Microstructural Characterization of CdZnTe(CZT) Crystal Ingot Grown by Bridgman Method at KAERI

Kyuhong Lee [a], Han Soo Kim [a], Jang Ho Ha [a,*], Young Soo Kim [a], and Hyo Jeong Choi [a, b]
[a]*Korea Atomic Energy Research Institute, Daedeok-daero 989-111, Daejeon, Republic of Korea*
[b]*WCU Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea*
[*]*Corresponding author: jhha@kaeri.re.kr*

1. Introduction

$Cd_{1-x}Zn_xTe$ crystal is an important wide band-gap II-VI compound semiconductor which is one of the most attractive radiation materials for room temperature detector, especially for gamma rays [1]. However, the electrical and radiation detection properties of CZT crystal vary widely. They have been attributed to several metallurgical defects such as dislocation, grain- and twin-boundary, Cd vacancy, and secondary phase (Te inclusion and precipitation, etc.) [2]. They act as trapping sites of carriers, and significantly degrade the detector's performance. To reduce these defects, doping elements such as Indium is applied [3]. That method compensates Cd vacancies.

In this study, 1 inch-diameter In-doped CdZnTe ingots were grown by Vertical Bridgman Method. We conducted several microstructural analyses such as X-ray diffraction, edge-pit density (EPD), and ICP-MS analysis.

2. Methods and Results

2.1. Crystal Growth and Machining

We have grown 1-inch diameter CdZnTe ingots doped with 5 ppm and 7 ppm Indium using vertical Bridgman furnace which is designed by KAERI (fig. 1). After carrying out the cleaning process of the quartz ampoules, the compound of Cd, Zn, and Te (6N purity) were introduced into the carbon coated ampoule with indium. And then, the vacuuming and sealing of ampoule followed by the growth process at a rate 0.8 mm/h.

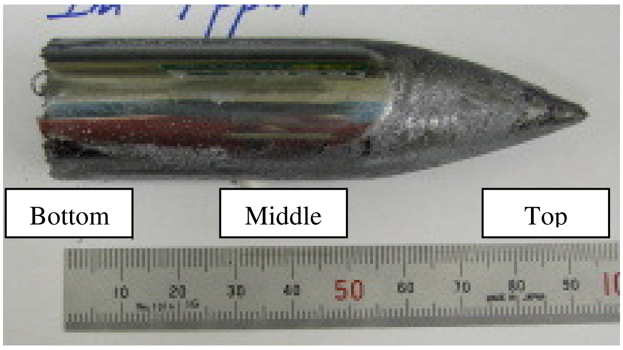

Fig.1. A Photography of a 1 inch diameter CdZnTe crystal ingot doped with 7 ppm In.

CdZnTe ingots were cut into 10 mm thick cylindrical shapes perpendicular to the axial direction and etched by a solution 20 ml H_2O, 15 ml HNO_3, 5 ml HF, and 0.4 g $AgNO_3$ to reveal the grain- and twin-boundaries. For x-ray diffraction analysis and EPD test, the thick etched wafers were cut in the size 10 x 10 x 5 mm^3 along twin boundaries. Twinning planes are lying exclusively in CZT {111} planes [4].

2.2. ICP-MS analysis

We analyzed chemical composition of three CdZnTe ingots having different doping concentration, CZT(no doping), CZT5IN(5 ppm In), and CZT7IN(7ppm In) at the position of top, middle, and bottom as indicated fig. 1 by ICP-MS. The results are given in Table I.

Table I. Chemical analysis of CZT(no doping), CZT5IN (doping with 5 ppm In) and CZT7IN (doping with 7 ppm In) by ICP -MS

Specimen		**Cd**	**Zn** (wt.%)	**Te**	**In** (ppm)
CZT	top	42.1	3.9	54.1	n/a
	middle	42.4	3.7	54.0	n/a
	bottom	41.4	4.4	54.0	n/a
CZT5IN	top	44.8	2.2	53.5	63.6
	middle	44.6	3.0	53.5	5.3
	bottom	44.9	2.6	52.3	14.9
CZT7IN	top	44.0	3.4	52.8	101.9
	middle	44.3	3.0	51.9	7.7
	bottom	46.9	2.2	51.3	13.5

The results show that during the growth process, Te-rich melt was formed due to Cd evaporation. Also, in the middle part of ingots the concentration of doped Indium was well controlled. In CZT crystal, 1~2 wt.% Te-rich melt leads to obtain high resistivity because Te_{Cd} acts as a deep donor in the middle of the band gap [5]. At the same time, Te-rich melt also give rise to a larger concentration of Te inclusions and precipitates.

2.3. X-ray diffraction analysis

We have conducted a crystallographic analysis using X-ray diffraction (XRD). The surface which was investigated by X-ray was parallel to the twin boundary and grinded with 4000 grid SiC paper. Fig. 2 shows the

XRD results of three different specimens from the middle parts of ingots.

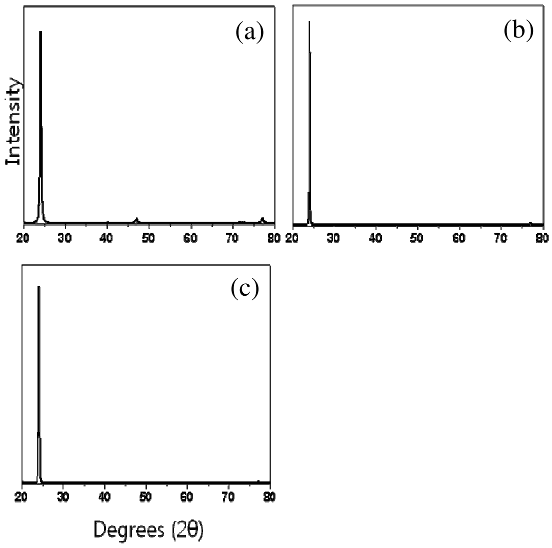

Fig. 2. X-ray diffraction patterns of the specimens from the middle part of (a) CZT, (b) CZT5IN, and (c) CZT7IN

The results show that the CZT ingots well grew. In addition, the cut specimens well obtained within single grain and were aligned along [111] direction regardless of doping concentration. For analysis of crystalline quality, the high resolution X-ray diffraction (HRXRD) can be applied.

2.4. Edge-Pit Densities

One of the main defects of CZT is a dislocation. The density of dislocation in a given material is calculated by measurement of the corresponding etch pit density with chemical etching. Etch-pit density was investigated on (111) planes. The mechanically polished specimens were immerged at Nakagawa solution (30 ml HF, 20 ml H_2O_2, 20 ml H_2O) for 1 minutes. The results of average EPDs were given in Table II.

Table II. Average etch-pit densities

Specimen	**Average EPD per cm^{-2}**
CZT	4.3×10^3
CZT5IN	7.6×10^3
CZT7IN	4.7×10^3

Average EPDs were 4.3×10^3, 7.6×10^3, and 4.7×10^3 in doping concentration order. Usually, EPD range of suitable CZT crystals for radiation detector is $10^3 \sim 10^4$ cm^{-2}. Therefore, the grown crystals are qualitative enough for radiation detector.

3. Conclusion

We have successfully grown the In-doped CZT crystal ingots which have 25 mm diameter using vertical Bridgman furnace designed at KAERI. From the results of XRD and EPD tests, we have concluded that the grown CZT ingots have good crystal qualities. Also, indium doping concentrations have not affected the crystal qualities as for microstructural properties. These findings suggested that our designed furnace is suitable for growing high quality CZT crystals for fabricating radiation detectors. Further research on the physical and radiation properties of the grown crystals will be conducted in another study.

ACKNOWLEDGMENT

This work has been carried out under the R&D program of the MEST (Ministry of Education and Science Technology)

REFERENCES

[1] R.B. James, T.E. Schlesinger, J.C. Lund, and M. Schieber, in: R.B. James, T.E. Schlesinger (Eds.), Semiconductors for Room Temperature Nuclear Detector Applications, vol. 43, Academic Press, New York, p. 334, 1995.

[2] C. Szeles, S.E. Cameron, J.O. Ndap, and W. Chalmers, Advances in the crystal growth of semi-insulating CdZnTe for radiation detector applications. IEEE Trans. Nucl. Sci., Vol.49, pp. 2535-40, 2002.

[3] V. Babentsov, J. Franc, A. Fauler, M. Fiederle, and R.B. James, Distribution of zinc, resistivity, and photosensitivity in a vertical Bridgman grown $Cd_{1-x}Zn_xTe$ ingot, Journal of Crystal Growth, Vol. 310, pp. 3482-87, 2008.

[4] G. Li, S.J. Shih, Y. Huang, T. Wang, and W. Jie, Nanostructures of defects in CdZnTe single crystals. Journal of Crystal Growth, Vol. 311, pp.85-89, 2008.

[5] X. Zhang, Z. Zhao, P. Zhang, R. Ji, and Q. Li, Comparison of CdZnTe crystals grown by the Bridgman method under Te-rich and Te-stoichiometric conditions and the annealing effects. Journal of Crystal Growth, Vol. 311, pp.286-91, 2009.