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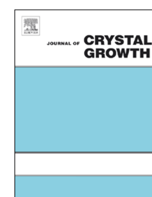

Bulk growth of uniform and near stoichiometric cadmium telluride

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ABSTRACT

Crystal growth of bulk cadmium telluride (CdTe) ingot with 64 mm diameter and 75 mm height was accomplished in a modified vertical Bridgman configuration with the aim of achieving minimal nonstoichiometry related second phases (SP) defects such as inclusions and precipitates. As-grown crystal wafers were characterized with respect to infrared microscopy, bulk resistivity, low-temperature photoluminescence (PL) and foreign impurity concentration. Except for grain boundaries and twins, the wafers were found to be completely free of SP of sizes $>1\ \mu m$ and the distributions at different parts of the grown boule were found to be identical. Star shaped inclusions were observed at some places near the mid-section of the ingot, which were tentatively identified as Cd inclusions. At room temperature, the crystal exhibited high bulk resistivity values of 10^7–$10^8\ \Omega$ cm, which was found to be in conformity with the low density of nonstoichiometric defects. GDMS results indicated that the concentration of unintentional impurities was low enough for the electrical behavior to be explained uniquely on the basis of native defects.

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1. Introduction

Cadmium telluride and its alloy cadmium zinc telluride (CdZnTe) have been used as room temperature radiation detectors [1,2] as well as substrate material for HgCdTe (MCT) epitaxial growth [3,4]. In addition their complete transparency to IR up to 30 μm renders CdTe/CdZnTe a unique advantage over some of the conventional substrate choices such as Si, Ge, sapphire, since removal of the substrate after growth is not desired. However the presence of structural defects such as grain boundaries, twins, inclusions and precipitates in the substrate is known to adversely affect the quality of the deposited epilayer [5]. These defects are also known to deteriorate carrier transport in detector grade crystals [6]. Inclusions and precipitates originate as a result of the inherent deviation from stoichiometry in CdTe melt at growth temperature. The accepted viewpoint about the formation mechanism of these SP defects is that inclusions form as a result of morphological instability at the crystallization front, whereas precipitation occurs due to condensation of native defects during post-growth cooling which is a consequence of the retrograde behavior of the CdTe solidus [7]. The sizes of occurrence of inclusions are typically 1–20 μm and therefore IR microscopy is a convenient tool for their characterization. These inclusions are observed in varying size and distributions depending on the adopted crystal growth techniques. Modified vertical Bridgman technique is one of the most robust bulk growth methods for CdTe/CdZnTe growth with provision for in situ post-growth thermal processing [8]. Irrespective of the growth methods, as-grown crystals are always seen to have these SPs and post-growth thermal treatment is almost inevitable for their reduction. Typically CdTe/CdZnTe post-processing is carried out on thin wafers in the presence of elemental Cd or Cd–Zn alloy source and complete elimination of the inclusions requires long annealing time [9]. It has also been reported that tellurium inclusions act as potential sites for impurity gettering, which are released upon thermal annealing [10]. These impurities can diffuse throughout the crystal and affect its transport properties. Inclusion free, as-grown crystal has been obtained by the vertical gradient freeze growth method using a controlled Cd pressure [11]. The aim of this paper is to present a simpler and faster way of achieving near stoichiometric as-grown CdTe crystals without requiring any separate Cd reservoir and modifications to the furnace or ampoule design. The characteristics of such near stoichiometric crystals in terms of the extended defects as well as point defects will be discussed.

2. Experimental

2.1. Crystal growth

All the growths were performed in a vertical Bridgman setup. 6N5 grade CdTe purchased from 5N Plus Inc, Canada, was used as the charge material. The exact stoichiometry of the starting raw

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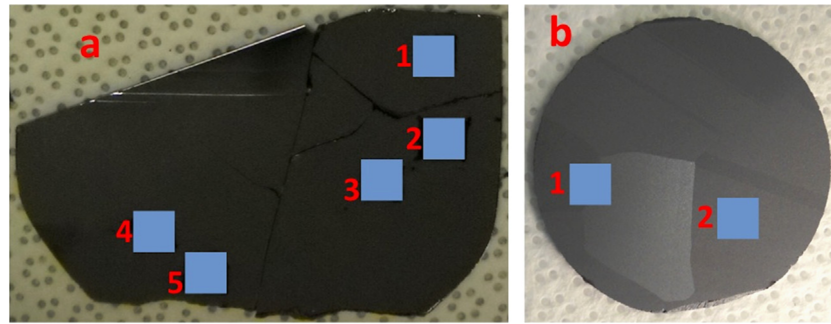

Fig. 1. IR mapped regions on the (a) axial slice, which cracked during polishing, and (b) radial slice.

material was unknown, however it is believed to be slightly tellurium rich. Pure cadmium in the amount of approximately 6×10^{18} atoms/cm^3 was added to the charge. The ampoule used for the growth was made out of GE 214 quartz at Technical Glass Products. The ampoule tip was conical in shape with a cone angle of 45° and the inner wall was coated with graphite. A fitting quartz insert was kept inside the ampoule on top of the charge for sealing purpose. The open volume left inside the ampoule was ~200 cm^3. The amount of raw cadmium telluride used is ~1000 g. The ampoule was then evacuated and simultaneously baked to remove residual gases. After a proper vacuum of ~10^{-7} Torr was reached the ampoule was sealed and then loaded into the furnace. The growth was performed with an imposed growth rate of 2 mm/h and an imposed axial temperature gradient of 20 °C/cm. Prior to starting the growth, the charge material was melted and convective melt mixing (soaking) was performed with the ampoule tip at 1150 °C. Post-growth crystal cooling to room temperature was performed at the rate of 4–10 °C/h. It should be noted that the entire residence time of the ampoule inside the furnace was 12 days, which included raw material melting, growth and post-growth cooling to room temperature. Crystals of diameter ~64 mm and length ~75 mm were grown.

2.2. IR microscopy

IR microscopy was performed in order to analyze the shape, size and distribution of secondary phases (SP) in the wafer. It is believed that the observed SP are mostly tellurium inclusions, precipitates and voids. IR microscopy cannot distinguish between inclusions and voids. Other techniques such as TEM could possibly distinguish them. Only those measuring >1 μm were considered for our study. Depth of field (DOF) method was used to take the image of each SP. In the DOF method, a microscope's focal plane is moved through the depth of the crystal. DOF applies an automated scheme to capture a picture in *Z*-direction from the first plane and then move into the crystal to capture the next picture in the second plane. After the microscope's focus has moved the entire depth of the crystal, it compiles all "in focus" planes into a single picture. Next, the position of the camera shifts to a new *xy* coordinate and the process is repeated until the entire CZT piece has been examined. Then the DOF images of entire crystal are tiled together to comprise a complete view of all SP in the crystal. Image Pro software was used to count the dark SP in the tiled image and it reports selected parameters such as mean diameter, area, roundness and aspect ratio of the SP. In the analysis, objects are removed which are not SP by the software. These objects can be dark objects such as surface defects or a scratch-like artifact. Data are exported to Origin software and the vol.% and density of the SP can be calculated (estimated) based on mean spherical SP diameter. The mean diameters are calculated by approximating the inclusions to spherical shapes and then taking the statistical mean over the range of the distribution of diameters.

For this study, a radial slice towards the first to freeze section of the ingot and a vertical slice were cut and IR mapped to study the distribution of SPs in both axial and radial directions.

2.3. Low-temperature photoluminescence measurement

Low-temperature PL experiments were carried out at 7 K and above using a closed cycle helium cryostat. The 488 nm line of argon-ion laser was used as the excitation source. The PL spectra were collected with a SPEX 1877D Triplemate spectrometer. A liquid nitrogen cooled charge-coupled device camera was used to detect the luminescence spectra.

2.4. Sample preparation and measurement

The ingot was cut into slices using a diamond wire saw. The surface preparation steps for IR microscopy involved mechanical polishing with 1 μm de-agglomerate alumina paste followed by surface cleaning with ammonium hydroxide water solution with a pH value of 10 and a final light chemical etching with 0.5% bromine methanol solution for 10 s. For *I–V* measurements, $10\times10\times2$ mm^3 samples were cut from slices cut next to the ones shown in Fig. 1 and prepared the same way as described for IR measurements. Gold chloride contacts were deposited on both 10×10 mm^2 faces of the samples. Current voltage characteristics were obtained by the two probe measurement technique.

The regions selected for IR mapping are marked as square shapes on the slices as shown in Fig. 1. Each of these mapped regions was ~7.5×7.5 mm^2 in area. Some of these regions contained grain boundaries and twins.

3. Results and discussion

3.1. Secondary phases (SP)

Analysis of infrared microscopy results from different single crystal regions of the ingot indicated absence of SP >1 μm. Regions near the first to freeze section of the ingot were seen to be completely free of any type of SP. However at regions of grain boundaries there were inclusions with sizes close to 1 μm even at the first to freeze sections. The IR images of a grain boundary at region 1 of the radial slice and a completely single crystal region 2 are shown in Fig. 2. For better view a section of the single crystal micrograph is magnified. It is observed that the grain boundary is decorated with inclusions whereas the regions in the immediate vicinity of the boundary were free of any type of SP.

Similarly, in the axial SP distribution shown in Fig. 3, it was observed that the single crystal regions were free of tellurium inclusions >1 μm. In region 2, the inclusions were observed to decorate the twin boundary. We have also observed star shaped secondary phase defects even in the single crystalline regions,

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