Magneto-hydrodynamic damping of convection during vertical Bridgman–Stockbarger growth of HgCdTe

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Abstract

In order to quantify the effects of convection on segregation, Hg_{0.8}Cd_{0.2}Te crystals were grown by the vertical Bridgman–Stockbarger method in the presence of an applied axial magnetic field of 50 kG. The influence of convection, by magneto-hydrodynamic damping, on mass transfer in the melt and segregation at the solid–liquid interface was investigated by measuring the axial and radial compositional variations in the grown samples. The reduction of convective mixing in the melt through the application of the magnetic field is found to decrease radial segregation to the diffusion-limited regime. It was also found that the suppression of the convective cell near the solid–liquid interface results in an increase in the slope of the diffusion-controlled solute boundary layer, which can lead to constitutional supercooling.

1. Introduction

For nearly four decades, the usefulness of applied magnetic fields in crystal growth from the melt has been recognized. The fundamental basis for the interaction between magnetic fields and convection was first discussed in Refs. [1–5]. The basic mechanism for the interaction of an applied magnetic field and a molten semiconductor involves the electrical currents induced by the movement of a conductor in the presence of a magnetic field. Early experiments by Utech and Flemings [6,7] investigated the effects of a magnetic field on tellurium-doped indium antimonide grown in a horizontal furnace by directional solidification. Their results indicated that vertical magnetic fields of 1300 and 1750 G were sufficient to suppress turbulence in the melt. This eliminated the temperature fluctuations which caused melting and resolidification of the growth interface and an associated fluctuation in the dopant concentration in the crystal grown in zero field.

Temperature and solutal gradients in the melt during growth almost always result in buoyancy-driven convection. Frequently, this convective flow is oscillatory [8] and gives rise to a fluctuating rate of crystal growth, which, in turn, produces a microscopically non-uniform distribution of dopant in the crystal. The universal effect of an applied magnetic field is the damping of the convective turbulence in the melt, which produces a more homogenous dopant distribution [9–13].

The majority of the experimental studies with magnetic fields has been focused on the growth of GaAs, Si and Ge by the Czochralski growth process.
In these systems, small (2–5 kG) fields were applied to suppress turbulent convection. Limited work [6,12–16] has been conducted on the magnetic effects of crystal growth in a vertical Bridgman–Stockbarger configuration and out of these experiments only two involved the II–VI compounds of HgCdTe and HgZnTe.

The Hg-based II–VI semiconductor compounds are important for applications in infrared detection and imaging, particularly for a broad range of wavelengths from 0.8 µm to the far-infrared spectrum beyond 30 µm. The crystal growth of these Hg-based II–VI systems is characterized by a destabilizing horizontal temperature gradient due to a difference in the thermal conductivities of the melt and the crystal at the growth interface in the presence of a containing crucible and the release of latent heat. Additionally, a stabilizing vertical solutal gradient is produced by the rejection of the denser constituent (HgTe in the case of HgCdTe) into the melt. These phenomena, coupled with a large solutal-to-thermal expansion coefficient ratio ($\beta_C/\beta_T \Delta T_T = 100$) and a large thermal-to-solutal diffusion coefficient ratio ($\alpha_T/D_T = 200$), give rise to double diffusive convection during the growth of these binary semiconductors, where $\Delta T_T$ is the radial temperature difference, $C_0$ is the starting composition, $\beta$, and $\beta_T$ are, respectively, the solutal and thermal expansion coefficients and $\alpha_T$ and $D_T$ are the thermal and solutal diffusion coefficients, respectively. If this buoyancy-induced convection is large as compared to the solidification velocity, it can interfere with segregation near the solid–liquid interface resulting in a non-homogenous crystal. It is believed that the reduction of convection should be advantageous in maintaining the solid–liquid interface shape required to minimize the crystal defect densities while maximizing compositional variation transverse to the crystal growth direction.

This paper focuses on the influence of the magnetic field on mass transfer in the melt and radial segregation at the solid–liquid interface. We begin with a description of the charge crucible configuration, followed by a brief discussion of the Bridgman–Stockbarger growth system used for the experiments. Results of the axial and radial compositional distributions with and without the presence of the magnetic field are, then, described.

2. Experimental procedure

2.1. Sample preparation

The starting materials were triple-distilled instrument grade Hg from Bethlehem Apparatus and six nines grade Cd and Te from Johnson Matthey. The ampoules were made from 8 mm ID × 12 mm OD commercial grade, T08, fused silica quartz. A tapered section was formed on the quartz ampoule to enhance the probability of single crystal growth. An internal layer of graphite was formed on the ampoule as described in Ref. [16] to prevent the adhesion of HgCdTe to the ampoule walls. The elements were weighed out for Hg$_{1-x}$Cd$_x$Te (x = 0.2), loaded into the ampoules and sealed off under 10^-4 Torr vacuum. The Hg$_{1-x}$Cd$_x$Te ingots were compounded by a homogenization process that has been described in detail elsewhere [16]. The formed ingots were 14 cm long and weighed approximately 47 g.

2.2. Directional solidification growth system

The ingots were regrown by directional solidification in the presence of a stationary axially aligned magnetic field as shown schematically in Fig. 1a. The Bridgman–Stockbarger crystal growth system consisted of five heated zones with the booster and cold zone separated by a 2 cm adiabatic zone. A 0.3 cm thick heat extraction plate was placed between the adiabatic zone and cold zone to produce high axial gradients. The ampoule was supported by an inconel 625 cartridge assembly shown in Fig. 1b and remained stationary during crystal growth. Translating the furnace instead of the cartridge minimized any movement and vibrations of the sample and allowed the crystallization to take place in the homogenous region of the magnetic field. The superconducting magnet is manually set to the desired field strength (up to 50 kG) and is held constant during the entire growth process. The thermal profile was chosen in order to produce a gradient of approximately 80°C/cm on the ampoule wall at the position of 706°C, the solidus temperature for the steady-state growth [17]. The thermal profile was translated at a relatively slow rate of 0.2 µm/s in order to avoid constitutional supercooling [18].
2.3. Characterization

The effect of convection on segregation was determined by measuring radial and axial compositional variations in the grown crystals. For this study, the average $x$ values ($x$ is the mole fraction of CdTe) of wafers cut transverse to the growth direction were determined by high precision density determinations and the values of the crystal lattice constant published by Woolley and Ray [19] as described in detail elsewhere [20,21].

For $x$ values of 0.18 or larger, the radial microdistribution of cadmium telluride was quantitatively determined from the transmission edge of the IR transmission spectrum. The details of this highly automated transmission-edge mapping technique are described in Ref. [22]. Briefly, the hardware consists of a Fourier transform spectrometer specially equipped with a software controllable $xy$ stage driven by stepper motors. The stage can position the sample throughout a 2.54 cm square in 50 μm steps. Spectra are then analyzed to obtain the cut-on wavelength.

Fig. 1. (a) Schematic representation of the magnetic Bridgman–Stockbarger growth system. (b) Containment cartridge utilized for the magnetically stabilized growth of HgCdTe.
and the mole fractions of CdTe are calculated from the compositional dependence of the energy bandgap. For those samples with a cadmium telluride content of less than \( x = 0.18 \), the radial compositional variations were determined by energy dispersive X-ray spectroscopy analysis (EDX) using pseudo-binary solid solutions as standards [23].

3. Results and discussions

3.1. Axial compositional distributions

Fig. 2 shows the limiting axial compositional distributions for directional solidified HgCdTe. The two experimental curves [21], illustrate the effects of varying translation rates. The translation rates for ingots MCT-L6 and MCT-L7 were 0.310 and 0.068 \( \mu m/s \), respectively. Solidification at the slower rate results in the build up of a much longer solute boundary layer. Hence, the stabilizing solutal forces are expected to be less during the growth. This reduced stabilizing force can lead to the increase of natural convective mixing, which results in a more uniform radial segregation. However, the axial compositional profile never reaches a steady-state value. Therefore, improved radial segregation is gained at the expense of less uniform axial composition. If the translation rate is increased, as in MCT-L6, shorter transients result in steady-state axial compositional distribution, but radial segregation increases by two orders of magnitude. These results are in qualitative agreement with the numerical calculations of Motakef [24,25]. His results indicate that radial segregation increases initially with decreasing Peclet mass transfer number reflecting the reduction in the mixing of the melt, which results in increased non-uniformity of melt composition at the growth interface. This suggests that improved material compositional uniformity requires sufficiently fast growth rates to produce short initial transients and a simultaneous reduction of radial segregation caused by convective effects.

Fig. 3 shows the axial compositional distribution profiles for two crystals: curve MCT-D2 was obtained for growth without a magnetic field and curve MCT-4 for growth with melt stabilization by a 50 kG axial magnetic field. The theoretical curve based on a one-dimensional diffusion equation is also shown.

![Fig. 2. Axial compositional limits of directional solidification for HgCdTe.](image-url)
Fig. 3. Comparison of the experimental axial compositional distribution to the one-dimensional diffusion model.

Fig. 4. Schematic representation of the convective melt flows and solute boundary layer configurations for directional solidification growth of HgCdTe with and without magnetic stabilization.
The curve for MCT-D2 indicates that, as expected, during solidification in zero field the distribution of CdTe undergoes an initial transient, then a steady-state region followed by a final transient. This compares well with the curve calculated from an exact numerical solution to the one-dimensional diffusion equation for an \( x = 0.2 \) alloy [26,27]. The curve for MCT-4 (50 kG field) shows a similar initial transient and steady-state section. However, a sharp increase in the CdTe content is observed near the last-to-freeze end just before the final transient. To ensure that this rise was not due to measurement error, IR compositional measurements were taken at various axial locations. There was excellent agreement between the two measurement techniques, see Fig. 3. This rise in CdTe content may be explained by constitutional supercooling ahead of the interface.

Fig. 4, shows a schematic of the convective melt flows and solute boundary layer configurations for the no-field and field cases. In the no-field case, a region with intense convection (as compared to the growth rate) caused by radial thermal gradients is assumed to occur between a bulk of diffusion-controlled melt and the growth interface as proposed by Kim and Brown [28] to explain axial segregation patterns seen in HgCdTe crystal growth experiments by Szofran and Lehoczky [29]. Hence, the axial temperature gradient in the melt is sufficient to avoid constitutional supercooling due to the flatness of the compositional profile and normal solidification proceeds. In the case of growth in the presence of a stabilizing magnetic field, the elimination or reduction of convection allows for the build up of the diffusion-controlled solute boundary layer closer to the solid–liquid interface. As the axial temperature gradient is held constant, this stiffer solutal boundary layer produces a region in the liquid ahead of the interface that is at an actual temperature below its equilibrium liquidus temperature. Accordingly, this can lead to homogeneous nucleation of solid-phase particles, richer in Cd (higher \( x \)) than the bulk melt, which float upwards because their densities are less than those of the melts. This phenomenon of buoyant rising of solid particles, or Stokes migration, has been observed during vertical Bridgman–Stockbarger growth experiments of HgCdTe [30,31] and HgCdSe [32] and is consistent with the results from the growth of the MCT-4 ingot. Conclusive evidence of this phenomenon is demonstrated in Fig. 5, which illustrates a back-scattering electron micrograph of a quenched HgZnTe ingot showing Zn-rich precipitates that have migrated to the top of the boule due to Stokes migration brought about by constitutional supercooling [33].

3.2. Radial compositional distributions

3.2.1. Radial segregation: initial transients

Fig. 6 shows the radial compositional variations for wafers 2.5 cm from the first-to-freeze portion of ingots MCT-D2 (zero field) and MCT-4 (50 kG field) as determined by IR transmission-edge measurements. The pattern of low Cd content at the center (high Hg content) and high Cd content along the edge of wafer #2.2, prepared from the MCT-D2 ingot, is consistent with other results obtained previously in the absence of a magnetic field. As noted earlier, the vertical directional solidification of Hg-based II–VI systems is characterized by double diffusive convection and a concave (toward the solid) growth interface. Thus, the denser Hg-rich melt tends to accumulate at the center of the crucible resulting in the radial compositional profile shown in Fig. 6a.
Fig. 6b shows the radial profile for growth in the presence of the stabilizing magnetic field. The order of magnitude improvement in radial homogeneity clearly indicates that the magnetic field was efficacious in suppressing convective effects on segregation. Fig. 6c shows the composition variation across the diameter of the two samples. Compositional variations in other wafers in the initial transient region show similar behavior.

3.2.2. Radial segregation: steady-state region

In an effort to quantify the effects of the magnetic field on the radial segregation, the experimental results were compared to the analysis of the lateral solute segregation associated with a curved solid-liquid interface during steady-state unidirectional solidification of a binary alloy as derived by Coriell and Sekerka and described in detail in Ref. [34]. Briefly, they solved the species continuity equation for the radial solute concentration in the solid crystal at the solid–liquid interface with the assumptions of no convection in the liquid and that the solid–liquid interface could be represented by a Fourier series. Their work showed that in the limiting case, the transverse segregation in the solid is proportional to the deviation of the interface from planarity, the proportionality factor being just the product of the unperturbed concentration gradient and the distribution coefficient given by

$$\Delta C/C_0 = (k - 1)(R/D_L)\Delta \xi,$$

(3.1)

where $\Delta C$ is the difference in composition at the edge and center of the wafer, $k$ is the equilibrium segregation coefficient, $R$ is the translation rate and $\Delta \xi$ is the interface deflection. These calculations are applicable for crystal growth in a stabilizing mag-
netic field where the field strength is sufficient to suppress convection. The solid–liquid interface deflection necessary for the calculations was determined experimentally by quenching samples with and without a magnetic field. The quenched interface obtained in the presence of a magnetic field was symmetric about the growth axis and had a maximum deflection (concave toward the solid) of 1.1 mm, which was a factor of 3 less than that obtained without the magnetic field. Similar effects on the solid–liquid interface were found in gallium-doped germanium grown in the presence of a 30 kG axial magnetic field [35].

Fig. 7 shows a comparison of the experimental and the calculated diffusion-limited radial segregation, where the diffusion-limited regime was determined by varying the translation rate in Eq. (3.1). For this calculation, the steady-state equilibrium segregation coefficient, $k = 4.2$, was determined experimentally by measuring the compositional change across a quenched interface in the steady-state region of crystal growth. The mass diffusion coefficient, $D_L = 5.5 \times 10^{-5}$ cm$^2$/s, was determined by a best fit of the experimental axial composition data to the one-dimensional diffusion-limited model of Clayton et al. [36] and is consistent with the value obtained by Lehoczky et al. [21]. The figure summarizes previous data for MCT-L6 and MCT-L7, as well as, the data from MCT-D2 and MCT-4. The multiple data points for MCT-L6 and MCT-L7 are for three wafers analyzed in the steady-state region and are described in Ref. [21]. The comparison of the various experimental and calculated results strongly suggest nearly diffusion-limited growth and, thus, signifi-

![Fig. 7. Comparison of experimental and diffusion-limited radial segregation.](image-url)
stantly improved compositional homogeneity can be obtained with magnetically stabilized Bridgman–Stockbarger growth systems.

4. Conclusions

An axial magnetic field was applied during crystal growth experiments in order to damp the velocity of the melt via magneto-hydrodynamic interactions. The resulting reduction in convection significantly altered the overall mass transfer and redistribution process. The primary influence of convection on mass transfer in the melt and segregation at the solid–liquid interface can be summarized as follows:

(1) The axial compositional distribution was relatively unaffected during the initial transient and steady-state growth portions of the solidification process. An abrupt rise in the CdTe content was observed near the end of the ingot and has been attributed to constitutional supercooling brought about by the magnetic suppression of convection near the solid–liquid interface, which results in an increase in the slope of the diffusion-controlled solute boundary layer.

(2) In conventional growth, the Hg-based II–VI systems are characterized by double diffusive convection and a concave growth interface. This results in the accumulation of Hg-rich material at the center of the melt just ahead of the growth interface, which in turn increases the interface curvature because of the nature of the HgTe–CdTe pseudo-binary phase diagram. These effects tend to enhance the radial segregation.

(3) For growth in a 50 kG magnetic field, the convection intensity was sufficiently damped, which allowed the interface curvature and radial composition to approach diffusion-limited growth conditions. It should be remarked that the present study indicates that the interaction of the thermal, solutal and momentum fields in HgCdTe systems are highly coupled. The modification of these complex interactions, through, for example, the application of a magnetic field can significantly alter the interface morphology and compositional homogeneity. Therefore, any attempts at modeling these systems should involve the fully coupled form of the governing equations.

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