Improvement of charge collection efficiency of the CdZnTe detectors by decreasing the Te inclusions

Hyojeong Choi¹, Jeong Min Park²,* and Jong-Seo Chai¹,*

¹ Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon-Si, Gyeonggi-do, 16419, Republic of Korea
² Korea Atomic Energy Research Institute, 29, Geumgu-gil, Jeongeup-si, Jeollabuk-do, 56212, Republic of Korea
* Authors to whom any correspondence should be addressed.
E-mail: jmp1024@kaeri.re.kr and jschai@skku.edu

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Abstract
CdZnTe is a promising material for room-temperature radiation semiconductor detectors. However, their radiation response performance might be deteriorated owing to defects within the material such as Te inclusions. This study employs the Cd thermal annealing process to reduce the size of these Te inclusions. An ampoule containing Cd powder and CdZnTe was sealed under the vacuum conditions of 2.5 × 10⁻⁵ Torr for Cd-vapor annealing. Subsequently, the ampoule was annealed at 783 K for 64 h. An IR camera was used to observe the distribution of Te inclusions in the CdZnTe before and after annealing. As a second experiment, NH₄F + H₂O₂ passivation was performed to suppress the increased leakage current due to Cd-vapor annealing. Then an ²⁴¹Am radioisotope source was used to obtain a radiation response spectrum. The improved charge collection efficiency was about 35%.

1. Introduction

Thus far, many studies have been conducted on CdZnTe (CZT), which is a material used for the fabrication of nuclear radiation detectors. Its high atomic number enables a strong response under X-/gamma-ray, its wide band-gap enables the use of room-temperature radiation detectors, and its fast electron transport ability enables excellent energy resolutions [1, 2]. However, Te inclusions, which are a major defect that occur during the Bridgman growth process, deteriorate the X- and gamma-ray properties and reduce the energy resolution of CZT [3]. CZT is grown using a Bridgman furnace with excess Te to achieve high resistance; under this process, however Te inclusions are introduced throughout the CZT ingots [4–6]. As a solution, this work presents a novel method to remove or reduce Te inclusions and improve the properties of CZT via thermal annealing of the grown CZT.

Thermal annealing is typically performed under Cd-vapor to remove Te inclusions [7]. Under this method, Cd-ions interact with the Te inclusions to eliminate or reduce them. When CZT is annealed at high temperatures under a Cd-vapor atmosphere, the Cd particles are diffused into the sample and react with the excess Te, such as the Te inclusions and Te precipitates. Hence, the Te-rich particles are replaced with the crystalline material [8–11]. Furthermore, the resistivity of CZT decreases with an increase in the dislocations. Yang et al [12] conducted thermal annealing under Zn-vapor after Cd-vapor annealing to determine the specific resistivity of CZT. Egarieewa et al [10] analyzed the thermal annealing conditions required to remove and reduce Te inclusions; they reported that long-term thermal annealing at a low temperature of 783 K is more effective in reducing thermal stresses and irregular Cd inclusions than short-term thermal annealing at a high temperature of ~1,170 K.

Many existing studies have attempted to reduce the Te inclusions in CZT using Cd-vapor annealing. Although Te inclusions are reduced via Cd-vapor annealing, the resulting CZT does not function as a radiation detector owing to a decrease in its resistivity. In this study, we performed Cd-vapor annealing after passivation and compared the obtained results with those for a Cd-annealed sample. Cd-vapor annealing was performed at a low temperature of 783 K, and the distribution of Te inclusions and resistivity of the sample before and after
annealing were compared. Notably, gamma-ray response spectra were not measured after Cd-vapor annealing owing to the high leakage current, as reported by Yang et al. [12]; hence, another sample was passivated using the NH4F + H2O2 solution, and Cd-vapor annealing was performed for this sample under the same conditions [13]. The gamma-ray response spectrum and a peak shift of 59.5 keV (241Am) were observed before and after passivation and Cd-vapor annealing. The charge collection efficiency (CCE) was improved after passivation and Cd-vapor annealing [14]. The variations in the Te inclusions within the CZT sample and the changes in the CCE of the passivated sample, caused by Cd-vapor annealing, are presented herein.

2. Experimental methods

2.1. Crystal growth

A Cd0.9Zn0.1Te:In (7 ppm) ingot with diameter of 1-in was grown using the 6-zone vertical Bridgman method. High-purity CZT (99.9999%) and 4.59 × 1018 of In were placed in a quartz ampoule with an inner diameter of 1-in, which was coated with carbon to prevent interactions between CZT and the quartz ampule. All handling before crystal growth were performed in an argon-purged glove box to avoid impurities. Subsequently, the quartz ampoule was sealed in a vacuum below 10−5 Torr. The quartz ampoule was placed in a 6-zone vertical Bridgman furnace for crystal growth. The thermal gradient of the furnace was 12 °C/cm, and the length of the grown CZT ingot was 8 cm. Figure 1 shows the image of the grown 1-in CZT ingot, obtained at the Korea Atomic Energy Research Institute (KAERI).

Because of the temperature gradient in the vertical or horizontal directions of the Bridgman growth furnace, the tendency of Te inclusions may be different depending on their locations in one ingot. The samples were prepared and used from wafers obtained at the same location from two ingots grown under identical conditions to identify the Te inclusion. The exact vertical position of the sample from the ingot growth start direction (tapered part) was 8 mm. It was then sliced into a wafer with a thickness of 6 mm; the third wafer was used in this study. Precipitate can be broadly divided into inclusions, occlusions, and surface adsorbate, which were observed using an IR camera. Here, we considered the Te inclusions. The distribution was clearly distinct from the inclusions. The samples were obtained from the third wafer and analyzed considering Te inclusions [15]. The samples were named as ARDISCZT0301A and ARDISCZT0101PA, as shown in table 1.

2.2. Sample preparation

The grown ingot was sliced into a wafer using a diamond wire saw and then diced into a cube to fabricate a radiation detector. The diced CZT samples were polished using 800, 2,500, and 4,000 grit SiC papers, and then further polished using alumina powder with sizes 1, 0.3, and 0.05 μm. Dimensions of the fabricated sample were 4 mm × 4 mm × 1.17 mm.

First, Te inclusions in the sample along the Z-axis were measured using a NIKON ECLIPS LVdia-N IR camera. Au electrodes were deposited on the upper and lower portions of the sample to measure the electrical properties. Figure 2 depicts the electrical properties before post-processing. The leakage current in the I-V spectrum was measured using the Keithley 4200 semiconductor characterization system at an input voltage ranging from −200 to 200 V.

2.3. Post processing

Previous studies have shown that Te inclusions in a CZT sample are eliminated or their distribution is reduced when the CZT sample is subjected to post-processing such as annealing. In particular, the Te inclusions move toward higher temperatures [10].

ARDISCZT0301A was subjected to thermal annealing in a 1-zone horizontal furnace to demonstrate the defect of Cd-vapor thermal annealing. The sample was ground and polished, as described in Subsection 2.2, to remove the Au electrodes after measuring the electrical properties. The sample and 0.5 g of Cd powder (99.9999%) were placed in a quartz ampoule and subsequently sealed under the vacuum conditions of ∼10−5 Torr. The sealed quartz ampoule was placed in an OTF-1200Z 1-zone furnace (MTI Co.) and annealed at 783 K for 64 h, as shown in figure 3. The Cd powder remaining in the sample was then removed and the surface of the sample was polished after thermal annealing to obtain clear IR camera image.

2% Br-MeOH etching offers the advantages of a better ohmic contact and physical damage removal during the polishing process. A Te-rich CZT surface is formed when using 2% Br-MeOH etching. The leakage current of CZT is increased owing to this Te-rich surface. The Te-rich surface of CZT is most effectively oxidized using NH4F + H2O2 passivation, which creates a stoichiometric surface. In addition, the surface corrosion of CZT can be prevented via passivation [16].

ARDISCZT0101PA was etched using 2% Br-MeOH and subsequently passivated with 10% NH4F + H2O2 aqueous solutions. To compare the resistivity of the Cd-vapor annealed samples with and without passivation,
ARDISCZT0101PA was passivated before Cd-vapor annealing. The passivation reaction is defined as

\[
\begin{align*}
\text{Cd}_0.9\text{Zn}_{0.1}\text{Te} \text{(Surface)} + \text{H}_2\text{O}_2 & = 0.9\text{Cd(OH)}_2 + 0.1\text{Zn(OH)}_2 + \text{Te} \\
\text{Te} + 2\text{H}_2\text{O}_2 & = \text{H}_2\text{TeO}_3 + \text{H}_2\text{O} \\
\text{H}_2\text{TeO}_3 + \text{H}_2\text{O}_2 + \text{H}_2\text{O} & = \text{Te(OH)}_6, \\
\text{Te(OH)}_6 + 6\text{NH}_4\text{F} & = \text{TeF}_6 \uparrow + 6\text{NH}_3 \uparrow + 6\text{H}_2\text{O}. 
\end{align*}
\]

(1)

3. Results and discussion

Te inclusions were measured at a random sample depth using the NIKON ECLIPS LVDIA-N IR CAMERA. The IR camera images revealed that the bulk of CZT was transparent; however Te-inclusions appeared black. The distribution of the Te inclusions was clarified by correcting the background of the measured images.

Table 1. Name of samples with respect to growing conditions.

| Name          | Material | Ingot number | Sample number | P (Passivation) | A (Annealing) |
|---------------|----------|--------------|---------------|-----------------|---------------|
| ARDISCZT0301A | CZT      | 1 (0428)     | 1*            | X               | O             |
| ARDISCZT0101PA| CZT      | 3 (0707)     | 1*            | O               | O             |

Note.
* Sample from wafer at the same ingot location.
Subsequently, the sample position before and after Cd-annealing was fixed based on the Te inclusions with a specific shape. Using the IR camera images, the area and number of Te inclusions were calculated with Leopard 2009 (http://www.zootos.com) to measure the changes in the Te inclusions before and after Cd-annealing. Figure 4 shows the IR camera images captured at heights of (a) 0.00 mm, (b) 0.215 mm, and (c) 0.30 mm along the Z-axis for ARDISCZT0301A. These are the original image before annealing, image before annealing with inclusions, original image after annealing, and image after annealing with inclusions, respectively. As shown in the figure 4(a), random phenomena is not associated with the sample properties and occurred between the slice glass and IR camera holder.

Table 2 summarizes the distribution of Te inclusions in ARDISCZT0301A, as shown in figure 4. As indicated in figures 4(a), (b), and (c), the number of Te inclusions decreased after annealing. In addition, it was confirmed that the area of the Te inclusions was reduced, as compared with the total area; this is because the minimum area of the Te inclusions after annealing was larger than that before annealing owing to the removal of small-sized Te inclusions. The minimum area of the Te inclusions after annealing is 6.165 μm² in figure 4(b) and 5.945 μm² in...
Therefore, it was confirmed that Te inclusions with sizes smaller than 6 μm² can be removed using Cd-vapor annealing.

Figure 5 presents the IR camera image that was captured by focusing on the hexagonal-shaped Te inclusion of ARDISCZT0101A observed before and after Cd-annealing. These images captured before and after annealing are presented on the left and right sides, respectively. The disappearance of the small-sized Te inclusions was identical to that observed for ARDISCZT0301A; however, the area of the hexagonal Te inclusions did not decrease significantly. Figures 5(a) and (b) are IR camera images captured at the same height; however, the focus of these images is different. Thus, the inclusions inside the red circle appear to be shifted along the Z-axis. Egarievwe et al. [10] reported that Te inclusions migrate toward a higher temperatures. As this experiment was conducted in a 1-zone furnace, it was assumed that no thermal gradients existed. Additionally, the migration along the X-, Y-, and Z-axes was confirmed based on the distance between the two inclusions (that is, 389.033 μm and 413.342 μm). Both samples were subjected to the same annealing conditions in terms of the annealing temperature and amount of Cd powder; the results varied slightly because the distance between the sample located in the quartz ampoule and the Cd powder could not be matched precisely.

Table 3 summarizes the distribution of Te inclusions in ARDISCZT0301A before and after annealing. As shown in figures 5(a) and (b), the number of Te inclusions decreased after annealing. Contrary to the results presented in table 3, both the minimum and maximum areas of the Te inclusions decreased, as the minimum

| ARDISCZT0301A | Figure 4 (a) | Figure 4 (b) | Figure 4 (c) |
|---------------|-------------|-------------|-------------|
|               | Before      | After       | Before      | After       | Before      | After       |
| Number of Te inclusions [#] | 68          | 23          | 6           | 3           | 6           | 3           |
| Inclusions of area/Total area | 7.034 × 10⁻⁸ | 4.451 × 10⁻⁸ | 3.887 × 10⁻⁶ | 3.295 × 10⁻⁶ | 1.074 × 10⁻⁷ | 4.157 × 10⁻⁸ |
| Minimum area of Te inclusions [μm²] | 38.656      | 42.171      | 4.844       | 6.165       | 3.303       | 5.945       |
| Maximum area of Te inclusions [μm²] | 3096.067    | 2463.499    | 3186.028    | 2727.107    | 56.374      | 18.718      |
area of the Te inclusions was larger by approximately 6 μm². Based on the IR camera images of ARDISCZT0301A and ARDISCZT0101PA, it was confirmed that the Te inclusion were removed even when using the 1-zone furnace.

Figure 6 shows a comparison of the resistivity before and after Cd-vapor annealing with and without passivation. The resistivities of ARDISCZT0301A and ARDISCZT0101PA were $2.18 \times 10^8$ and $4.56 \times 10^5$ Ω·cm, respectively. It was confirmed that the resistivity difference before and after Cd-vapor annealing amount to a factor of 1,000 depending on whether passivation.

Peak channel shifts of 59.5 keV were observed using a $^{241}$Am radioactive source. The radiation response spectra were measured using nuclear instrument modules, such as eV550 preamplifier (eV product Inc.), 527A shaping amplifier (ORTEC Co.), 927 multi-channel analyzer (ORTEC Co.), and Maestro 7.01 software (ORTEC Co.). As shown in figure 7(a), the radiation spectrum of ARDISCZT0301A was obtained at an input voltage of -300 V and a shaping time of 0.5 μs for a life time of 600 s before Cd-vapor annealing. The single peak fitting result demonstrates that the peak center was located at 118.31. The full width half maximum (FWHM) of 16.58% was observed to be an appropriate value for applying the counting mode radiation detector. The center of the peak channel was shifted to 156.47, which is 32% higher than the peak before Cd-vapor annealing, performed under identical measurement conditions. Therefore, the CCE increased drastically. However, the FWHM of 37.79% was significantly degraded after Cd-vapor annealing owing to the increased leakage current, as reported in [3, 10, 12]. Figure 7(c) shows the radiation spectrum obtained under an input voltage of −120 V. As shown in figures 7(b) and (c), both peak center values were approximately identical. Thus, the maximum
CCE of ARDISCZT0301A was achieved at $-120\,V$. As the leakage current decreased with the input voltage, the FWHM at an input voltage of $-120\,V$ was two times smaller than that at an input voltage of $-300\,V$. Consequently, the Te inclusions were removed or reduced after Cd-vapor annealing, and the CCE increased the trap of the reduction in the charge carriers. Additionally, with the removal of the high resistivity Te anti-sites, the leakage current increased and the FWHM degraded. The CCE and $\mu h \tau_h$ are defined in [19] as:

$$CCE(V) = \frac{\mu_e \tau_e E}{D_h - \epsilon} (1 - e^{E/\mu_e \tau_e})$$

(2)

$$\mu_h \tau_h = \frac{\epsilon \mu_e \tau_e}{D_h - \epsilon}$$

(3)

where $\mu$ is the total attenuation coefficient, $\mu_e \tau_e$ is the mobility life time products of electrons, $\mu_h \tau_h$ is the mobility life time products of holes, $E$ is the electric field, $\epsilon$ is a correction factor, and $D$ is the thickness of the detector. The CCE depends on $E$, $\mu \tau$, and the thickness. As shown in equation (3), as the density of Te inclusion is reduced, the trapped charges are reduced and a uniform $E$-field is created. This is identical to the effect of increasing $E$ and $\mu \tau$.

Figure 7 shows the $59.5\,\text{keV}^{241}\text{Am}$ energy spectra before and after annealing. It is evident that the CCE increased with the number of charge carriers increased. In other words, additional charge carriers were created after Cd-annealing. As the distribution of the peaks increased, the number of counts of the central peak was lowered; however, the total number of events in the area of the peak corresponding to $59.5\,\text{keV}$ remained the same. Furthermore, the resolution deteriorated because the resistivity was lowered via Cd-annealing [12]. From the fitted peak center between figure 7(a) and Fig. Figure 7(b), the calculated CCE was increased about 35%. Te inclusions act as trap sites were reduced by annealing as shown in figure 4. Owing to this, $E$-field inside of the
CZT sample was generated uniformly. Consequently, more charge carriers were created after annealing at same bias at $-300 \text{ V}$, and a channel of peak center was shifted from 118.31 to 160.47.

A method of additionally performing Te-vapor annealing after Cd-vapor annealing has been examined [20] to solve the problem of the FWHM deterioration owing to the leakage current.

4. Conclusion

This study demonstrated that the CCE can be improved by performing Cd-vapor annealing on passivated CZT samples. Thus far, gamma-ray energy spectra have not been discussed in existing studies because the resistivity decreased to a maximum of $10^5 \Omega \cdot \text{cm}$ after Cd-annealing. It was possible to observe the spectrum by minimizing the reduction in the resistivity using passivation. However, the energy resolution was reduced because the leakage current increased with the decreasing resistance. Cd annealing can effectively improve the CCE because it reduces the density of the Te inclusions generated in the CZT sample bulk. However, there are significant disadvantages when obtaining the radiation energy spectrum, such as a reduction in the resistance, which may require additional post-processing. In the future, we plan to develop a two-step annealing process, to perform Te-vapor annealing after Cd-vapor annealing to compensate for the reduction in the resistivity.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Jeong Min Park  https://orcid.org/0000-0003-4893-6521

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