Post-growth Annealing of Bridgman-grown CdZnTe and CdMnTe Crystals for Room-temperature Nuclear Radiation Detectors

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Abstract

Bridgman-grown cadmium zinc telluride (CdZnTe or CZT) and cadmium manganese telluride (CdMnTe or CMT) crystals often have Te inclusions that limit their performances as X-ray- and gamma-ray-detectors. We present here the results of post-growth thermal annealing aimed at reducing and eliminating Te inclusions in them. In a 2D analysis, we observed that the sizes of the Te inclusions declined to 92% during a 60-hour annealing of CZT at 510 °C under Cd vapor. Further, tellurium inclusions were eliminated completely in CMT samples annealed at 570 °C in Cd vapor for 26 hours, whilst their electrical resistivity fell by an order of 10^2 . During the temperature-gradient annealing of CMT at 730 °C and an 18 °C/cm temperature gradient for 18 hours in a vacuum of 10^{-5} mbar, we observed the diffusion of Te from the sample, so causing a reduction in size of the Te inclusions. For CZT samples annealed at 700 °C in a 10 °C/cm temperature gradient, we observed the migration of Te inclusions from a low-temperature region to a high one at 0.022 $\mu\text{m/s}$. During the temperature-gradient annealing of CZT in a vacuum of 10^{-5} mbar at 570 °C and 30 °C/cm for 18 hours, some Te inclusions moved toward the high-temperature side of the wafer, while other inclusions of the same size, i.e., 10 μm in diameter, remained in the same position. These results show that the migration, diffusion, and reaction of Te with Cd in the matrix of CZT- and CMT- wafers are complex phenomena that depend on the conditions in local regions, such as composition and structure, as well as on the annealing conditions.

Keywords: CdZnTe and CdMnTe, Nuclear radiation detectors, Te inclusions, Thermal annealing in Cd vapor, Te diffusion and migration, Temperature gradient annealing

1. Introduction

Cadmium zinc telluride (CdZnTe or CZT) and cadmium manganese telluride (CdMnTe or CMT) are some of the semiconductor materials that have proven to be good candidates for applications as room-temperature nuclear-radiation detectors [1-4]. CZT has found usages in medical imaging [5] and in astrophysics for measuring celestial gamma-ray photons [6]. Bridgman-grown CZT and CMT crystals often contain Te inclusions that limit their performances as X-ray- and gamma-ray-detectors [7]. These Te inclusions form from the evaporation of Cd (due to the high pressure), and the deposition of segregated Te from the decomposition of the melt. Te inclusions were observed to act as localized centers where different impurities gather, and may affect electrical compensation and cause charge trapping [8]. The trapping of charge carriers generated by ionizing radiation entails fluctuations of the collected charges, so degrading the energy resolution of thick ($> 5\text{-}15\text{ mm}$) detectors [9, 10]. While efforts have been made to control the formation of Te inclusions in Bridgman-grown CZT and CMT, their presence persists because the crystals are grown in Te-rich environments to ensure the high resistivity needed for the detector's room-temperature operation. Post-growth thermal annealing is a reasonable alternative to removing these performance-limiting Te inclusions.

There are two basic approaches to the post-growth thermal annealing of CZT- and CMT-crystals. The first one involves annealing the material at elevated temperatures in a Cd-rich atmosphere. Then, Cd diffuses within the sample and reacts with the excess Te, so replacing the Te-rich particles with crystalline material. The strain introduced by forming new CZT in place of Te particles may increase the number of dislocations in the material. This procedure also reduces the material's resistivity. Reportedly, annealing in a combination of Cd-rich and Zn-rich atmospheres maintains high resistivity [11]. The second thermal-annealing approach involves inducing movement of the Te inclusions under temperature gradients and their accumulation at the sample's high-temperature side, leaving the higher-quality regions of the crystal with fewer smaller particles.

In previous experiments we recorded that annealing in a Cd vapor effectively removes Te inclusions from CZT, and there was migration of Te inclusions for annealing in a temperature-gradient field [12]. While many of the small-size Te inclusions were eliminated after annealing in a Cd vapor at 923 K for 24 hours, the larger inclusions remained; and the size-reduction for larger inclusions become possible in two cases: 1) annealing at higher temperature of 1100 K for a shorter time of 60 minutes, and, 2) a two-cycle annealing at 1100 K for 15 minutes per cycle [12]. It has been reported that annealing under a Cd vapor pressure at high temperatures above $\sim 1170\text{ K}$ generates a large quantity of irregular Cd inclusions in the

CZT matrix [13]. Thus, depending on the crystal composition and structure, annealing at lower temperatures and longer time could have the advantage of less heat stress on the CZT matrix compared to annealing at high temperatures. In the present work, we show that both elimination of small-size Te inclusions and the size-reduction of large Te inclusions in CZT wafers can also be achieved at lower temperature and longer time of up to 60 hours. We also present further results of post-growth annealing of CZT- and CMT- crystals under Cd vapor and a temperature gradient. The discussion of the new results focused on 1) the Te diffusion in the detector material, 2) the reduction in the size of Te inclusions, 3) the migration of Te inclusions, and, 4) the resistivity of the wafers.

2. Experimental Procedures

Wafers were cut from Bridgman-grown CZT- and CMT-ingots ranging from 2.5 mm- to 5.25 mm-thick, 5.0 mm to 10.4 mm long, and 5.0 mm- to 7.6 mm-wide. The samples were mechanically polished with 800-grit and 1200-grit silicon carbide abrasive papers, and then polished on multi-tex pads with alumina powder (Al_2O_3) of decreasing size from 3- to 0.1-microns. Each sample was sealed in a quartz ampoule under vacuum of 10^{-5} mbar. For annealing under Cd vapor, we placed Cd at one end of the ampoule and sealed it with the sample. The sealed ampoules were placed in a predetermined region of an annealing furnace. In each annealing run, the location of the ampoule was determined by setting the heating elements to give a furnace-temperature profile that would give the desired annealing temperature, the Cd temperature for annealing under a Cd atmosphere, and a temperature gradient for temperature-gradient annealing. Fig. 1 shows an example of the profile of the furnace's temperature used in this experiment. For annealing under Cd vapor, the distance between the sample and the Cd material was determined from the profile of the furnace's temperature and the desired temperatures for the sample and Cd.

Fig. 1. An example of a profile of the furnace temperature used in this experiment. The top of the profile could be moved up or down to get the desired annealing-temperature and temperature-gradient.

To study diffusion of Te inclusions, the reduction in their size, and their migrations, we used infrared (IR) transmission microscopy to image them both before and after annealing; also, we then obtained the resistivity of the samples by current-voltage (I-V) measurements. The matrix of the CZT- and CMT-crystals is transparent to IR light, while the Te inclusions are opaque. The samples were marked to track the locations and orientations of the Te inclusions that we studied. For I-V measurements, planar Au electrical contacts were placed on two opposite surfaces of the rectangular-shaped samples by an electroless chemical-deposition method, wherein AuCl_3 5% solution droplets are pipetted on to the samples' surface and the excess solution removed via a liquid-absorbing soft felt paper. The I-V measurement system consists of a sample mount enclosed in an aluminum box fitted with electrical leads connected to a Keithley 237 high-voltage source and a low-current measure unit.

After I-V measurements and before sealing the samples in ampoules for annealing, the Au electrical contacts were removed by polishing with a 1200-grit silicon-carbide abrasive paper, followed by polishing on multi-tex pads with Al_2O_3 powder of decreasing size from 3- to 0.1- microns. Polishing was repeated after annealing to remove any rough surfaces caused by heating the samples. Smoothing the surface allows a more uniform entry of IR light into the matrix of the CZT and CMT-samples while preventing the image of a rough surface from obscuring images of Te inclusions. The IR images were taken with a Nikon industrial microscope Eclipse LV100 fitted with an IR light source, an IR camera, a motorized xyz-translation stage, and image-capturing and analysis software. The following sets of annealing experiments were carried out:

1. Annealing of CZT at 510 °C under Cd vapor for 60 hours, after which the reduction in size of Te inclusions was measured.
2. Annealing of CMT crystals at 570 °C in Cd vapor for 26 hours. The elimination of Te inclusions and change in resistivity were studied.
3. Temperature-gradient annealing of CZT at 30 °C/cm and CMT at 18 °C/cm under a 10^{-5} mbar vacuum for 18 hours at 570 °C and 730 °C , respectively. This set of experiments yielded details of the diffusion and migration of Te inclusions.
4. Annealing of CZT at 700 °C under Cd vapor at 650 °C for 30 minutes at 10 °C/cm temperature gradient. The migration of the Te inclusions under temperature gradient was measured.

3. Results and Discussion

The results are discussed under three categories: Thermal annealing in Cd vapor; annealing under a temperature gradient; and, temperature-gradient annealing in Cd vapor.

3.1. Thermal Annealing in Cd Vapor

In previous experiments we recorded that many of the small-size Te inclusions were eliminated after annealing in a Cd vapor at 923 K (~ 650 °C) for 24 hours while the larger inclusions remained, and observed size-reduction for larger inclusions in two cases: 1) annealing at higher temperature of 1100 K (~ 827 °C) for a shorter time of 60 minutes, and, 2) a two-cycle annealing at 1100 K for 15 minutes per cycle [12]. The results in the present work show that both elimination of small-size Te inclusions and the size-reduction of large Te inclusions in CZT wafers can also be achieved at lower temperature of 510 °C and longer time of 60 hours – see Table 1 and Fig. 2 which showed up to 96% size reduction of large inclusions in a 2D analysis. Annealing at this relatively low temperature and longer time reduces the generation of large quantity of irregular Cd inclusions reported for annealing at much higher temperatures above ~1170 K [13].

Table 1 shows the size reductions for seven selected Te inclusions in CZT annealed at 510 °C for 60 hours in Cd vapor. The areas of the Te inclusions were calculated using NIS-Elements Nikon imaging software. This reduction could result from Te diffusing outside the CZT matrix, or the Te reacting with Cd that diffuses within the CZT matrix from the Cd-rich atmosphere, thus replacing the excess Te with crystalline material. The dominant cause of size reduction in this case is the reaction of Cd with Te as illustrated in Fig. 2 that shows the almost linear dependence of the size-reduction on the pre-annealing

sizes of the Te inclusions, i.e., larger inclusions provide a larger surface area for reaction with Cd. The percent size reduction is almost constant, averaging 92%.

Table 1

Percentage size reduction of Te inclusions in CZT annealed at 510 °C for 60 hours in Cd vapor.

Before annealing (μm^2)	After annealing (μm^2)	Size reduction (%)
311.2	24.6	92.1
235.2	9.1	96.1
359.8	37.4	89.6
280.7	21.2	92.4
196.1	29.2	85.1
311.2	16.6	94.7
333.4	15.9	95.2

Fig. 2. Linear dependence of size-reduction on the pre-annealing sizes of the Te inclusions – larger Te inclusions provide larger surface area for reacting with Cd. The percent size reduction is approximately constant.

Depending on the annealing temperature and the Cd-rich atmosphere, increasing the annealing time could completely eliminate the Te inclusions. Figure 3 shows the IR images of CMT before and after annealing in 570 °C in Cd vapor for 26 hours, at which the Te inclusions were completely eliminated through the reaction of Cd and Te. The electrical resistivity of the CMT sample was reduced by an order

of 10^2 , as shown by the I-V curves in Fig. 4. Similar reductions in the electrical resistivity of CZT annealed in Cd vapor were reported in the literature, where a second step of annealing in Te-rich atmosphere was used to restore the resistivity [12]. During annealing in Cd-rich atmosphere, extra Cd interstitials are introduced into the CZT matrix, a process which may cause a loss of compensation between deep-level Te antisites, Cd interstitials, and the Cd vacancies that are responsible for the high resistivity in CdTe and its associated tertiary compounds, CdZnTe and CdMnTe [12,13]. The result is a shift of the Fermi level towards the bottom of the conduction band or to the top of the valence band [12]. Much success was reported in increasing the resistivity of CZT by annealing in Te-rich atmosphere [14]; in some cases with restoration to $10^9 \Omega\text{-cm}$ from the range of 10^3 and $10^5 \Omega\text{-cm}$ [15].

Post-growth annealing processes lowered the resistivity of the CZT- and CMT-materials. This effect, illustrated in Fig. 4, compares the current-voltage measurements of Bridgman-grown and modified floating-zone-grown CMT crystals before and after annealing. The results of current-voltage measurements on CMT wafer annealed at 570°C in Cd vapor for 26 hours showed a reduction in electrical resistivity by an order of 10^2 .

Fig. 3. Te inclusions are completely eliminated from a CMT wafer annealed at 570°C in Cd vapor for 26 hours.

Fig. 4. I-V curve of CMT wafer annealed at 570 °C in Cd vapor for 26 hours, showing a reduction in electrical resistivity by an order of 10^2 .

(a) Before annealing

(b) After annealing

Fig. 5. Size reduction and elimination of Te inclusions in 2.5 mm x 6.9 mm x 7.0 mm CMT wafer annealed at 730 °C and 18 °C/cm temperature gradient for 18 hours.

3.2. Annealing under Temperature Gradient

We recorded the migration of Te inclusion under *temperature gradient annealing in a Cd over pressure* atmosphere [12]. The present work differs in that Cd was not added in the ampoule to anneal in Cd over pressure atmosphere. Thus, any Cd in the ampoule's atmosphere in the present work would only come by diffusion from the CZT wafer and thus would create a much less Cd atmosphere. We observed the migration, size reduction, and complete elimination of Te inclusions during temperature-gradient annealing under vacuum of 10^{-5} mbar. The size reduction and elimination of Te inclusions from some regions of the wafers, without annealing in Cd-rich atmosphere, is

a significant result; it is prominent in CMT annealed at 730 °C and 18 °C/cm temperature gradient for 18 hours (Fig. 5). This could be due to the diffusion of Te from the sample, as well as the reaction of Te within the matrix during annealing. This explanation is further supported by the 2D size distribution of Te inclusions, in a $2.2 \times 10^6 \mu\text{m}^2$ area of the CMT wafer, shown in Figure 6. The size of the CMT wafer was 2.5 mm x 6.9 mm x 7.0 mm, is fairly thin compared to the size of the CZT wafer, 5.2 mm x 7.6 mm x 10.3 mm. The IR images of the CMT and CZT wafers are shown respectively in Figs. 5 and 7. The CZT wafer was annealed at 570 °C, and in a 30 °C/cm temperature gradient for 18 hours.

(a) Before annealing

(b) After annealing

Fig. 6. Size distribution of Te inclusions in a $2.2 \times 10^6 \mu\text{m}^2$ area of a CMT wafer annealed at 730 °C and 18 °C/cm temperature gradient for 18 hours. The diameters of the Te inclusions were measured within $\pm 1 \mu\text{m}$.

Fig. 7. CZT wafer size of 5.2 mm x 7.6 mm x 10.3 mm annealed at 570 °C and 30 °C/cm temperature gradient for 18 hours. The Te inclusions are about 10 μm in diameter. Some inclusions remained in the same position, while other migrated towards the wafer's high temperature side.

3.3. Temperature-gradient Annealing in Cd Vapor

Annealing under a temperature gradient and in Cd-rich atmosphere is expected to result in both a size reduction of the Te inclusions and their migration. In previous experiments, we observed both effects during the 10 °C/cm temperature-gradient annealing of CZT at 700 °C under Cd vapor at 650 °C for 30 minutes; we also noted voids left behind by the migrating inclusions [16]. Further analysis showed that the Te inclusions migrated toward the high-temperature side of the wafer at an average speed of about 0.022 μm/s.

Conclusions

We experimentally studied three major types of post-growth annealing practices for CZT- and CMT-crystals for X-ray and gamma-ray detection applications: Annealing in a Cd-rich atmosphere at constant temperature, annealing in a temperature gradient, and temperature-gradient annealing in a Cd-rich atmosphere. Under 2D IR image analysis, we observed that the area of Te inclusions in CZT was reduced by about 92% after 60-hours annealing at 510 °C under Cd vapor. Tellurium inclusions were eliminated completely in CMT samples annealed at 570 °C in Cd vapor for 26 hours, and the electrical resistivity was reduced by an order of 10^2 . We also recorded a significant reduction in size of Te inclusions and their elimination in a CMT wafer annealed at 730 °C and at an 18 °C/cm temperature gradient for 18 hours under a vacuum of 10^{-5} mbar. Since there was no Cd-rich atmosphere, we believe this could be due to diffusion of Te from the sample, and to the reaction of Te within the matrix during annealing. For CZT samples annealed at 700 °C in a 10 °C/cm temperature gradient, we observed Te inclusions migrating from a low-temperature region to a high one at a rate of 0.022 $\mu\text{m/s}$.

Another interesting phenomenon observed for the temperature-gradient annealing of CZT in vacuum of 10^{-5} mbar at 570 °C and 30 °C/cm for 18 hours is the movement of inclusions of 10 μm in diameter towards the high-temperature side of the wafer, while other inclusions of the same size remained in the same position. These phenomena, along with complete elimination of Te inclusions from some regions of CMT during both constant-temperature annealing in Cd vapor and temperature-gradient annealing, highlight the complexity of Te migration, diffusion, and reaction with Cd in the matrix of CZT and CMT wafers. These processes depend on the conditions in local regions, such as composition and structure, as well as the annealing conditions.

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