on the concentration of the solute (Fig. 9). When solidification starts, the solute is rejected uniformly into the melt leading to the formation of a high concentration zone right next to the interface. As the flow develops, the relatively large vertical velocity pushes the solute very rapidly down to the bottom of the melt cavity. The weak horizontal velocity component of the flow then slowly shifts the solute to the other end of the melt. There the large velocity rapidly shifts the solute up to the free surface from where it is convected back to the interface. Note that during this process the solute is transported into the melt mainly through diffusion. The flow behavior described above results in the solute being periodically brought back to the interface. This (cyclic) process of solute trans-
Fig. 8. Calculated contours of streamlines, concentration and temperature at times $\tau = 2$ and $\tau = 4$ for the solidification of SbGe under the influence of a uniform magnetic field.

Fig. 9. Calculated history of the solid-liquid interface concentration under the influence of a uniform magnetic field.

The advantages of a magnetic gradient are brought out by looking at the temperature profiles in Fig. 8. The surface tension driven velocity at the free surface gradually curves the top portion of the isotherms towards the interface. Since the magnetic field is such that only the horizontal component of the velocity is damped, the flow along the interface to the bottom wall takes place unhindered. The bottom wall diverts the flow to the right into the melt. This flow pattern causes the isotherms at the bottom to gradually spread out while the isotherms are close together at the free surface. That is, the flow pattern leads to large difference in temperature gradients across the length of the interface. This has an adverse effect on the quality of the crystal. The difference in temperature gradients across the interface leads to a variation in the growth rate along the interface of the crystal. The variation in the growth rate results in thermal stresses as well as inhomogeneous solute concentration in the crystal. The small value of the horizontal velocity at the free surface and the larger ver-
The preceding two subsections illustrate the difference in the quality of the crystal produced by using a magnetic field gradient as compared to a crystal produced by using a uniform magnetic field. The uniform magnetic field damps out only one component of the melt velocity (in this case the surface tension induced motion) whereas the magnetic field gradient damps out all components of the melt velocity thereby leading to a better crystal quality.

3.2 Horizontal Bridgeman growth (HBG) of Sb-doped Ge

GeAs is used in a variety of applications including semi-conductor photodiodes, rectifiers and solar cells, electronic devices, mirrors, optical systems, radiation divisors for laser engineering, infra-red devices, fluorescent tubes and special glass. In this example, we investigate the effect of a magnetic field gradient on the horizontal Bridgeman growth of Antimony doped Germanium (Fig. 12).

3.2.1 Bridgeman growth system

A schematic of the apparatus used in the HBG system is shown in Fig. 12. The ampule is 10 cm long and 5 cm wide. The ampule is made of pyrolytic boron nitride (PBN) with a thickness of 1 mm. The furnace closely envelops the crucible. A seed of thickness 5 mm is initially placed on the left side of the configuration and the ampule is filled with charge. The power to the furnace is increased slowly from the right. The charge...
starts melting from the right and the temperature profile in the furnace is increased until the entire charge along with a part of the seed has melted (melt back process). The furnace maintains a temperature gradient of 10 K/cm (≈ 25 K/in) in the melt zone and a higher gradient of 30 K/cm (≈ 75 K/in) in the solid zone. The temperature profile increases to the right along the length of the ampule until 40 K superheat is reached after which a constant temperature is maintained. Similarly, the temperature decreases to the left along the length of the ampule until 40 K undercooling is reached beyond which a constant temperature is maintained. To maintain the stoichiometry of the crystal, arsenic gas at a predetermined pressure is maintained over the free surface of the melt. The ampule properties were taken from [17] and the thermophysical properties of the crystal and melt from [8]. The following assumptions are made:

- A quasi-steady state assumption for the modeling of the radiation effect.
- Properties of the crucible and ampule are assumed to be independent of temperature.
- The crucible is assumed to radiate like a black body.
- The thickness of the ampule is assumed small and that it reaches thermal equilibrium much faster than the melt.

Let the ampule thickness be $\delta_a$. At any instant, let the temperatures on the melt side and the furnace side of the ampule be $T_{in}$ and $T_{out}$, respectively. The heat from the furnace is radiated to the ampule outer wall and conducted across the ampule thickness to the material in the ampule. The heat conducted across the ampule is given by $k_a \frac{T_{out} - T_{in}}{\delta_a}$, where $k_a$ is the thermal conductivity of the ampule. The radiation heat flux received by the ampule outer wall is $\sigma \epsilon (T_1 - T_{out})$, where $T_1$ is the temperature of the furnace, $\sigma$ is the Stefan-Boltzmann constant and $\epsilon$ is the emissivity of the ampule. To simplify the analysis, this radiation term is linearized about the melting temperature $T_m$. The linearized radiant heat flux received by the ampule outer wall takes the following form:

$$ q_{rad} = 4 \sigma \epsilon T_m^3 (T_\infty - T_{out}) \quad (3.1) $$

Heat balance across the ampule inner and outer walls results in the following equations:

$$ -k \frac{\partial T}{\partial z} = k_a \frac{T_{out} - T_{in}}{\delta_a} \quad (3.2) $$
\[
\frac{k_a}{\delta_a} \frac{T_{\text{out}} - T_{\text{in}}}{T_{\infty} - T_{\text{out}}} = 4\sigma \epsilon T_m^3 (T_{\infty} - T_{\text{out}}) \tag{3.3}
\]

Eq. (3.3) is used to evaluate an expression for \(T_{\text{out}}\). Substituting this expression for \(T_{\text{out}}\) in Eq. (3.2), a relation between the thermal gradient at the melt/ampoule interface and the furnace temperature is calculated. In non-dimensional form it is given as follows:

\[
- \frac{\partial \theta}{\partial z} = \frac{h_1 L}{k} (\theta_{\infty}(x) - \theta) \tag{3.4}
\]

where \(L\) is the characteristic length scale of the system, \(h_1 = \frac{k_1}{1 + \frac{k_1}{4\sigma \epsilon T_m^3}}\), and \(\theta_{\infty}(x)\) is defined appropriately based on the imposed furnace temperature gradients. This gives us Neumann boundary conditions for the horizontal bottom wall. The Neumann condition applied on the free surface similarly takes the following form:

\[
\frac{\partial \theta}{\partial z} = \frac{h_2 L}{k} (\theta_{\infty}(x) - \theta) \tag{3.5}
\]

with \(h_2 = 4\sigma \epsilon m T_m^3\), where \(\epsilon_m\) is the emissivity of the material (SbGe). Eqs. (3.4) and (3.5) are applied to both the solid and melt parts of the boundaries \(\Gamma_b\) and \(\Gamma_t\), with \(k\) referring to the conductivity of the crystal or the melt, respectively. The crystal is slowly pulled to the left. Directional solidification takes place and a single crystal is produced. To bring out the advantages of using a magnetic gradient on the growth of single crystals, a fairly large pulling rate of about 10 cm/hr was chosen.

3.2.2 Reference growth problem

The horizontal Bridgeman growth of Antimony doped Germanium under standard conditions (normal earth gravity, no magnetic field) was simulated. At early times, the thermal gradients in the originally quiescent melt cause surface tension gradients on the free surface as well as density gradients in the bulk liquid. This leads to combined buoyancy and thermocapillary convection in the fluid. The fluid velocities are maximum at the top free surface in regions close to the moving solid-liquid interface. Continuity of the fluid flow slowly leads to counter-clockwise circulation of the melt filling the entire cavity (Fig. 13). As the solidification process proceeds further, the solid-liquid interface starts to curve, with more solid volume formed at the bottom compared to the top part of the cavity. The bottom part manages to keep up with the moving imposed thermal gradients at the melt-ampule interface but the aggressive flow towards the interface from the hotter melt causes the front to move very slowly at the top. This trend continues and can be clearly seen in Fig. 14.

The initially flat interface gradually becomes very skewed. In crystal growth a more or less planar interface is desired. This can be achieved either by increasing the thermal gradient or by reducing the pulling rate. Both these measures have major economic consequences. The streamline contours in Fig. 13 show that once the flow pattern has developed (by \(\tau = 0.7\)) it remains steady. It can be clearly seen that the flow is basically constrained to the edges of the system with a weaker secondary cell formed at the right bottom of the melt. Notice also that there is
Fig. 13. Calculated contours of streamlines, concentration and temperature at times \( \tau = 2 \) and \( \tau = 4 \) for the HBG of SbGe without the application of a magnetic field.

Fig. 14. Solid-liquid interface position with time for the HBG of SbGe with a pulling speed of 10 cm/hr and without the application of a magnetic field.

Fig. 15. Calculated history of the solid-liquid interface concentration for the HBG of SbGe without the application of a magnetic field.

A stratification of the isotherms in the middle region of the melt. This would result in the fluctuation of the temperature on the interface and cause the formation of defects and striations. Striations are the non uni-

form deposition of the dopant on the interface. These have a significant effect on the life of a semiconductor component.

The isopleths have an almost identical structure to the flow pattern (Fig. 13). Initially a high concentra-
Fig. 16. Calculated contours of streamlines, concentration and temperature at times \( t = 2 \) and \( t = 4 \) for the HBG of SbGe under the action of a magnetic gradient.

A formation spot is formed at the left top of the melt domain. This is then forced down by the thermocapillary induced convection. Interestingly, the flow carries the rejected solute down to the bottom of the melt, then across the bottom wall, up the other wall and right back to the interface. In the meantime, the concentration of the solute in the ‘flow stream’ gradually reduces due to diffusion. This periodic recycling of the dopant at the interface causes a fluctuation in the dopant concentration on the interface and hence on the solid. This phenomenon can be seen in the time history of the concentration at the interface given in Fig. 15. The concentration excess in front of the interface forms until about \( t = 1 \) after which it is removed by the strong flow patterns. The flow recirculates the solute back to the interface as seen by the fluctuations in the concentration profile with time. Note that these fluctuations become further apart and weaker as time progresses. This is because along with convection the solute is also diffused slowly into the middle relatively quiet zone in the melt. A correlation between the frequency of these concentration jumps at the interface with the length of the crystal growth chamber and the thermal conditions is estimated in the next section.

### 3.2.3 Effect of magnetic field gradient

As seen in the above section, the crystal growth of SbGe in the horizontal Bridgeman growth configuration at higher crystal pulling rates led to a wavy interface and cyclic fluctuations in the temperature and concentration of the solute at the solid-melt interface. Calculations are carried out for crystal growth under the action of a uniformly imposed
magnetic field gradient of about $1.6 \, T^2/cm$.

Two weak rolls develop at $\tau = 0.015$ in the upper left and bottom left of the melt domain. These rolls gradually grow and increase in strength. At $\tau = 0.05$ these rolls interact to form an elongated elliptical roll that diffuses out into the melt occupying the whole domain by $\tau = 2.0$ (Fig. 16). Thereafter the flow pattern remains steady. Notice that the maximum strength of the stream function is 0.6 as compared to a maximum of 17.9 in the case of the reference problem.

The notion of a quiescent fluid is indeed appropriate in this case. This state of small velocities in the whole melt region continued until the end of simulation. The consequences of very small velocities is immediately seen in the isotherms in Fig. 16 (compare with the isotherms in Fig. 13). The isotherms are nearly parallel to the interface all through the simulation and they closely follow the movement of the externally imposed temperature gradient. This suggests that the heat transfer is nearly conduction-based, with minute local convection effects.

Fig. 17 shows the interface positions at various times. Note the significant difference between the interface profiles in the two cases in Figs. 14 and 17. Initially, the melt-crystal interface is planar in both cases. In the reference case, with increasing time, the surface tension induced back flow at the top of the melt causes the interface growth velocity at the top surface to become extremely small. The planar front quickly deteriorates. With the application of the magnetic field gradient, the interface stays planar with uniform temperature distribution all along the interface. The impact of the application of a magnetic field gradient on the growing front is seen in Fig. 18.

The standard deviations of the curvature (deviation from a planar interface) of the preceding two cases (an applied magnetic field gradient and without a magnetic field) are plotted as a function of time. Note the significant differences in the standard deviation of the interface for the two cases. This has a direct impact on
Fig. 19. Calculated history of the solid-liquid interface concentration in HBG of SbGe under the influence of a magnetic gradient.

The concentration profiles at the interface.

Fig. 19 shows the interface concentration profile with time. The concentration is mainly diffusion-based with nearly uniform concentration all throughout the entire simulation. It must be noted that the concentration on the interface increases very slowly albeit uniformly due to the accumulation of the solute in front of the interface. The slow moving flow could still produce long time-period, low amplitude oscillations in the concentration at the interface (due to recirculation), but this was not observed during the entire simulation.

The concentration profiles at two points on the interface corresponding to \( z = 0.5 \) and \( z = 0.9 \) are shown in Fig. 20. The dotted line is the concentration profile under the action of a magnetic field gradient whereas the solid line is for the reference case (no magnetic field). The fluctuations that are present during the growth of the crystal under normal conditions cause rapid deterioration of the component produced (formation of dislocations, striations, etc.). In comparison, the magnetic field gradient has the effect of smoothing out the deleterious fluctuations in concentration and temperature. A fast Fourier transform (FFT) analysis of the concentration fluctuations evaluated at the two points \( (z = 0.5, z = 0.9) \) was carried out. The power versus the wave-number plot is shown in Fig. 21.

The effect of the application of the magnetic field is clearly seen. The power spectrum for this case is almost flat signifying that there are no fluctuations in the concentration. The dominant frequency extracted from the FFT (for the reference case) had a time period of around 0.06 dimensionless time units. As noted in the previous section, the developed flow for the reference problem consists of a roll that circulates all around the edges of the melt. The mean dimensionless velocity of this large scale flow pattern was about 89. The total circumferential distance that the flow recirculates was about 5.6. The time it took for the flow to recirculate all the way to the same point on the interface is thus 5.6/89 \( \sim 0.062 \). This compares well with the dominant time period of concentration fluctuations evaluated using the FFT analysis (0.06). One can thus conclude that the concentration fluctuations at the melt-solid interface are mainly due to the recirculation of the convected solute back to the interface by the large scale flow patterns. This would mean that larger aspect ratio configurations would initially give large time period fluctuations of the interface concentration and as the growth proceeds this time period would decrease. Under the influence of a magnetic gradient there is very less fluctuation of the concentration as seen by the almost flat and smooth power-wavenumber variation.
4 Conclusions

There are a few significant differences in the application of a magnetic field and in the application of a uniform magnetic field gradient. As seen in the developments presented here, the Kelvin force does not depend on the velocity of the particle under consideration, whereas the Lorentz force depends implicitly on the direction as well as the magnitude of the velocity of the particle. This has immediate consequences while attempting the control of melt flow during the growth of the crystal. Given the recent rapid developments in the field of superconducting magnets and Magnetic Resonance Imaging (MRI), the commercial production of these magnetic gradients is very feasible [18–22]. Further, there are many commercially available gradient field production coils that could be incorporated into existing crystal growth furnaces. More significantly, the Kelvin force does not depend on the electrical conductivity of the fluid, as is the case with the Lorentz force. Hence, magnetic gradients could be used for the control of solidification of molten metals and organic substances.

We have investigated the effects of an imposed magnetic gradient on the directional solidification of a dilute alloy and on the crystal growth of a semi-conductor. Comparison with simulations of the growth under normal (no magnetic gradients) conditions show that the application of a magnetic gradient has a very promising effect on the evolving structure of the solid. The effect of the magnetic gradient is two-fold: First, it offers the possibility of increasing the growth rate while maintaining a planar interface. Second, the fluctuations in the concentration and temperature that are detrimental to the quality of the crystal can be removed to a large ex-
tent. The effect of this technique on the stresses induced during crystal growth is also being looked into. The commercial availability of small scale magnetic gradient generators could lead to the local control of the flow structure. The magnetic gradient affects the flow patterns in the melt region while the imposed thermal gradients affect the growth speed. Thus, the magnetic fields could be properly oriented and varied along with suitable variations in the thermal gradients to obtain a tailor made interface and large growth rates with low stress levels.

The use of magnetic field gradients has been found to neutralize buoyancy induced motion. This has a direct consequence on the speed of growth of the crystal as well as the quality of the crystal. It has to be noted that the magnetic fields required increase very quickly with increase in the characteristic length scale of the crystal system. Small scale systems like MEMS and magnetically active systems like ferrofluid systems can be affected by very small, off the shelf, magnetic gradient coils. Finally, the control of protein crystallization using a magnetic field gradient among other parameters is an interesting concept of current research interest.

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References


