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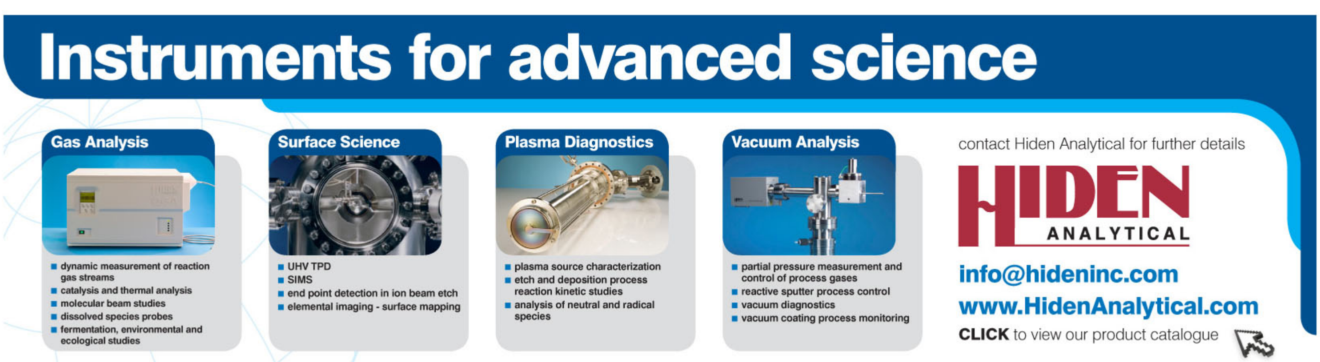

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Growth of Bi doped cadmium zinc telluride single crystals by Bridgman oscillation method and its structural, optical, and electrical analyses

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The II-VI compound semiconductor cadmium zinc telluride (CZT) is very useful for room temperature radiation detection applications. In the present research, we have successfully grown Bi doped CZT single crystals with two different zinc concentrations (8 and 14 at. %) by the Bridgman oscillation method, in which one experiment has been carried out with a platinum (Pt) tube as the ampoule support. Pt also acts as a cold finger and reduces the growth velocity and enhances crystalline perfection. The grown single crystals have been studied with different analysis methods. The stoichiometry was confirmed by energy dispersive by x-ray and inductively coupled plasma mass spectroscopy analyses and it was found there is no incorporation of impurities in the grown crystal. The presence of Cd and Te vacancies was determined by cathodoluminescence studies. Electrical properties were assessed by I-V analysis and indicated higher resistive value (8.53×10^8 Ω cm) for the crystal grown with higher zinc concentration (with Cd excess) compare to the other (3.71×10^5 Ω cm). © *2010 American Institute of Physics*. [doi:10.1063/1.3275054]

I. INTRODUCTION

For the past few years, cadmium zinc telluride semiconductor compounds [$Cd_{1-x}Zn_xTe$ (CZT)] have gained attention due to numerous applications in the area of medical imaging, radiation sensors, photorefractive, etc.[1–3] Due to its relatively wide band gap energy, CZT can operate even at room temperature and does not require cryogenic cooling as required for Si/Ge based detectors. The title compound has both high density and high atomic number and might be useful for stopping high-energy radioactive sources and has a large cross section for photoelectric interactions.[4,5] Te precipitates are one of principal defects that form during cooling of melt-grown CdTe or CZT crystals when grown Te-rich.[6] Zhang *et al.*[7] reported that CZT wafers grown under Te-rich conditions contain large-size Te precipitates with density of high-10^3–low-10^4 cm^{-2} and IR transmission less than 60%. Yang *et al.*[8] quoted that the impurity gettering in Te inclusions originated from the diffusion mechanism during crystal growth and segregation mechanism during crystal cooling.

The performance of gamma and x-ray detectors mainly depends on the high resistive CZT materials, which limits the surface leakage currents. Several measurements have been carried out in order to determine its optimal zinc concentration; however, dopant concentration seems to be necessary in order to compensate for residual impurities and also to obtain high resistivity materials. Earlier report shows the incorporation of Bi as a dopant in CdTe single crystal enhanced its resistivity.[9] By keeping the surface leakage current in mind, in the present communication we are reporting high resistive Bi doped cadmium zinc telluride single crystals with two different zinc concentrations, viz., 14 at. % (CZT1) and 8 at. % (CZT2), respectively. The crystals were grown by Bridgman oscillation (BRO) method with and without platinum support. In the BRO method, the furnace has been oscillated in clock and anticlockwise direction about 15° during 30 min at a superheating temperature of 15 °C before starting the crystal growth process. During this operation, the material is getting homogenized mixing and smashing down the tellurium inclusions, respectively, as an important step for the production of large grain size in CZT bulk crystals.[10,11] The cut and polished grown ingot was subjected to different characterization analyses in order to know its suitability for device fabrications.

II. EXPERIMENTAL

A. Crystal growth

The title compound has been grown by BRO method by optimizing its growth conditions. In this experiment, Bi has been taken as the dopant (1×10^{19} at/cm^3) and the CZT crystal have been grown in two different zinc concentrations (14 and 8 at. %) namely CZT1 and CZT2, respectively. It is worth noting that the growth experiment of CZT1 has been carried out with a platinum tube as the ampoule support, which is also acts as a cold finger. It also enhances the crystalline quality of the grown crystals. The commercially purchased high purity (6*N*) raw materials (Cd, Zn, Te Pure Metals, and Bi Alfa Aesar) were used as the charge materials for the present crystal growth. Before starting the growth process, the ampoule has to be cleaned and graphitized as per the procedure reported.[11] Then, the raw materials were charged into the quartz ampoule and evacuated. After attaining the required vacuum, the ampoule was sealed using a

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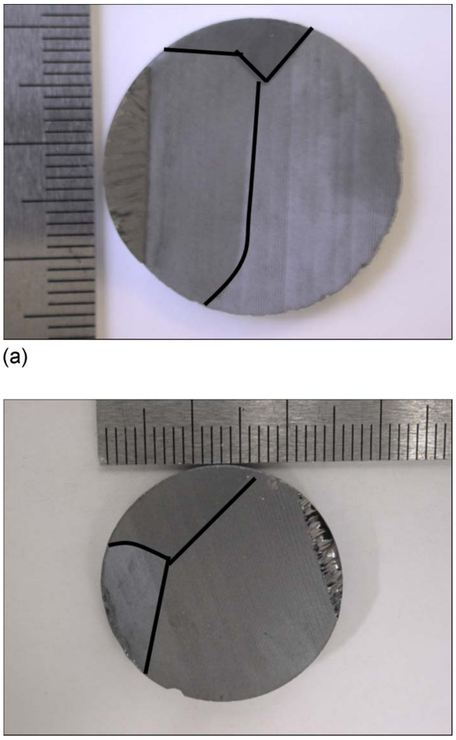

FIG. 1. (Color online) As grown single crystal of Bi doped CZT (a) 14 at. % Zn and (b) 8 at. % Zn.

glass rod. Then, the ampoule was circularly covered by eleven thermocouples in order to control its temperature precisely. The temperature was monitored and recorded with PICOLOG software. Then the whole ampoule setup was carefully kept in the center of the Bridgman furnace. The furnace temperature was carefully controlled by a Eurotherm controller with an accuracy of ±0.1 °C.

In the current experiments, a growth rate of 0.4 mm/h has been adopted and two different temperature gradients [4.5 °C/cm for CZT1 (with Pt tube) and 6 °C/cm for CZT2 (without Pt tube)] were employed following the cool down velocity of 5 °C/h. The platinum tube, which is used for the ampoule support, has the same dimension of the quartz ampoule. The bottom portion of the CZT ampoule is in touch with the Pt tube support. It is acting as a cold finger and it will transport the heat from the crystallized materials to the cold part of the Pt tube. The details were given in our earlier report.[11] After a time span of 3–4 weeks, good quality single crystals of 27 mm in diameter and 90 mm in length have been harvested [Figs. 1(a) and 1(b)]. The wafers of 2–3 mm thickness were cut from the grown ingot and the samples were lapped and polished with alumina powders. Then, the crystals were etched with Br_2-Methanol solution (2%, 2 min). Immediately after the etching, gold contacts were made by vapor thermal deposition on both sides of the samples by following the Au contacts in order to analyze the grown crystal characteristics for possible detector applications.

B. Characterization

The presence of Bi and other possible impurity concentrations have been analyzed by using inductively coupled plasma mass spectroscopy (ICP-MS) with ELAN-6000 (PE-Sciex) mass spectrometer. Cathodoluminescence (CL) measurements were carried out by Leica 440 scanning electron microscopy (SEM) and Hitachi 2500 SEM equipped with R5509 Hamamatsu photomultiplier tube at liquid nitrogen temperature with the electron beam energy of 20 kV. The presence of stoichiometric composition has been found from energy dispersive by x-ray (EDX) analyses using a Leica 440 SEM equipped with a Bruker AXS QUANTAX system. The resistivity of the grown ingot was determinated from the current-voltage (I-V) measurements using a Keithley electrometer (Model 6514) and ET NHQ 105L DC high voltage power supply.

TABLE I. Chemical compositions by EDX.

CdZnTe:Bi	[Zn] (at. %)	[Bi] (at. %)
Set of CZT1 samples	14	0.7–0.8
Set of CZT2 samples	7–8	0.7–0.8

III. RESULTS AND DISCUSSIONS

The chemical composition of the grown ingots was examined by EDX at room temperature. The observed results were tabulated (Table I). The measurement confirms the presence of Bi and zinc compounds and no other foreign impurities were presented other than those tabulated. This confirms the purity of the CZT ingots, which were grown by BRO method. The ICP-MS measurement (Zn, Cd, and Te the resolution limits are ppt range) shows similar results, which is supportive evidence of the stoichiometric compositions. There are no remarkable changes in the observed results for the CZT1 and CZT2 crystals.

CL is a technique which is used to detect the defects in solids/single crystals. In a present experiment the cut and polished crystal was subjected to CL analysis with electron beam energy of 20 keV. The recorded spectrum is shown in Figs. 2(a) and 2(b). CL spectra of CZT1 shows only emission and that is related to band gap transition. No other emissions were observed, indicating that concentration of vacancies of Cd and Te (which are responsible of A-band and 1.1 eV band, respectively) have been reduced significantly. On the other hand, the crystal 2 (CZT2) shows a very intense band centered at 1.1 eV. This band is related to Te vacancies.[12] Moreover, another band centered at 0.8 eV is observed and it is comparable in intensity to 1.1 eV band. The nature of this band is related to Cd vacancies. The origin of A-band is related to Cd vacancies too, but it is well known in samples doped with Bi this A-band is not present.[13] It is clearly understood that the dopant Bi occupies Te and Cd positions in the CZT host lattice, thus increasing the Te aggregate concentration. These Te aggregates decrease the resistivity and recent studies have shown that Te precipitates[14] affect the device performance with regard to radiation detection. In the samples, which have been presented in this work, have a concentration of Te precipitates between 30% and 40%, with a size between 1 and 3 μm.

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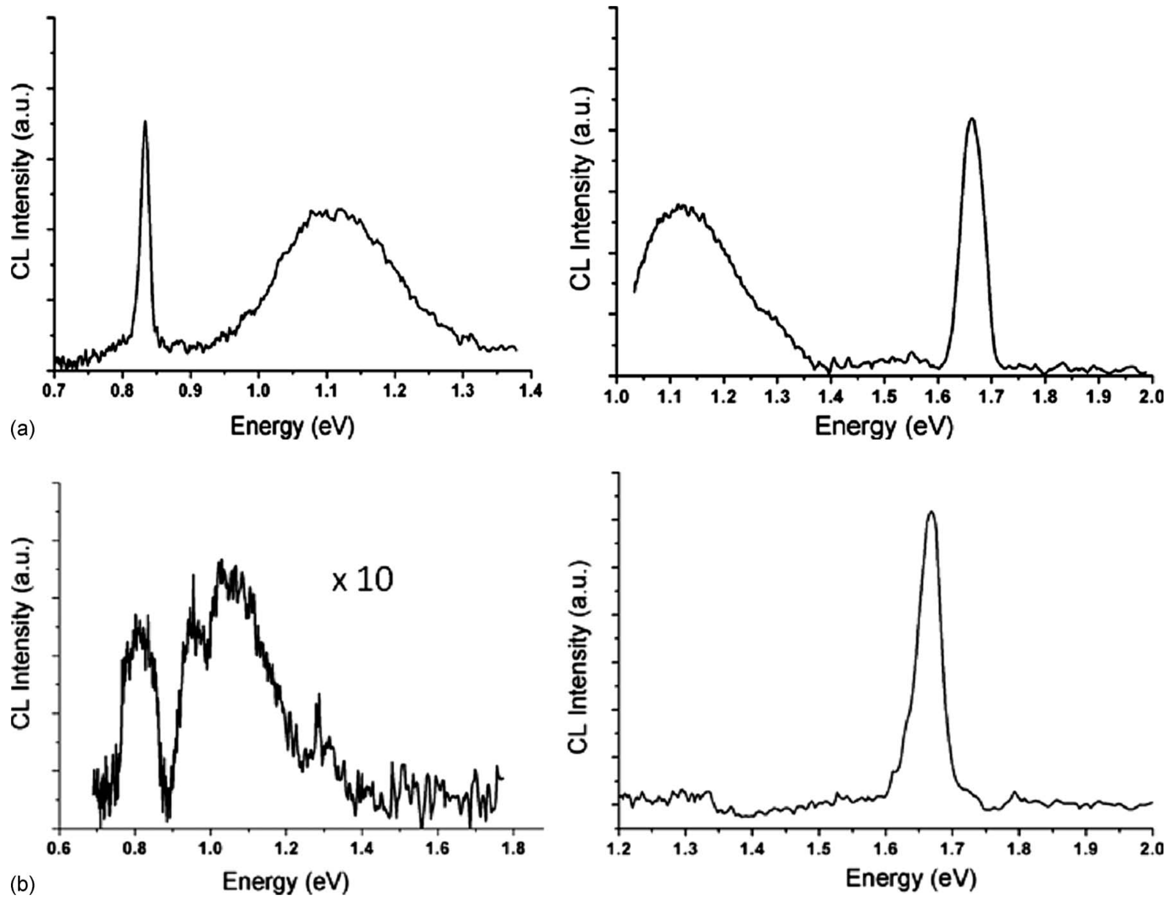

FIG. 2. (a) CL spectra of set CZT1 (high resistivity) at 77 K. (b) CL spectra of set CZT2 (low resistivity) at 77 K.

The electrical characterization measurements were carried out for both crystals, which were grown with and without Bi as dopants. A typical I-V curve of CZT1 sample is shown in Fig. 3. The applied voltage for the present measurement is between −500 and 500 V and the recorded I-V curve agrees well with Ohm's law and thus can be used to calculate the resistivity of the single crystals. But at the same time the CZT2 crystal does not show the higher resistivity, which might be due to tellurium segregation during growth that reduces the resistivity of the crystals. The calculated resistivity for CZT1 and CZT2 were 8.53×10^{8} and 3.71×10^{5} Ω cm, respectively. It was obvious that the Cd excess in the CZT1 growth and the different zinc composition well compensated by Cd vacancies that decrease the free-carrier concentration and, therefore, increase the resistivity of the crystals. Excess Cd leads to poor crystals in terms of radiation detection because it generates too much change in conductivity, producing material that has less semi-insulating properties.

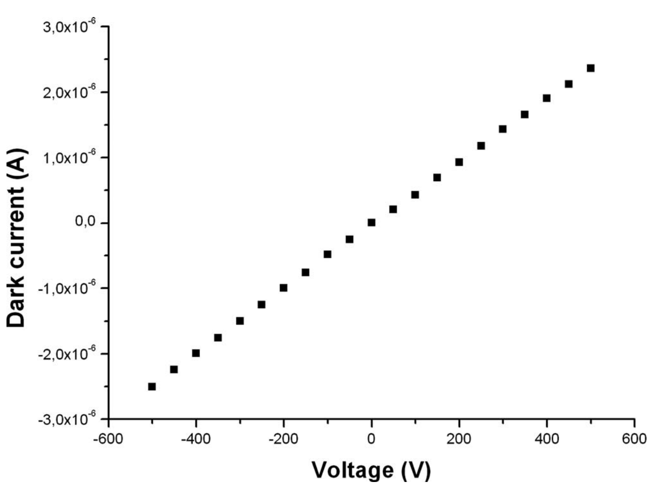

FIG. 3. I-V curve for set of CZT1 samples at room temperature.

IV. CONCLUSIONS

The II-VI compound semiconductor material of Bi doped CZT has been grown with two different zinc concentrations by BRO method by optimizing its growth conditions. The grown single crystals were characterized by different characterization analyses in order to determine its suitability for device fabrication. The EDX and ICP measurements show the stoichiometric composition of the compounds (Cd, Zn, and Te) with the calculated amount of bismuth. The CL measurement indicates the concentration of vacancies of Cd and Te (which are responsible of A-band and 1.1 eV band, respectively) have been reduced significantly. The higher zinc concentration with Cd excess shows high resistivity value in comparison with the lower Zinc concentration. It is also concluded that Cd vacancies decrease the free-carrier concentration.

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