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A method of promoting single crystal yield during melt growth of semiconductors by directional solidification

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ABSTRACT

For certain semiconductors with important applications, the existing unseeded bulk directional solidification crystal growth technique from the melt usually results in poor quality multi-crystalline ingots which causes the low yield of the commercial growth process. The multi-grained crystal growth is mainly caused by the large supercool of the melt, which not only results in a large section of ingot solidifying uncontrollably under spontaneous nucleation but also prohibits the ideal growth condition that small single crystal nuclei form at the very tip of the ampoule and grow into large single grains. To promote nucleation under the condition of small supercooling, a method was employed to induce nucleation by mechanical perturbation at a critical time during growth. The technique was applied to the bulk crystal growth process of $Cd_{1-x}Zn_xTe$ ingots. The comparison between the crystalline quality of the crystals grown with and without the mechanically induced nucleation shows that the yield of single crystalline can been vastly improved with the application of the technique.

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1. Introduction

For certain semiconductors with important applications, the commonly used growth method of directional solidification from a melt, including the Bridgman–Stockbarger technique or vertical gradient freeze, has the nature of extensive supercooling of the melt during growth. For instance, the measurement of differential thermal analysis (DTA) of the $Hg_{0.80}Zn_{0.20}Te$ melt revealed a supercool of 52 °C [1] as a freezing temperature of 743 °C was observed comparing to the equilibrium liquidus temperature of 795 °C for the melt. It implies that the melt does not solidify until it is 50 °C below the equilibrium liquidus temperature and this has been verified in the directional solidification of a $Hg_{1-x}Zn_xTe$ ($x=0.22$) melt that a 4 cm long supercooled solid, with a value of x greater than 0.5, was spontaneously formed in the first freeze part of a 10 cm long ingot [2]. Supercool of 50 to 80 °C were also observed in other semiconductors systems with strategically important applications, such as HgCdTe [3]. A curve for the DTA measurements of a CdTe ampoule is shown in Fig. 1, which plots the ΔT, the difference between the temperature of the furnace and that of the CdTe sample, against the furnace temperature. The sample was heated up rapidly to above its melting point of 1090 °C and was soaked for 9 h before a furnace cooling rate of about 10 °C/min commenced. During the cooling of the furnace, the sample temperature stayed at 1090 °C and started to decrease when the furnace reached 1040 °C, i.e., a supercool of 50 °C. The high supercool not only results in a large section of ingot solidifying uncontrollably with spontaneous nucleation but also prohibits the ideal growth condition that small single crystal nuclei form at the very tip of the ampoule and grow into large single grains and, consequently, results in the low yield of single crystal.

To prevent the undesired formation of a large multi-grained spontaneous nucleation, i.e., to promote nucleation under the condition of small supercooling, it is proposed to apply a short-time mechanical perturbation to the growth ampoule when the melt at the ampoule tip is just below the liquidus temperature. It is also desirable to provide a method that can be readily implemented with existing fabrication systems to promote the single crystal growth of semiconductors. The technique was implemented to the directional solidification process of $Cd_{0.80}Zn_{0.20}Te$ crystals, previously reported in Ref. [4], by adding a solenoid AC vibrator, which was bound to the growth ampoule, with a frequency of 60 Hz and an adjustable magnitude. The high-frequency shaking of the ampoule causes local inhomogeneity in the supercooled melt, which promotes the nucleation in the melt and, consequently, a small section of solid, usually single or double grain, was formed at the growth tip which grows continuously throughout most of the ingot length.

2. Crystal growth

The crystal growth of $Cd_{0.80}Zn_{0.20}Te$ by directional solidification has been reported in detailed early in Ref. [4]. It will be described briefly here.

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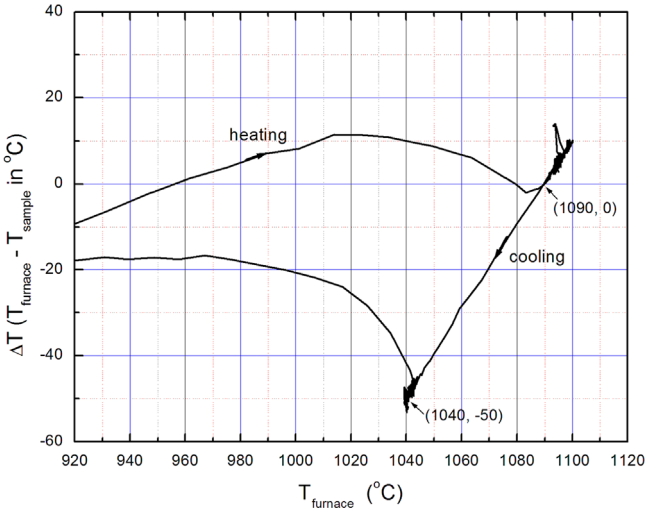

Fig. 1. A curve for the DTA measurements of a CdTe ampoule. The difference between the temperature of the furnace and that of the CdTe sample, ΔT, is plotted against the furnace temperature.

2.1. Homogenization of starting material

The starting elements of Cd, Zn, and Te were high purity; either six-nines grade from Johnson Matthey or seven-nines grade from 5N Plus. The small chunks of the elements were mixed and loaded inside fused silica ampoules. A heated zone (maximum temperature of 520 °C) was translated over the vacuum-sealed ampoules at a translation rate of 1 cm/h, to initiate the Te-rich eutectic exothermic reaction. The ampoules were then loaded inside a closed fused-silica tube, evacuated to 10^{-3} Torr, which was placed inside a tubular rocking furnace for the melting and mixing of the charge. After the zone pass, the spongy-looking material was heated up to 1070 °C, soaked for 36 h, then raised to 1160 °C, rocked for 3 to 5 h before casting by turning off the furnace power. The ampoules were opened and the homogenized samples were retrieved for crystal growth.

2.2. Crystal growth

The growth ampoules were made of fused silica of inner diameters either 20 or 40 mm with a tapered end at the growth tip. After the starting material has been loaded inside the growth ampoule, a fused silica basket holding about 2 g of pure Cd was fixed below the seal-off cup at the top of the ampoule and served as the Cd reservoir to control Cd overpressure during growth. The ampoules were then sealed under a vacuum better than 10^{-5} Torr.

As shown schematically in Fig. 2, the growth ampoule has a fused silica rod extending from its tapered tip which was supported by a fused silica tube vertically fixed by a lathe chuck on the floor. The mechanical perturbation provided for the present growth experiments was a commercially available 60 Hz solenoid AC vibrator, which was coupled to the base of the supporting fused silica tube by a plastic strap. The magnitude of the perturbation was adjusted by varying the power input of a variable voltage power supply, Variac, from 0 to 120 V. The vertical Bridgman growth furnace, as shown in Fig. 2, had four independently controlled electrical-resistance heating zones. They are, starting from top to bottom, the Cd reservoir zone, the hot, booster and cold zones. The Cd reservoir was kept between 805 to 820 °C to control the Cd overpressure during growth. The hot zone and booster zone provided a maximum of 1185 °C for the melt and, together with the cold zone, a thermal gradient of about 10 °C/cm between the liquidus and solidus temperature of 1145 and 1115 °C, respectively, for the composition of $Cd_{0.80}Zn_{0.20}Te$. Fig. 2 also illustrates schematically the thermal profile inside the furnace bore and the initial position of the growth ampoule with the sample staying above the liquidus temperature, T_L. The specific procedures for the growth of CdZnTe crystals with mechanically induced nucleation are the followings:

1. Position the growth ampoule along the thermal profile inside the furnace such that the sample would be completely melted when the furnace temperature settings have been reached.
2. Heat up the furnace to the desired thermal profile so that the sample is completely melted as shown in Fig. 2.
3. Soak the sample for 48 h as the furnace translates upward at a rate of 1.0 to 1.25 mm/h.
4. When the ampoule tip is at a position in the furnace where the temperature is 3 to 8 °C below the liquidus temperature, the mechanical tapping was applied using the solenoid vibrator for 20 s at a voltage of 50 V.
5. Continue the growth by translating the furnace at a rate of 1.0 to 1.25 mm/h until the sample section is completely below the solidus temperature.
6. Cool down the settings of the furnace and retrieve the grown sample

Growths of $Cd_{0.80}Zn_{0.20}Te$ crystals, both 20 mm and 40 mm in diameter, have been processed with and without the mechanical perturbation. The grown ingots were sliced by wire saw and the patterns of crystallinity were observed and studied.

3. Results

The growth environments and procedures for the 20 mm diameter ingots of CZT-37 and CZT-38 were implemented as similar as possible except that the mechanical tapping was introduced to the latter but not the former. The detailed sample composition and mass as well as the growth parameters are given in Table 1. Figs. 3 and 4 show the photographs of CZT-37 and CZT38 ingots, respectively. Fig. 3(a) shows the slicing of the roughly 7 cm long ingot of CZT-37. Fig. 3(b) shows that the cross section at 1.5 cm from the tip has at least five grains and some twinning. The cross sections at 1.8 cm and 2.5 cm, given in Fig. 3(c), also exhibit multiple grains. Fig. 4(b) shows that the slices cut at 1.5 cm and 1.8 cm from the ingot CZT-38, as given in Fig. 4(a), exhibit a mono-crystalline structure. The cross section at 1.5 cm has some twinnings which disappeared at the cross section of 1.8 cm. The longitudinal cut of the remaining ingot shown in Fig. 4(c) extends the mono-crystalline structure through the ingot till the last 1.5 cm section. The single crystallinity has been confirmed from the measured X-ray diffraction spec tra across the diameter shown in Fig. 4(c). Several 40 mm diameter ingots have also been processed with and without mechanical disturbance. Without the mechanical perturbation, as shown in Fig. 5(a), the as-grown ingot of CZT-16 shows multiple crystalline grains with twins. Another grown ingot without mechanical tapping, CZT-20, as shown in Fig. 5(b), also exhibits multiple grains. The ingot of CZT-36, grown with the mechanical perturbation, slid inside the growth ampoule after growth process, as shown in Fig. 6(a), and shows twins in the tapered shoulder area as given in Fig. 6(b). These twins were limited to the first 1.5 cm section, as shown in the axially sliced section of the first 2.5 cm sample in Fig. 6(c), and the ingot developed into one major and one minor crystalline grains. The cross section area at 2.5 cm, given in Fig. 6(d), shows the major grain covers more than 70% of the sample.

4. Discussions

In general, the semiconductors needed for certain special applications, such as the three systems discussed above, the HgCdTe and HgZnTe crystals for infrared detection and CdZnTe for X-ray and gamma ray detection, require high purity starting materials to control