Overcoming Zn Segregation in CdZnTe with the Temperature Gradient Annealing

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Abstract

The availability of large volume crystals with the same energy gap in melt-grown CdZnTe(CZT) is restricted due to the Zn segregation in CdTe hosts. We observed the migration of Zn in the solid phase along the positive temperature gradient direction both *in-situ* and post-growth temperature gradient annealing (TGA) of CZT. Diffusivity of Zn obtained from the *in-situ* TGA was approximately 10^{-5} (cm²/s) order and completely different mechanism with that of post-growth. The CZT ingots obtained through *in-situ* TGA have uniform Zn and resistivity of $10^{10}\Omega\cdot\text{cm}$ orders. The CZT detectors fabricated from *in-situ* TGA applied ingots exhibit 10 % of energy resolution for 59.5 keV peak of ²⁴¹Am.

Keywords: A1. Segregation, A2. Bridgman technique, B1. Cadmium compounds, B2. Semiconducting II-VI materials

1. Introduction

CdZnTe (CZT) is the leading candidate material for large-volume room temperature X- and gamma-ray detectors. The energy resolution and uniformity

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of CZT detectors have been considerably improved during the past 10 years, prompted by advances in crystal growth and material purification technologies. In addition, the available volumes of commercial detectors gradually increased from a few cubic millimeters to a few cubic centimeters [1].

The segregation coefficient (k) is defined as the ratio of impurity (or elements) concentration in the solid phase to that of in the liquid phase, and it is an important physical property of a material under study [2, 3]. It affects the doping profile and the ingot uniformity of materials grown from the melt [4]. Generally accepted segregation coefficient of Zn in a CdTe host is 1.3 although its values can vary from 1.05 to 1.6 depending on the growth method and the Zn content [1, 4, 5, 6, 7, 8, 9].

The reported segregation coefficient of Zn is of higher unity so that Zn composition in CZT ingots decreases from the first-to-freeze part to the last-to-freeze part. The Zn non-uniformity on gamma-ray spectrometers would be a major obstacle to achieving statistically limited energy resolution in CZT detectors [10]. However, M. Azoulay *et al.* achieved a more uniform Zn distribution by using Cd/Zn reservoir by a modified vertical gradient freeze method [6]. They used a Cd/Zn reservoir to replenish Zn effectively to the melt through the vapor phase. With issues of non-uniformity results from Zn, researchers have begun to pursue use of new materials such as CdMnTe(CMT)[11] which have high yields and allow use in a large volume single detector with the relatively small diameter ingot.

We have reported preliminary results on an anomalous Zn segregation in CdTe in a previous publication [12]. During the crystal growth process by the vertical Bridgman method, a CZT ingot remained at 700-800 °C for a week within the temperature gradient field of 10 °C/cm owing to the moving system's failure. For

this ingot, we observed an unusual Zn distribution where the segregation behavior of Zn in CdTe looked like to be a less than 1, as shown in Fig. 1(a). This indicated that segregation of certain elements might be resolved by diffusion within the solid phase. Based on this observation, we tried to overcome the Zn segregation in CdTe by using *in-situ* and post-growth temperature gradient annealing (TGA).

2. Experiment

CZT detectors were grown by the Bridgman method from a melt mixture of CdTe(6N), ZnTe(6N), and 2-5 atomic percent of excess Te and 3-10 ppm of indium. The resistivity of these detectors was $0.8\text{-}5 \times 10^{10} \text{ } \Omega\text{cm}$ of resistivity, and their electron mobility-lifetime product was $0.9\text{-}5 \times 10^{-3} \text{ cm}^2/\text{V}$. A typical growth rate and an interface temperature gradient were 6 mm/day and 10-15 °C/cm, respectively. During the cooling process, we intentionally applied *in-situ* TGA on CZT ingots in order to reproduce Zn diffusion within the solid phase. The *in-situ* TGA condition was 850 °C for 32 h with the temperature gradient of 10 °C/cm.

The "as-grown" ingots were sliced parallel to their growth direction and then finished by fine mechanical polishing to avoid potential stoichiometric changes that may occur after chemical etching. The typical CZT slabs were 1-in. wide, 3-4 in. long, and 3-mm thick. The Zn composition in CZT ingots was measured by using electron probe micro-analysis(EPMA). The measurements by EPMA cannot provide an accurate Zn composition such as ppm level reading but their accuracy is good enough to provide a Zn profile along the CZT slab.

To demonstrate that the thermo-migration of Zn is a common feature of CZT materials, we repeated similar post-growth annealing experiments by using smaller CZT samples ($5 \times 5 \times 2 \text{ mm}^3$) cut from the conventionally grown CZT wafers un-

der Cd and Te overpressure with a temperature gradient.

We performed qualitative stoichiometric analysis of the samples by using micro-X-ray fluorescence (μ -XRF) available at BNL's National Synchrotron Light Source (X-27A). This allowed for a fast and non-destructive mapping of large sample areas in fine steps. The μ -XRF instrument could trace 1 ppm elemental compositions at a spot. We used 100- μ m or 500- μ m steps depending on the sample's scanning area. The quantitative changes in stoichiometry were also estimated by photoluminescence (PL) measurements at 4 K [13].

For the pulse height measurement at room temperature, the planar CZT detector was installed in a holder and the cathode side of the detector was irradiated. The signals from the positively biased anode were measured by using a capacitively-coupled eV Products 550 preamplifier. The data acquisition system included a spectroscopic shaping amplifier and a multi-channel analyzer (MCA).

3. Results and Discussion

Fig. 1 (b) shows the μ -XRF maps for the CZT slabs cut from the ingots to which the TGA were applied during the crystal-cooling processes. The CZT slabs were mechanically polished only during the final step by using the 0.9- μ m-alumina powder. The Zn profiles in CZT slabs, to which the TGA were applied, were fairly uniform, as shown Fig. 1(b). In general, this is not a common Zn behavior for CdTe, and it indicates thermo-migration/diffusion of Zn within in the solid phase.

The Zn distribution using a classical segregation law for the directional freezing can be evaluated by the following equation:

$$C_s = C_0 k (1 - g)^{k-1} \quad (1)$$

where C_0 is the initial concentration and g is the solidified fraction. In general, Zn segregates with a coefficient of 1.3. In this case, Zn composition along the growth direction follows the classical segregation law as shown in Fig. 2 [9]. Open and closed circles in Fig. 2 represent the Zn composition obtained from the EPMA measurement for the TGA applied CZT slabs. As shown in the figure, the theoretical curve and the experimental data do not match in the segregation behaviour. The segregation coefficient of two TGA applied CZT slabs which were obtained by fitting EPMA data to classical segregation law were 0.61 and 1.01 for the slab 1 (TGA for 72 h at 750 °C) and the slab 2 (TGA for 32 h at 850 °C), respectively.

Fig. 3(a) shows a Zn profile measured for "as-grown" 1-inch-thick CZT wafers sliced perpendicularly to the growth direction. Since the Zn composition was uniform throughout the entire wafer, thus we discontinued with the μ -XRF measurements during the measurement process. Some CZT samples were sliced in the wafers with dimensions of $5 \times 5 \text{ mm}^2$ and were annealed under Cd overpressure at 700/600 °C (CdZnTe/Cd) for 72 h, with a temperature gradient of 20 °C/cm. The annealed CZT samples were mechanically polished to remove Cd contaminated layers (500- μm) prior to starting the μ -XRF measurements. By contrast, the Zn profiles of the annealed sample exhibited prominent changes that correlated with the temperature gradients vs. thermo-migration of Zn, even in a relatively small area ($1 \times 2.5 \text{ mm}^2$) as shown in Fig. 3(b). We noted the same tendency in a CZT slab cooled in presence of a temperature gradient. A similar pattern was confirmed for the CZT sample annealed under Te overpressure at 700/800 °C (CdZnTe/Te) for 72 h, with the temperature gradient of 40 °C/cm, as shown in Fig. 3(c). In Fig. 3(b), the temperature gradient was applied to the sample in the horizontal direc-

tion, while in Fig. 3(c) it was applied in the perpendicular direction. We note that the Zn variation perpendicular to the direction of temperature gradient was only minor. These TGA experiments, performed with "as-grown" ingots and small individual samples, led us to conclude that Zn concentration becomes high along the positive temperature gradient field. We again state that in the control sample annealing experiments performed at isothermal conditions, we did not observe any significant differences for Zn under either Cd- or Te-overpressure.

We quantitatively analyzed Zn migration via PL measurements. Fig. 4 shows the PL spectrum for an "as-grown" CZT sample. We observed a donor-bound ($D^\circ X$) and an acceptor-bound exciton ($A^\circ X$) around 1.659- and 1.648-eV, respectively. In addition, strong intensity of donor-acceptor pair (DAP) recombination band was apparent at 1.595 eV and disappeared after Cd annealing. The A-center peak, reflecting the complex of Cd vacancies and compensating dopant, was visible at 1.453 eV in "as-grown" samples but it also disappeared after Cd annealing. In case of Cd annealing, the Cd vacancies filled by the Cd atoms under Cd overpressure and the reduction of Cd vacancies resulted in the disappearance of the DAP and the A-center, $(V_{Cd} - In_{Cd})^-$. We calculated Zn composition from the exciton peak - before annealing it was about 9.73 %, but after annealing it decreased to 7.42 % after annealing. Zn composition was calculated by using the following relations [13]:

$$E_g(x, 4K) = 1.606 + 0.520x + 0.254x^2, \quad (2)$$

where E_g is the bandgap at 4 K and x is the Zn composition.

Considering all the experimental conditions, the only factor causing Zn migration in the CZT ingots/samples [14] was the temperature gradient. Previously, the rate of diffusion of zinc in CdTe at a negligible concentrations gradient has been

determined to be $10^{-9} \sim 10^{-10}$ cm²/s in the range of 800 to 900 °C [15, 16] . This compares favorably with the value for the self-diffusion of Cd in CdTe. The diffusion length can be estimated using following equation:

$$L_D = \sqrt{Dt} \quad (3)$$

where D is diffusivity (cm²/s) and t is time (s). The uniform Zn distribution cannot be explained only by the self-diffusion process considering the length of CZT ingots is about 7 cm. The diffusion length of Zn is 10⁻²-cm order in case of the 10⁻⁹ (cm²/s) diffusivity. To satisfy our *in-situ* annealing condition, the diffusivity should be in the order of 10⁻⁵ (cm²/s).

Aslam *et al.* reported that the addition of Cd and Te to the diffusion source did not affect the diffusivity of Zn at any temperature. Studies of Zn self-diffusion in ZnTe with ⁶⁵Zn elucidated that self-diffusion is controlled by native defects concentrations that depend only on thermal disorder, rather than on deviations from stoichiometry [15, 17]. In the post-growth TGA experiment [12], thermo-migration velocity did not show any Cd or Te pressure dependence. However, the diffusion mechanism of Zn in *in-situ* and post-growth TGA looked completely different in point view of thermo-migration velocity. In case of *in-situ* TGA, the fast diffusion dominates with diffusivity in the order of 10⁻⁵ (cm²/s). **In general, for fast diffusion involves defects in in both interstitial and substitutional sites [16]. In *in-situ* TGA, temperature gradient on the CZT ingots yield a concentration gradient of Cd vacancies and provides a pathway for Zn migration toward high concentrations of Cd vacancies for achieving chemical equilibrium. We need further investigation is required to clarify this behavior.**

The Two TGA, namely *in-situ* TGA and post growth TGA, give a notable difference in resistivity after the annealing process. The bulk resistivity of CZT

samples cut from *in-situ* TGA ingots was found to be $0.5 - 1 \times 10^{10} \Omega \cdot \text{cm}$, which is similar in value obtained from the normally cooled CZT ingots. However, the resistivity decreased to 10^3 - $10^6 \Omega \cdot \text{cm}$ after the post-growth TGA of the whole ingots or wafers regardless Te and/or Cd overpressure.

Figure 5 shows the pulse height spectrum of ^{241}Am taken with CZT detector which came from *in-situ* TGA applied CZT ingot. Full width half maximum (FWHM) of 59.5 keV is 10.06% and that is similar value to other CZT detector which did not going through the TGA.

4. Conclusion

In summary, we observed Zn migration in CZT ingots and in prepared small samples annealed under a temperature gradient. We demonstrated that Zn composition in both CZT ingots and wafers can be adjusted by using the proper thermal conditions as with the temperature and its gradient, thereby controlling the speed of Zn migration and the distribution of Zn in the material. The mechanism behind the fast diffusion with a diffusivity in order of $10^{-5} \text{ (cm}^2/\text{s)}$ order is not clear but it might be related to the defects in both interstitial and substitutional sites.

This approach described here can be used for fabrication of large-volume CZT crystals with uniform distribution of Zn that are required for highly effective large-area X- and gamma-ray detectors and for generating large-area CZT substrates for growing HgCdTe epilayers for infrared detectors. Besides for "as-grown" CZT ingots and wafers, our approach may also have impact on methods for modifying the zinc composition in and around spatially extended defects, such as high-angle grain boundaries, twins and possibly cellular networks. This new understanding is likely to have significant implications for manufacture of II-VI electronic

devices.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (NRF-2015M2B2A9032788 and NRF-2015M2A2A4A01045094) and the U.S. Department of Energy Office of Defense Nuclear Nonproliferation Research and Development, DNN R&D.

References

- [1] R. B. James, T. E. Schlesinger, J. Lund, and M. Schieber, *Semiconductors and Semimetals Vol. 43: Semiconductors for Room Temperature Nuclear Detector Applications*, (Academic Press, NY, 1995).
- [2] S. Terterian, M. Chu, and D. Ting, J. Electron. Mater. **33**, 640 (2004).
- [3] M. Schieber, T. E. Schlesinger, R. B. James, H. Hermon, H. Yoon, and M. Goorsky, J. Cryst. Growth **237-239**, 2082 (2002).
- [4] P. Capper, J. E. Harris, E. S. O’Keefe, C. L. Jones, and I. Gale, Adv. Mater. Opt. Electron. **5** (2), 101 (1995).
- [5] C. Szeles, S. E. Cameron, S. A. Soldner, J. Ndap, and M. D. Reed, J. Electron. Mater. **33**, 742 (2004).
- [6] M. Azoulay, S. Rotter, G. Gafni, R. Tenne, and M. Roth, J. Cryst. Growth **117**, 276 (1992).
- [7] P. Fougères, L. Chibani, M. Hageali, J. M. Koebel, G. Hennard, A. Zumbiehl, P. Siffert, and M. Benkaddour, J. Cryst. Growth **197**, 641 (1999).

- [8] Y. Tao, and S. Kou, J. Cryst. Growth **181**, 301 (1997).
- [9] A. Zappettini, M. Zha, L. Marchini, and D. Calestani, Cryst. Eng. Comm. **14**, 5992 (2012).
- [10] J. E. Toney, T. E. Schlesinger, and R. B. James, IEEE Trans. Nucl. Sci. **45**(1), 105 (1998).
- [11] K. H. Kim, Chansun Park, Pilsu Kim, Shinhaeng Cho *et al*, J. Korean. Phys. Soc. **66** (11), 1761 (2015).
- [12] K. H. Kim, A. E. Bolotnikov, G. S. Camarda *et al*, IEEE Trans. Nucl. Sci. **59** (4), 1510 (2012).
- [13] J. Franc, P. Hlidek, P. Moravec, E. Belas, P. Hoschl, L. Turjanska, and R. Varghova, Semicond. Sci. Technol **15**, 561 (2000).
- [14] A. Zappettini, L. Marchini, M. Zha, G. Piacentini, N. Zambelli, G. Benassi, and D. Calestani, Cryst. Eng. Comm. **15**, 2227 (2013).
- [15] N. Aslam, E. D. Jones, T. C. Q. Noakers, J. B. Mullin, and A. F. W. Willoughby, J. Cryst. Growth **117**, 249 (1992).
- [16] E. D. Jones, J. C. Clark, J. B. Mullin, and A. W. Brinkman, J. Cryst. Growth **138**, 274 (1994).
- [17] R. A. Raynolds and D. A. Stevenson, J. Phys. Chem. Solids **30**, 139 (1969).

Figure 1: μ -XRF images of CZT slabs ($22 \times 60 \text{ mm}^2$) exhibiting abnormal and uniform Zn distributions after *in-situ* TGA applied for (a) 72 h at 750°C and (b) 32 h at 850°C with the temperature gradient of $10^\circ\text{C}/\text{cm}$. The CZT slab annealed 72 h at 750°C exhibited an abnormally low Zn concentration in the first-to-freeze parts and high Zn concentrations in the last-to-freeze parts. However, the slab that was annealed *in-situ* for 32 h 850°C exhibited relatively uniform distribution of Zn. The color bar on the bottom indicates the counts of 12 keV Zn K_{α} signals. The streak that appears in the image is an artifact, arising from beam injection at the National Synchrotron Light Source(NSLS).

Figure 2: The Zn distribution along the growth direction after *in-situ* TGA applied for 72 h at 750 °C (closed circle) and for 32 h at 850 °C (open circle) with the temperature gradient of 10 °C/cm. The solid line indicates classical Zn distribution with segregation coefficient (k) of 1.3.

Figure 3: Distribution of Zn in (a) 1-in.-diameter wafer and (b) CZT samples that were temperature-gradient (ΔT) annealed at 700/600 °C (CdZnTe/Cd) with $\Delta T = 20$ °C/cm for 72 h under Cd overpressure and (c) samples that were annealed at 700/800 °C (CdZnTe/Te) with $\Delta T = 40$ °C/cm for 72 h under Te overpressure. The temperature gradients were applied to the horizontal in (b) and vertical in (c) each image. In both images, the Zn signal increased in the direction of the positive temperature gradient.

Figure 4: PL spectra of (a) the "as-grown" CZT sample and (b) the CZT sample annealed at 700/600 °C (CdZnTe/Cd) for 72 h under Cd overpressure with TGA of 40 °C/cm. Red-shift of exciton peak can be observed clearly owing to the migration of Zn.

Figure 5: Pulse height spectrum of ^{241}Am obtained by using a planar CZT detector at 300 K with 250 V. The CZT detector fabricated using *in-situ* TGA applied CZT ingot for 32 h at 850 °C. The shaping time was 1 μs . The 59.5 peak is asymmetric due to the hole tailing.