Homogenization of zinc distribution in vertical Bridgman grown Cd$_{0.96}$Zn$_{0.04}$Te crystals

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Abstract. One of the most pressing issues in the growth of high quality single crystal Cd$_{0.96}$Zn$_{0.04}$Te material, is to achieve homogenization of the high axial variation of Zn concentration, caused by the larger than unity segregation coefficient of Zn in CdTe. This is achieved in our crystals (i) by thermal annealing of the CdZnTe crystal, which redistributes the as grown Zn distribution by solid state diffusion of Zn (this solid state diffusion of Zn occurs at three stages (a) during the growth when the solidified crystal is near to the melting point temperature, (b) during the post growth annealing of the crystal at a high temperature and (c) during the cooldown to room temperature) and (ii) by the reduction of Zn segregation during the growth stage by enhanced convective mixing of the melt, through a proper choice of ampoule and furnace dimensions. By adopting suitable growth parameters and sufficient post growth annealing it has been possible to grow Cd$_{0.96}$Zn$_{0.04}$Te crystals, which have nearly 75% of their fraction within 1% Zn concentration variation.

Keywords. Bridgman growth; CdZnTe; Zn distribution; solid state diffusion.

1. Introduction

Bridgman grown single crystal, Cd$_{0.96}$Zn$_{0.04}$Te, is used as the lattice matched substrate material, for the growth of Hg$_{0.8}$Cd$_{0.2}$Te epitaxial layers required for high performance infrared detectors. The benefits of lattice matching with Hg$_{0.8}$Cd$_{0.2}$Te layer include, improved epilayer morphology, decrease in misfit dislocation density and reduced epilayer strain. It has been observed that a slight mismatch produces epilayers with a well resolved cross-hatch pattern and the lowest EPD. However, as the lattice mismatch increases the EPD increases and the epilayer morphology deteriorates resembling the epilayer grown on zinc free CdTe substrate (Rhiger *et al* 1997).

The growth of high quality single crystal, Cd$_{0.96}$Zn$_{0.04}$Te material is fraught with challenges due to a number of issues. One of the most pressing issue is to achieve homogenization of the high axial variation of Zn concentration, caused by the larger than unity segregation coefficient of Zn in CdTe. The segregation of Zn during the vertical Bridgman growth of these crystals leads to non-uniform Zn concentration on both axial and radial directions, severely reducing the yield of useful material.

This report is an attempt to understand the effects of the growth parameters on Zn distribution in vertical Bridgman grown CdZnTe crystals. Ten Cd$_{0.96}$Zn$_{0.04}$Te crystals grown in a variety of growth conditions (different furnace thermal gradients, growth speeds and ampoule dia./furnace radius ratios) and subjected to different post growth annealing and cooling treatments (different duration of post growth annealing and different rate of cooling to room temperature) were analysed for zinc distribution. The general observations from this analysis are presented in this report along with few typical Zn segregation curves and the approaches to be adopted for achieving a high degree of homogenization of Zn distribution in the vertical Bridgman grown Cd$_{0.96}$Zn$_{0.04}$Te crystals.

2. Experimental

The Cd$_{0.96}$Zn$_{0.04}$Te crystals were grown unseeded, in quartz ampoules in vertical Bridgman configuration (Bagai and Borle 1989; Gurumurthy *et al* 1998). The sample plates were cut from the central part of the crystal, along the growth direction, using an inner diameter annular saw. Since efforts were made to cut (111) oriented wafers, the sliced wafers were often slightly tilted to the growth axis. They were lapped and polished into 0·8–1·2 mm thick wafers, and then chemically etched with 0·5% Br-methanol solution.

Zn composition measurements were made on these Cd$_{0.96}$Zn$_{0.04}$Te wafers, using the room temperature transmission in the high energy band-edge region of the crystals. A Cary-5E (Varian) UV-Visible-NIR spectrophotometer was used to measure the RT transmission, with a wavelength accuracy of 0·4 nm, using a slit bandwidth of 1 mm and scanning the sample over 5 mm

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dia. circular areas. From the transmission measurement, the linear region of the band-edge was chosen and these data points were extrapolated to $T = 0$, to find out the cut-on wavelength at zero transmission (figure 1). The thickness correction and the composition calculations were carried out using the empirical equations developed by Johnson *et al* (1991). The measurements were made on the sample at the crystal centre, edge and mid-radius positions, and shifting the sample along its axis.

3.   Results and discussion

Some of the interesting general observations from the analysis of Zn distribution in ten $Cd_{0.96}Zn_{0.04}Te$ crystals are given below. As a measure of the degree of homogenization of Zn concentration (i.e. uniformity of Zn distribution), the solidified fraction wherein the Zn concentration varies gradually over 1% from its maximum value, was taken.

(I) It is observed that post growth annealing of the $Cd_{0.96}Zn_{0.04}Te$ crystal increases the homogenization of Zn distribution. The Zn distribution in crystal CZT179 (figure 2), grown at a growth speed of 1 mm/h and cooled to room temperature at a rate of 10°C/h after growth, has around 40% of its fraction within 1% Zn concentration variation. The Zn concentration is seen to go down to as low as 1·7%. The Zn distribution in crystal CZT175 (figure 3), grown at a growth speed of 1 mm/h, and annealed for 10 days at 1000°C, and then cooled to room temperature at the rate of 10°C/h, has nearly 75% of its fraction within 1% Zn concentration variation. This marked difference in the uniformity of Zn distribution between the two cases is a clear indication of the effectiveness of high temperature annealing in homogenization of Zn distribution. Upon high temperature annealing, the as grown Zn concentration gradient gets reduced because of the solid state diffusion of Zn. The high temperature annealing and the post growth cooldown results in a more uniform Zn concentration closer to 4%.
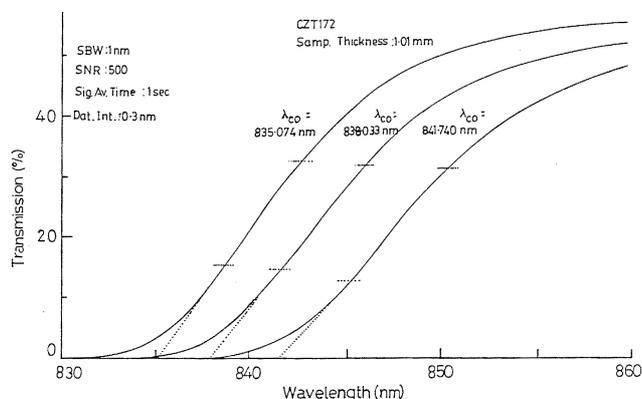
A simple least square fitting of the axial Zn distribution data along the centre of the crystal CZT179, to $Cs = kCo(1 - g)^{k-1}$, where Co is the initial nominal Zn concentration (Pamplin 1980), shows $k = 1.17$. The value of segregation coefficient of Zn in CdTe crystal reported in the literature varies over a range of 1·05–1·6 (Capper 1994), but is invariably around 1·1–1·3 for the typical low growth rates and the low thermal gradients used for high quality CdZnTe crystal growth. The Zn segregation coefficient calculated for Zn distribution along the centre of the crystal CZT175 is 1·11. This slightly lower value of the Zn segregation coefficient may be because of the role played by the post growth high temperature annealing which reduces the as grown Zn concentration variation.

(II) The redistribution of Zn by solid state diffusion is more efficient at higher temperatures, especially near the melting point of the crystal. This can be seen from the Zn distribution of crystal CZT171 (figure 4), which was grown at a growth speed of 0·5 mm/h, was not subjected to any post growth annealing, and cooled to room temperature naturally, has nearly 70% of its fraction within 1% Zn concentration variation. This high degree of uniformity in the Zn distribution, in an unannealed crystal can be explained by the lower growth speeds used. That is, at lower growth speeds the solidified part of the growing crystal is exposed to elevated temperatures (near melting point temperature) for longer duration than in the higher growth speed runs (it is nearly double the duration in the present case), which allows far more homogenization through solid state diffusion of Zn. This has occurred in spite of the higher axial segregation expected at the lower growth speed, because the as grown Zn distribution, is redistributed further by the solid state diffusion of Zn at near the melting point temperatures. The calculated Zn distribution coefficient is 1·10. The slope of the axial segregation profile of CZT171, would
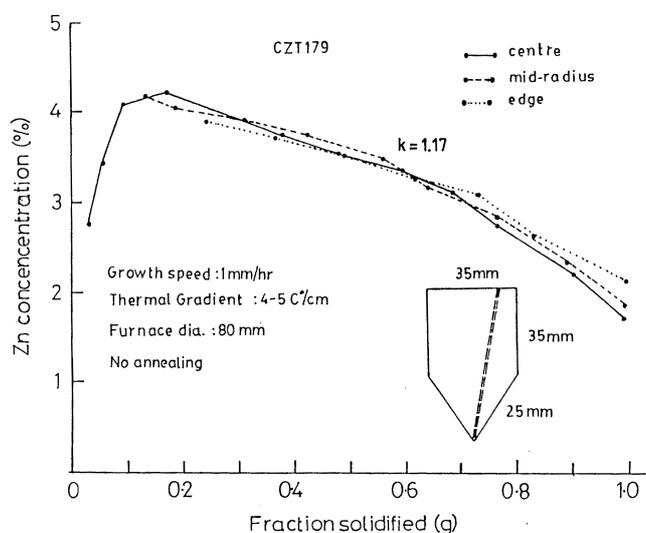
Figure 1.   Typical room temperature transmission at the high energy band-edge region of a $Cd_{0.96}Zn_{0.04}Te$ crystal.

Figure 2.   Zn distribution in crystal CZT179.

have been greater, had the effect of solid state diffusion of Zn been absent.

It is also observed that the crystals grown at lower growth speed possesses less radial segregation, as indicated by the almost overlapping segregation curves, at the centre, mid-radius and the edge of the crystal CZT171 (figure 4). This is because, lower growth rate leads to a more efficient removal of latent heat of solidification and hence a flatter solid–melt interface, and consequently less radial segregation.

(III) The axial and radial Zn distribution of a CdZnTe crystal is very useful in analysing the axial and radial homogeneity of the crystal, the growth conditions, the solid–liquid interface shapes, etc. For example, the axial and radial Zn distribution of crystal CZT184, is shown in figure 5. This crystal was grown at a growth speed of 0·5 mm/h, was not subjected to any post growth annealing and cooled to room temperature naturally. The wafer analysed was cut along the axis of the crystal, almost near to the centre of the ingot. The axial distribution of Zn concentration was measured along six locations of the wafer (figure 5a). It can be seen that at least 60% of the solidified fraction is within 1% Zn concentration variation (The probable reason for the lower yield homogeneous fraction for this crystal, compared to crystal CZT171, which was grown almost under similar conditions except for the different ampoule and furnace dimensions, is given in § 4 of this paper). The radial distribution of Zn concentration in this crystal was measured on the same wafer along its diameter at three different locations, namely the initial cone region, the main body and at the end portion. It can be seen that the radial uniformity of the Zn distribution is good at the main body of the ingot, indicating that the solid–liquid interface is nearly flat at this region. But the radial non-uniformity at the initial and end portions of the ingot, point out to a non planar solid–liquid interface at these places. It is known that (Azoulay *et al* 1990), because of the complex temperature distribution around the conical tip and its changing cross-

section, the interface is convex towards the melt at the bottom of the conical tip, which gradually changes and becomes nearly planar in the central part of the crystal, and then assumes a concave shape with a gradually increasing curvature to the last to freeze portion of the crystal, due to the end effects. However, a thorough investigation of the interface needs complete mapping of the Zn concentration using microprobes, and drawing the isoconcentration lines (Azoulay *et al* 1990) or other interface demarcation techniques (Wadley and Dharmasena 1997).

Also it can be seen that (figure 5b) the points of maxima and minima of Zn concentration distribution (which are also the maxima and minima of solid–liquid interface shapes), is shifted away from geometric axis of the grown crystal, showing that the crystal has been grown slightly asymmetric w.r.t. the furnace axis, as has been the present case (Bagai and Borle 1989).

(IV) There is a strong dependence of the axial Zn distribution of the grown crystals, on the ampoule dia. to furnace radius ratio. The homogenization of Zn distribution is found to be better in crystals grown in ampoules with an ampoule dia. to furnace radius ratio of 1·272, compared to the crystals grown in ampoules with the ampoule dia. to furnace radius ratios of 1·12, 1·06 and 0·875. This observation was valid for crystals grown at growth speeds of 1 mm/h and annealed at 1000°C for 10 days as well as for crystals grown at growth speed of 0·5 mm/h but unannealed (figure 6).

In vertical Bridgman growth, the heat and mass transfer dictates the growth interface and dopant segregation, and thus plays a crucial role in the crystal quality. The interaction between the heat and solute transport can be complex and can lead to unexpected results. There are two strong axisymmetric convective flow currents during the vertical Bridgman crystal growth (Kuppurao *et al* 1995), the lower clockwise flow cell caused by the release of latent heat of solidification near the solid–melt interface and the middle counter-clockwise flow cell
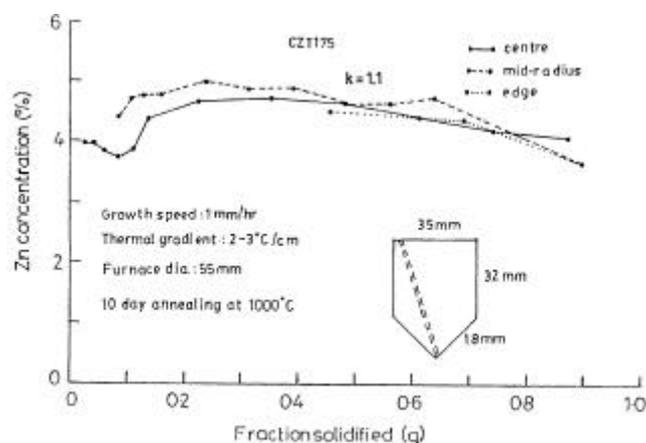

Figure 3. Zn distribution in crystal CZT175.
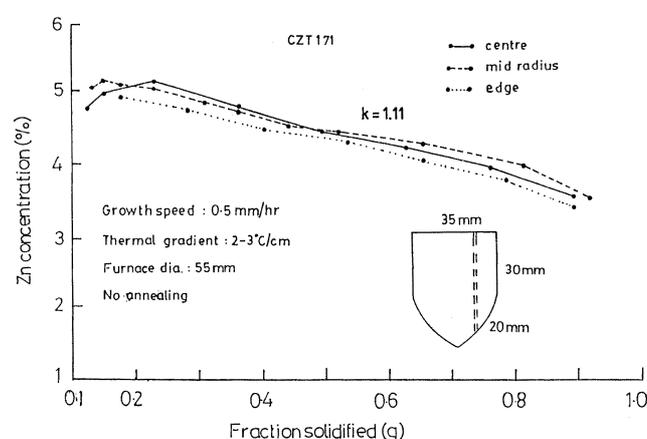

Figure 4. Zn distribution in crystal CZT171.

driven by the radial heat transfer from the hot-zone of the furnace to the melt. Work on modelling (Kim and Brown 1991; Kuppurao *et al* 1995; Xiao *et al* 1996) of the heat transfer, melt convection, solid–liquid interface shape and pseudo-binary segregation in vertical Bridgman grown binary alloys, have been carried out to study the effect of growth parameters, ampoule asymmetry and crucible rotation. Changes of ampoule radius and the slight asymmetries of the ampoule, alter the convective driving forces inside the melt. A suitable choice of ampoule dia. to furnace radius ratio, might lead to enhanced convective driving forces inside the melt, which give rise to a better solute mixing and hence lower segregation, but needs further theoretical and experimental investigation.

(V) In all the crystals the first to freeze portion was characterized by an anomalous segregation behaviour, where the concentration of Zn starts from a lower value, and increases to a maximum at about a length of 25 mm or solidified fraction of $\sim g = 0.2$, and then onwards follows the expected normal freezing behaviour. This initial solid phase at the tip region is also characterized frequently by polycrystalline material and higher radial segregation, and is observed in all crystals irrespective of the ampoule tip configuration (shape and length).
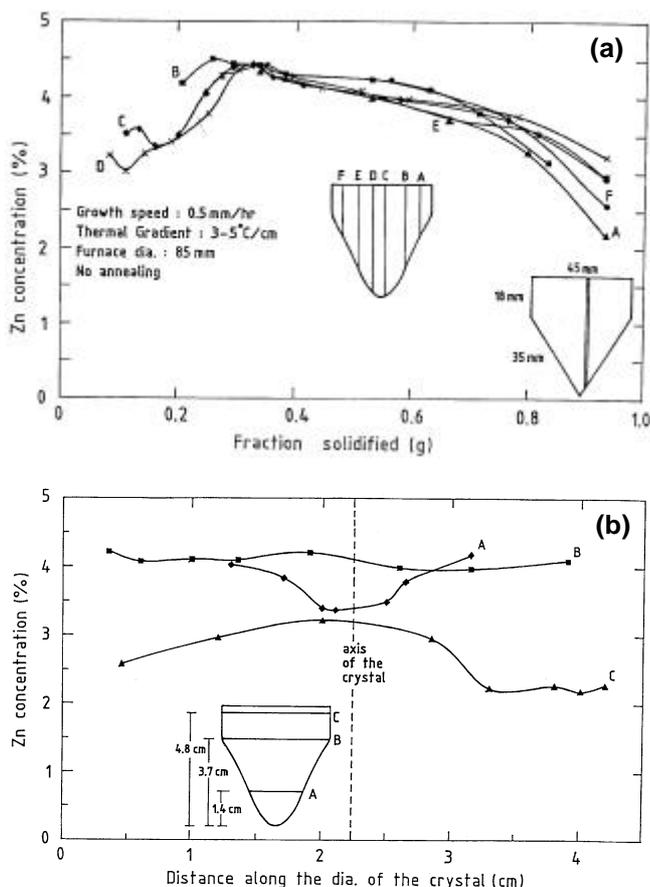
This anomalous segregation in the initial portion of the CdZnTe crystal has been observed by many workers (Muhlberg *et al* 1990; Azoulay *et al* 1992; Radhakrishnan *et al* 1998), and is associated with considerable supercooling of the tip region, under low gradient conditions. This kind of anomalous segregation behaviour is postulated to result from a burst of growth from the initially supercooled melt. In this initial portion, the growth is under conditions where melt mixing is not complete and the growth rate is varying, i.e. decreasing from the initial fast growth under non-equilibrium freezing conditions, to a slower steady-state equilibrium growth condition.

The variation (sudden fluctuations) in composition of CdZnTe near the tip of the crystals CZT175 (figure 3) and CZT184 (figure 5) are probably due to transient effects, such as temperature fluctuations and associated spontaneous nucleation at the beginning of the growth. The hump in the segregation curve, which is the maximum Zn concentration, is found to go down in magnitude and shift to the right upon long durations of post growth thermal annealing, due to the increased solid state diffusion of Zn.

(VI) Small changes in the furnace thermal gradient (within the range necessary for high quality crystal growth), had negligible effect on the homogenization of Zn distribution in the grown CdZnTe crystals.

(VII) The $Cd_{1-x}Zn_xTe$ crystals used for lattice matched substrates of IR sensor material $Hg_{1-y}Cd_yTe$, are grown world over (by substrate suppliers) with 4% nominal Zn concentration, probably because the lattice matched substrates for both the 8–12 μ atmospheric window IR sensor material—$Hg_{0.8}Cd_{0.2}Te$ (lattice matches with CZT substrate having 4.5% Zn concentration) and the 3–5 μ atmospheric window IR sensor material—$Hg_{0.7}Cd_{0.3}Te$ (lattice matches with CZT substrate having 4% Zn concentration), can be mined from the same ingot and becomes economical. However, for applications specific to $Hg_{0.8}Cd_{0.2}Te$, a higher yield of useful material will be obtained with CdZnTe crystals having an initial nominal Zn concentration of 4.5%.

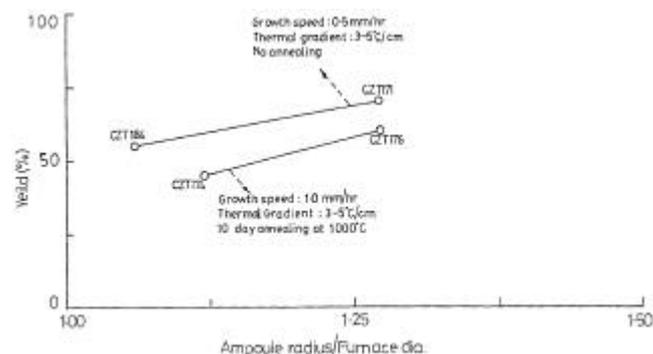**Figure 5.** (**a**) Axial Zn distribution in crystal CZT184 and (**b**) radial Zn distribution in crystal CZT 184.

Figure 6. Effect of the ampoule dia. to furnace radius ratio on the yield of homogeneous fraction of $Cd_{0.96}Zn_{0.04}Te$ crystal.

The empty volume above the melt inside the quartz ampoule used for synthesis and growth of the crystal should be taken into consideration while measuring the starting materials, since the elements Cd and Zn because of their higher partial pressures, fill this volume. Also to be taken into consideration is the ratio between the melt volume and the empty volume above the melt, and it should be kept constant so that the average Zn and Cd compositions do not shift above or below the initial nominal composition and remains reproducible.

4. Conclusions

A high degree of homogenization of Zn distribution was achieved in our Cd$_{0.96}$Zn$_{0.04}$Te crystals by adopting the following approaches.

(I) The as grown Zn distribution was distributed further by solid state diffusion, by thermal annealing of the CdZnTe crystal. This solid state diffusion of Zn occurs at three stages (a) during the growth when the solidified crystal is near to the melting point temperature, (b) during the post growth annealing of the crystal at a high temperature and (c) during the cooldown to room temperature.

(II) The reduction of Zn segregation during the initial growth stage by enhanced convective mixing of the melt, through a proper choice of ampoule and furnace dimensions.

By adopting suitable growth parameters and sufficient post growth annealing it has been possible to grow Cd$_{0.96}$Zn$_{0.04}$Te crystals, which have nearly 75% of their fraction within 1% Zn concentration variation.

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