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Two-step annealing to remove Te secondary-phase defects in CdZnTe while preserving the high electrical resistivity

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Abstract—The presence of Te secondary-phase defects (i.e., Te inclusions and Te precipitates) is a major factor limiting the performance of CdZnTe (CZT) X- and gamma-ray radiation detectors. We find that Te secondary-phase defects in CZT crystals can be removed through post-growth, two-step annealing without creating new trapping centers (i.e., prismatic punching defects). Two-step annealing (with the first in a Cd pressure and the second one in a Te pressure) was demonstrated to be effective in removing the Te secondary-phase defects, while preserving the electrical resistivity of the CZT detector. The first step involves annealing of semi-insulating CZT under a Cd overpressure at 700/600 (CZT/Cd) for 24 hours, which completely eliminated the Te-rich secondary-phase defects (Te inclusions). However, it resulted in a lower resistivity of the samples (down to $2 \times 10^{4-6}$ Ω·cm). A subsequent annealing step involves processing CZT under a Te ambient condition at 540/380 (CZT/Te) for 120 hours, which restored the crystal's resistivity to 6.4×10^{10} Ω·cm without creating new Te secondary-phase defects. However, Te inclusions reappeared in the case of unnecessarily long Te ambient annealing. Pulse height spectra taken with the two-step annealed CZT detectors showed improved detector performance due to a reduced concentration and size of Te secondary-phase defects.

Index Terms— CdZnTe, two-step annealing, high resistivity, real-time monitoring, pulse height spectra

I. INTRODUCTION

Distinct advantages of CdZnTe (CZT) and CdTe as room-temperature operating radiation detectors have been known for 30 years. However, the availability of large-volume (> 5 cm^3) CZT and CdTe commercial detectors only began about 5 years ago. CZT and CdTe are now used in next-generation high performance X-ray and gamma-ray radiation detection instruments for isotope identification and imaging for security and medical applications. Most commercial detectors are fabricated from crystals grown by the travelling heater method (THM), which can yield CZT/CdTe products with both high quality and economical feasibility. Charge carrier trapping at Te secondary-phase defects in CZT/CdTe is a factor limiting the performance of CZT detectors in term of charge collection efficiency (CCE) and energy resolution [1].

Commercial detector-grade CZT crystals are grown under Te-rich conditions regardless of the specific growth method. Therefore, the generation of Te secondary-phase defects (i.e., Te inclusions and Te precipitates) is inevitable. There are several reports on post-growth annealing of detector-grade CZT crystals under Cd/Te overpressure to eliminate these Te secondary defects. Annealing of CZT under Cd overpressure can eliminate Te-rich secondary phase defects completely. However, it leaves prismatic punching defects over the entire CZT volume [2]. It also decreases the resistivity of CZT to 1 ~ 100 Ω·cm. The prismatic punching defect is a kind of defect that deteriorates the uniformity of charge transport [3]. The uniformity of charge transport is affected more severely for larger prismatic punching defects. Generally, these prismatic punching defects are larger than the size of the original pre-annealed Te inclusions by 10-1000 times. The low resistivity of CZT annealed under Cd overpressure can be explained by annihilation of the (Te_{Cd} + V_{Cd}) complex by in-diffusion of Cd_i into the CZT lattice during Cd overpressure annealing, leading to loss of compensation. Te overpressure

annealing with a temperature gradient can remove Te inclusions by thermo-migration. However, it also gives a lower resistivity of CZT at 10^{4-6} Ω·cm. Two-step annealing (i.e., the first in a Cd pressure and the second in a Te pressure) has been demonstrated to be effective in order to preserve the resistivity of detector-grade CZT [4], [5]. However, after undergoing two-step annealing, CZT detectors will show more electron trapping and may lose spectroscopic properties [4], although they have high resistivity.

The objective of this study was to get rid of Te secondary phase defects in CZT crystals through a post-growth two-step annealing process, while preserving the resistivity of CZT detector without creating new trapping centers (i.e., prismatic punching defects). In addition, the variation of the leakage current in CZT during the two-step annealing process was monitored in real time.

II. EXPERIMENT

High resistivity CZT detectors (> 10^{10} Ω·cm) were grown by a seedless traveling heater method (THM). The size of the CZT crystal used in the experiment was typically 7 × 7 × 3 mm^3. Several CZT crystals were annealed under Cd overpressure at 700/600 (CZT/Cd) for 48 hours. CZT crystals annealed under Cd overpressure were etched with 2% Br-MeOH solution to remove the Cd-contaminated surface layer. Au electrode was formed by an electroless deposition method using a $AuCl_3$ solution. The size of the Au electrode was 4 × 4 mm^2. CZT detectors were placed on a specially designed sample holder, making it possible to measure the leakage current during annealing in Cd and Te over-pressures. The partial pressure of Te-rich semi-insulating CZT follows that of elemental Te up to 650 and saturates at about 18 mm-Hg [7]. The vapor pressure of the Te source was determined by vapor pressure of pure elemental Te which is

represented as follows:

$$\log_{10} P_{Te2} = -\frac{5690.2}{T(K)} + 4.719 \text{ (atm)}$$

where T(K) is absolute temperature. In our two-step annealing, CZT detectors were kept between 500 and 600 , while the Te source was kept between 300 and 650 .

The real-time current measurement system was sealed under a vacuum of 10^{-6} torr. We applied 1 V to CZT detectors and measured the leakage current every minute using a Keithley 237 electrometer. The heating and cooling rates of the CZT detectors were kept at below 0.5 per minute to minimize thermal stress and strain in the CZT. Before and after the annealing experiment, the material's resistivity was measured. For pulse-height measurements at room temperature, a planar CZT detector was installed in a holder, and the cathode side of the detector was irradiated with an Am-241 source. Signals from the positively biased anode were measured using a capacitively coupled eV Products 550 preamplifier. For the data acquisition, a spectroscopic shaping amplifier (ORTEC 672) and a multichannel analyzer (ORTECEASY- MCA-8k) were used.

III. RESULTS AND DISCUSSION

A. Cd annealing at 700/600 (CZT/Cd)

CZT samples were annealed at 700/600 (CZT/Cd) for 24 hours. CZT samples annealed in Cd overpressure were chemo-mechanically polished to remove the Cd contaminated surface layer prior to I-V measurement and second-step Te annealing. The resistivity of CZT samples were decreased from 1.95×10^{10} to 1.1×10^{5} Ω·cm after Cd overpressure annealing. However, Te-secondary phase defects were completely eliminated as shown in Fig. 2. This is the typical result observed for Cd overpressure annealed CZT. However, inadequate Cd overpressure annealing leaves star-shaped

prismatic punching defects in the same spot, which are a few orders of magnitude larger than the pre-annealed Te inclusions. These star-shaped prismatic punching defects can be revealed by the chemical etching with Nakagawa etchants or by white beam X-ray diffraction topography (WBXDT) [2]. Typical current-voltage characteristics of annealed CZT under a Cd overpressure are shown in Fig. 1b.

B. Te annealing at 540/380 (CZT/Te)

As a second step, CZT sample was annealed under a Te pressure at 540/380 (CZT/Te) for 120 h. The leakage current increased from 5×10^{-7} A to 3.5×10^{-2} A while temperature was increased from 23 to 590 over 20 h. However, the leakage current was slightly changed from 3.5×10^{-5} A to 2.7×10^{-5} A during the annealing at 500 for 120 hours. At the end of the Te annealing process, the leakage current of the CZT detector was decreased to 3.4×10^{-9} A. The activation energy obtained from the raising and lowering stages of the annealing processes are shown in Fig. 3. During the temperature rising stage, two different activation energies of 0.38 and 0.66 eV were obtained. On the other hand, two activation energies of 0.72 and 0.90 eV were obtained in the temperature lowering stage, indicating the successful two-step annealing from presence of the activation energy at 0.72 eV. The slopes during the raising and lowering temperature states changed at 392 and 440 in the Arrhenius plots, respectively.

Additional 240-hour annealing was applied to the same CZT sample to observe any changes in leakage current for extended annealing times. However, we did not observe any changes in the leakage current in spite of such additional Te annealing time. The CZT detector annealed under Te ambient for 360 h was chemo-mechanically polished to remove the damaged surface layer. The infrared transmission microscopy image and current-voltage characteristics of additional Te ambient annealing of CZT are

shown in Fig. 4 and Fig. 1c, respectively. The resistivity of the CZT detector was 6.4×10^{10} Ω·cm, which was slightly higher than the initial resistivity of the CZT detector. However, Te inclusions, which disappeared through Cd overpressure annealing, were observed in CZT annealed in a Te ambient condition for 360 h.

Cd-Te binding generated by Cd overpressure annealing might be in a meta-stable state. This meta-stable Cd-Te binding can break down during the Te ambient annealing step. Cd atoms from meta-stable Cd-Te binding can escape from CZT and combine with Te sources. According to Eq. 4, the Te pressure at 380 was extremely low at 7.7×10^{-2} mm-Hg. The role of the Te source was as a kind of Cd absorber, which could continuously allow the release of Cd atoms from CZT. For this reason, Te inclusions reappeared in CZT after Te ambient annealing. The Te source pressure at 380 was 1/26 of the Te partial pressure in Te-rich semi-insulating CZT at 540 [7].

Theoretical Cd diffusion (in and out) profiles were calculated using a complementary error function:

$$C(x)= C_0\{1- \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\}$$

where C_0 is the initial concentration of diffuser, D is the diffusion coefficient, x is the distance, and t is the time. In a previous experiment, Cd in-diffusion mechanism in Te-rich CZT follows diffusion via Cd vacancies [2]. However, Cd out-diffusion mechanism in Cd-rich CZT follows diffusion via Cd interstitials. Diffusion coefficients of Cd via Cd vacancies at 700 and 540 are 5.2×10^{-6} cm^2/s and 8.3×10^{-7} cm^2/s, respectively [8]. Te ambient annealing was done for 120 h followed by an additional 240 h. Both Te ambient annealing gave semi-insulating CZT of 10^{10} Ω·cm as shown in Fig. 1 (c). However, semi-insulating CZT obtained through Te ambient annealing for 120 h did not

provide any spectroscopic properties. The reason might be that CZT detector was not fully depleted due to such short annealing time. Theoretical diffusion lengths for 120 h and 360 h at 540 were 1.20 cm and 2.08 cm, respectively. Differential current-voltage measurements were done for a CZT detector that had been cut in half. It was attached to sapphire glass with conductive epoxy and polished by 200-μm steps. It proved that there were conductive layers in the middle of the CZT.

Another CZT sample was annealed in Cd overpressure and Te ambient under the same conditions except for the annealing time. An IR transmission image of the CZT detector annealed under Te ambient conditions for 250 h is shown in Fig. 5. Unlike previous results (see Fig. 4), Te inclusions were not observed in the CZT sample. This demonstrates that the Te inclusions size and concentration can be controlled with the Te ambient annealing time. Quantitative analyses for the Te ambient annealing time, Te inclusion size, and Te inclusion density are currently underway.

Pulse height spectra of Am-241 taken with as-grown and two-step annealed CZT detector are shown in Fig. 6. The gamma peak at 59.5 keV was normalized for quantitative comparison. The two-step annealed CZT detector showed improved detector performance. Especially, the hole tailing effect disappeared in the two-step annealed detector. Also, counts of low energy gamma peaks were increased more clearly. These phenomena indicated that the mobility-lifetime products of carriers were improved for two-step annealed CZT detectors. Two-step annealed CZT detectors have fewer Te inclusions depending on the Te ambient annealing time as shown in Fig. 4. However, their size and densities are notably reduced compared to those of as-grown CZT detectors. Therefore, the improvement in CZT detector performance can be attributed to the reduction in density and size of Te inclusions [9]. Large-volume CZT detector might show remarkable performance effects with two-step annealing.

V. SUMMARY

THM-grown CZT samples contain high concentrations of Te secondary-phase defects depending on the stability of the liquid/solid interface. Two-step annealing (i.e., first in Cd and the second in Te) successfully restored the initial resistivity of CZT with few remaining Te inclusions, depending on the Te ambient annealing time. The Cd-Te bonding formed during the Cd-overpressure annealing process is in a meta-stable state. Therefore, the removed Te inclusions can be reproduced in Te ambient annealing depending on the annealing time. A Te reservoir used in the second-step annealing acted as a Cd absorbent and provided minimum Te pressure for CZT. Two-step annealed CZT detector showed improved spectroscopic properties. However, the short-time annealed detector under Te ambient condition did not show any spectroscopic properties due to an un-depleted region in the central portion of the CZT sample. Complete characterization of Te inclusions and resistivity for two-step annealed CZT are underway to optimize the two-step annealing process to reduce and optimally control Te inclusions, while preserving the CZT's resistivity.

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REFERENCES

[1] A. E. Bolotnikov, N. M. Abdul-Jabber, O. S. Babalola, G. S. Camarda, Y. Cui, A. M. Hossain, E. M. Jackson, H. C. Jackson, J. A. James, K. T. Kohman, A. L. Luryi, and R. B. James, "Effects of Te inclusions on the performance of CdZnTe radiation detectors", IEEE Trans. Nucl. Sci., vol. 51, no. 5, pp. 2757-2764, 2008.

[2] K. H. Kim, A. E. Bolotnikov, G. S. Camarda, J. Franc, P. Fochuk, and R. B. James, "Prismatic punching defects in CdTe compounds", J. Cryst. Growth, vol. 390, pp. 1-4, 2014.

[3] G. Yang et al, "Post-growth thermal annealing study of CdZnTe for developing room-temperature X-ray and gamma-ray detectors", J. Cryst. Growth, vol. 379, pp. 16020, 2013.

[4] G. Piacentini, N. Zambelli, G. Benassi, D. Calestani, M. Pavesi, and A. Zappettini, "Two-step thermal process in tellurium vapor for tellurium inclusion annealing in high resistivity CdZnTe crystals", J. Cryst. Growth, vol. 415, pp. 15-19, 2015.

[5] A. Raulo, G. Hennard, M. Sowinska, R. B. James, A. Fauler, J. Freier, A. Held, and M. Fiederle, "Effects of Annealing on Bulk Properties of CdTe Detectors", IEEE Trans. Nucl. Sci., vol. 60, no. 5, pp. 3815-3823, 2013.

[6] K. H. Kim, Seokjin Hwang, Petro Fochuk, L. Nasi, A. Zappettini, A. E. Bolotnikov, and R. B. James, "The Effect of Low-Temperature Annealing on a CdZnTe Detector", IEEE Trans. Nucl. Sci., vol. 63, no. 4, pp. 2278-2282, 2016.

[7] K. H. Kim, J. Suh, A. E. Bolotnikov, P. M. Fochuk, O. V. Kopach, G. S. Camarda, Y. Cui, A. Hossain, G. Yang, J. Hong and R. B. James, "Temperature-gradient annealing of CdZnTe under Te overpressure", J. Cryst. Growth, vol. 354, pp. 62-66, 2012.

[8] E. D. Jones, N. M. Stewart, and J. B. Mullin, "Studies on the self-diffusion of cadmium in cadmium telluride in the temperature range 350-650 ˚C using anodic

oxidation", J. Cryst. Growth, vol. 130, pp. 6-12, 1993.

[9] P. Yu and W. Jie, "Effects of post-growth annealing on the performance of CZT:In radiation detectors with different thickness", Nucl. Instrum. Methods Phys. Res. A, vol. 737, pp. 29-32, 2014.

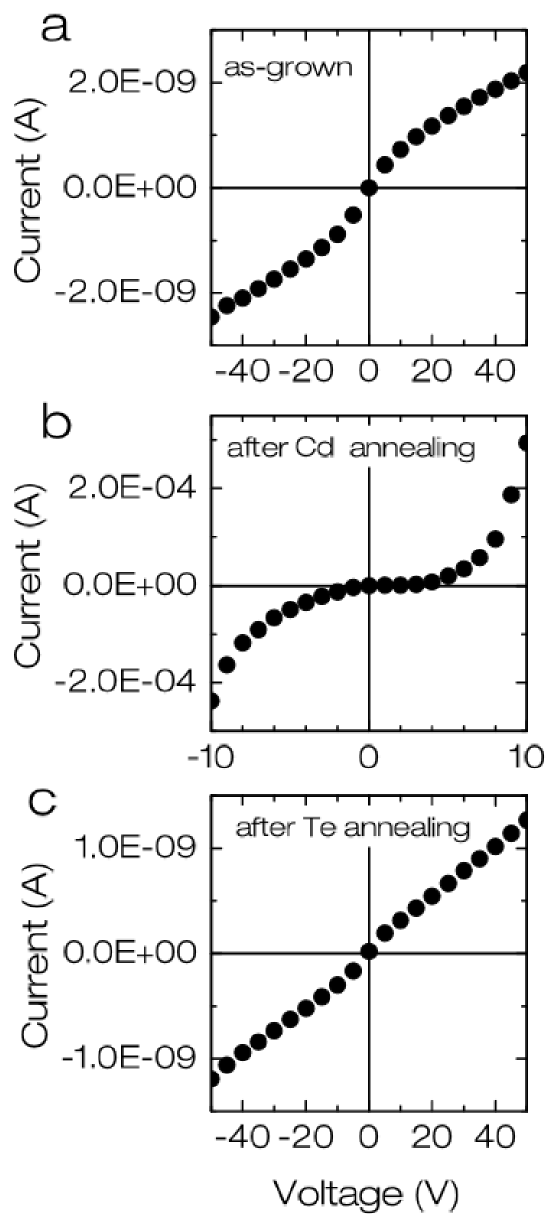

Fig. 1. Current-voltage characteristics of (a) as-grown, (b) annealed under Cd overpressure, and (c) two-step annealed CZT detector. The initial resistivity of the CZT detector was fully recovered following the two-step annealing process.

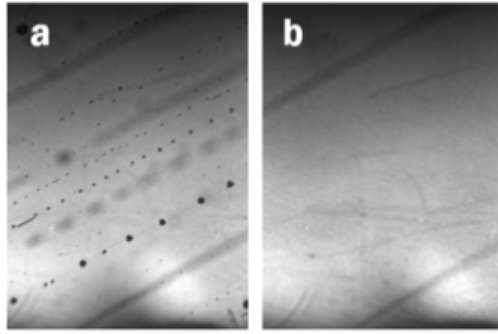

Fig. 2. IR microscope image of CZT samples taken (a) before and (b) after Cd-overpressure annealing at the same spot. Te secondary phase defects completely disappeared after Cd overpressure annealing. The image size is 1.1 × 1.5 mm^2.

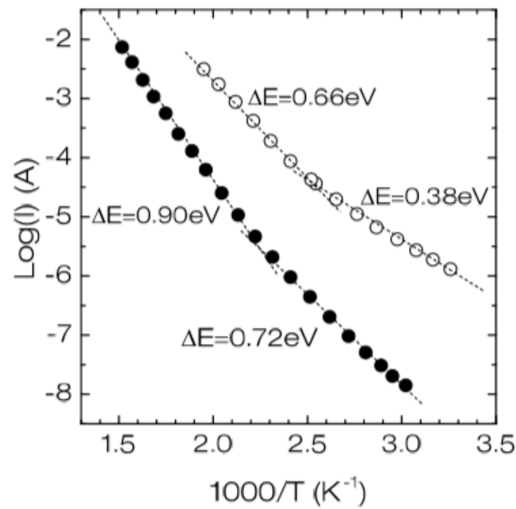

Fig. 3. Activation energy of CZT detector obtained while raising (open circle) or lowering (closed circle) the temperature. Two activation energies for both raising and lowering temperature were obtained. The activation energy of 0.72 eV indicates successful restoration of the resistivity through two-step annealing.

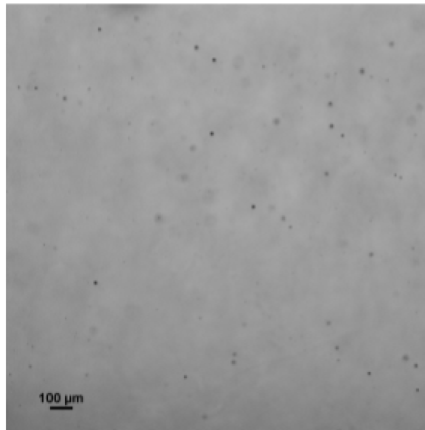

Fig. 4. IR transmission image of CZT sample taken after two-step annealing. Te inclusions which disappeared after Cd overpressure annealing re-appeared in the whole area of the CZT sample. The Te ambient annealing time was 350 h.

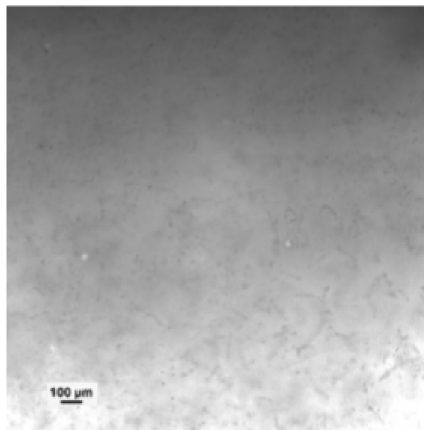

Fig. 5. IR transmission image of CZT sample taken after two-step annealing. CZT sample annealed in Te ambient condition for 250 h did not have any Te inclusions.

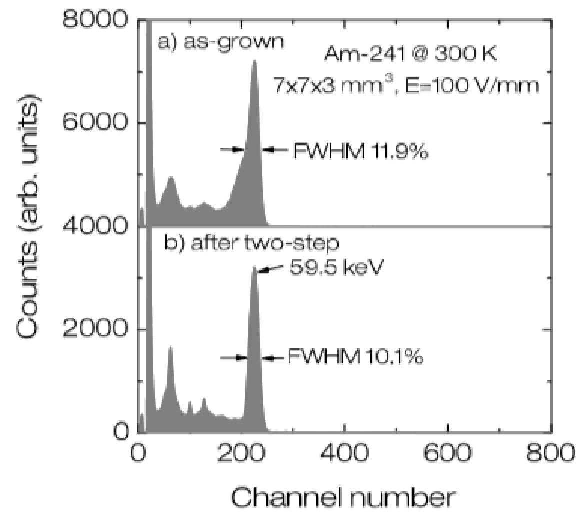

Fig. 6. Pulse height spectra of Am-241 taken with as-grown (top) and two-step annealed (bottom) CZT detector. The two-step annealed CZT detector showed improved detector performance with little or no hole tailing effect.