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Telluride (CZT) Crystals***

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Study on thermal annealing of cadmium zinc telluride (CZT) crystals

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ABSTRACT

Cadmium Zinc Telluride (CZT) has attracted increasing interest with its promising potential as a room-temperature nuclear-radiation-detector material. However, different defects in CZT crystals, especially Te inclusions and dislocations, can degrade the performance of CZT detectors. Post-growth annealing is a good approach potentially to eliminate the deleterious influence of these defects. At Brookhaven National Laboratory (BNL), we built up different facilities for investigating post-growth annealing of CZT. Here, we report our latest experimental results. Cd-vapor annealing reduces the density of Te inclusions, while large temperature gradient promotes the migration of small-size Te inclusions. Simultaneously, the annealing lowers the density of dislocations. However, only-Cd-vapor annealing decreases the resistivity, possibly reflecting the introduction of extra Cd in the lattice. Subsequent Te-vapor annealing is needed to ensure the recovery of the resistivity after removing the Te inclusions.

Keywords: Radiation detection, CZT, annealing, Te inclusions, dislocations.

1. INTRODUCTION

Much attention has focused on the excellent potential of cadmium zinc telluride (CZT) as a nuclear-radiation detector material. CZT's unique properties include a high average atomic number, large bandgap, and good electron-transport properties, along with the availability of materials with acceptable cross-sectional areas and thicknesses. These merits support high detection-efficiency and good energy-resolution when operating at room temperature [1-4]. However, largely, the development of CZT detectors still is limited by material defects, typically Te inclusions and dislocations. Using a delicate X-ray response micro-scale mapping system developed at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), we demonstrated, for the first time, that Te inclusions are the major impediment to good energy resolution in long-drift detectors [3]. More recently, we recognized that extended defects, e.g., dislocations, are another important performance-limiting problem, because they also act as trapping centers and lower the carrier-transport properties [4]. Consequently, we expect that before CZT detectors fully reach their potential and demonstrate the desired performance for large-volume devices, we must generate crystals relatively free from large inclusions and dislocations. However, the as-grown CZT crystals inevitably encompass them. The many efforts made to ameliorate this condition fall mainly into two groups. The first one is to optimize the growth processes. Nevertheless, simply adjusting parameters to realize these goals has proven to be difficult due to the complexities of growing nearly-stoichiometric CZT material. In contrast, the second one, post-growth annealing, offers more controllable, reproducible ways to modulate defects in CZT, and therefore, potentially is very promising. This realization is critical for the mass production of inexpensive, high-efficiency, high energy-resolution CZT radiation detectors.

At Brookhaven National Laboratory (BNL), we have built different facilities for investigating post-growth annealing, including using multiple-zone and single-zone-annealing furnaces, quartz-sealing systems, and related accessories. We used different CZT crystals to assess the effects of this approach. Here we report our findings, and discuss the factors affecting annealing behaviors.

2. EXPERIMENTAL PROCEDURES

The crystals investigated in this work were grown by different techniques, including the high-pressure Bridgman method (HPB), the conventional vertical Bridgman method (CVBM), and the travelling heater method (THM). We polished the surfaces of each crystal with a sequence of suspensions of alumina particles of 5 μm , 1 μm , and 0.1 μm . For the annealing experiments, the crystals were sealed in quartz ampoules with a Cd source under a vacuum of 10^{-5} Torr. Then, the sealed ampoules were put in the annealing furnace with predetermined temperature profile. Figs. 1 and 2, respectively, are photographs of sealed quartz ampoules and a two-zone annealing furnace.

Fig. 1. Sealed quartz ampoules with CZT crystals and Cd source.

Fig. 2. A two-zone annealing furnace used at BNL

CZT crystals are transparent to infrared (IR) light, while Te inclusions are opaque. Accordingly, Te inclusions can be seen in contrast images when IR light illuminates the crystals. Therefore, we used a customized IR transmission microscope to screen their size and distribution in CZT before and after annealing. A CCD camera collected the IR images, and quickly transferred them to a PC via a firewire cable. A XYZ-motorized translation stage, controlled with a C++ program specifically written for this task, allowed us to probe and relocate the microscope to an interesting region. This ability is very important for comparing changes in Te inclusions in the same region before and after annealing.

In the photoluminescence (PL) measurements, all the wafers were attached on a cold copper finger in a liquid helium cryostat that held the sample's temperature at 4.3 K. A 488-nm laser excited the sample. An iHR 550 tri-grating monochromator collected and analyzed the signals emitted from the crystals. Fig. 3 shows the set-up for the PL system.

Fig. 3. Low-temperature photoluminescence system developed at BNL

After etching the crystals' surfaces with a 2% bromine-methanol solution, we placed planar Au-CZT electrodes on the top and bottom surfaces of the crystals. Current–voltage (I-V) characteristic measurements were obtained via a Keithley 6487 picoammeter.

3. RESULTS AND DISCUSSION

Fig. 4 shows the IR images of a CZT sample annealed in a uniform temperature field at 700 °C for 60 hours; undoubtedly, annealing lowered the concentration of Te inclusions. At the same time, the size of the Te inclusions dropped from 5~8 μm down to 2-3 μm . Fig. 5 shows the IR transmission images of another CZT sample annealed at 700

°C for 10 hours with a temperature gradient of 10 °C/cm. Similarly, the concentration and size of Te inclusions were

lowered. However, we note that we did not observe a definitive migration of Te inclusions in such a small temperature gradient field. Since the size of Te inclusions in both as-grown CZT crystals is about 5~8 μm , i.e., relatively small ones, we also annealed CZT crystals with larger Te inclusions, 20 μm to 40 μm , under the same conditions (Fig. 6).

Surprisingly, the larger Te inclusions migrated even under our relatively small temperature gradient of 10 °C /cm at 700

°C. Since the annealing conditions are the same, clearly, the migratory behavior (and their rate) of Te inclusions is related to their size, viz., larger Te inclusions move more readily than do the smaller ones. One might expect that smaller

Te inclusions migrate within a large temperature gradient. So, to explore this, we raised the temperature gradient to 45 °C

/cm while keeping unchanged the rest of the annealing conditions. Interestingly, the smaller Te inclusions indeed started to move (Fig. 7).

Fig. 4 IR images of Te inclusions before and after the annealing in a uniform temperature field. (700 °C for 60 hours)

Fig. 5 IR images of small-size Te inclusions before and after the annealing in a temperature-gradient field of 10 °C /cm.

(700 °C for 10 hours)

Fig. 6. IR images of large-size Te inclusions before and after the annealing in a temperature-gradient field of 10 °C /cm.

Fig. 7 Migration of small-size Te inclusions during the annealing in a large temperature gradient of 45 °C /cm

We ascribed these migratory behaviors to the larger temperature difference between the cold end and hot end of Te inclusions brought by the greater temperature gradient. We consider that there are two mechanisms that remove Te inclusions during annealing: (1) Diffusion; and (2) thermo-migration. For the first one, Cd atoms will diffuse into the CZT matrix from the surrounding environment and form compounds with Te inclusions. Consequently, the Te inclusions dissolve as the Cd atoms bond to the excess Te within the CZT crystal. However, removing all Te inclusions will take a long time due to the slow diffusion of Cd atoms and will likely leave a large amount of excess Cd atoms distributed in the material. Thermo-migration is accounted for by the temperature difference between the cold end and the hot end of the inclusion after the temperature gradient is established. When the annealing temperature is higher than the melting point of Te, i.e., 449°C, Te inclusions will become liquid Te droplets embedded into the CZT. In this case, CZT will dissolve into the Te droplets from the hot end, while solidifying from the cold end and possibly from the relatively cold sides as well. Resultantly, Te inclusions will migrate from the low-temperature region of the ampoule to its high-temperature region. Since the surface tension of the small-size inclusions is high, this prevents the dissolution of CZT at the hot end and its solidification at the cold end. Also, when the temperature difference between the cold and hot ends is small, there is insufficient driving force to move the Te inclusions. In contrast, large-size Te inclusions have lower surface tension and a larger temperature difference between both ends. Similarly, heightening the temperature gradient also enlarges the temperature difference around the Te inclusions. Then, the difference between the dissolved CZT at the hot end and the solidified CZT at the cold end is greater, so promoting the migration of Te inclusions.

We noticed a change in the shapes of Te inclusions, from triangular or hexagonal into circular after the annealing, independent of the size of the Te inclusions in the as-grown crystals (see Fig. 8). This is consistent with our assumption that Te inclusions exist as liquid droplets at the annealing temperature. Their circular shape also reduces the surface energy of Te inclusions, which promotes migration. In addition, if two inclusions are located within a certain restricted range, they usually combine during the annealing (Fig. 9).

Fig. 8 Change in shape of Te inclusions before and after annealing (700°C and temperature gradient of 45 °C/cm).

Fig. 9 Te inclusions combine during the annealing (700°C and temperature gradient of 45 °C/cm).

To compare the changes in the density of dislocations, we used a Saucedo solution ($\text{H}_2\text{O}:\text{HNO}_3:\text{HF}+\text{AgNO}_3$) to reveal their etching pit density (EPD) [5]. As Fig. 10 illustrates, the EPD fell from $1.1 \times 10^4 / \text{cm}^2$ to $4.2 \times 10^3 / \text{cm}^2$ after the annealing at 700 °C. This signifies that the annealing releases stresses and reduces dislocations.

Fig. 10. Etching pit density of CZT crystal before and after the annealing

Fig. 11 shows the I-V curves of a CZT crystal before and after the annealing. Unfortunately, this process reduced the corresponding resistivity from $5.4 \times 10^{11} \Omega\text{-cm}$ to $4.2 \times 10^6 \Omega\text{-cm}$. The possible reason is that the only-Cd-vapor annealing that we employed also introduced extra Cd atoms after the Cd vacancies were compensated. Subsequent annealing steps in Te vapor might assure the recovery of the resistivity.

Fig. 11. I-V curves of CZT crystal before and after the annealing at 700°C under Cd overpressure

To understand this phenomenon better, we used low-temperature photoluminescence (PL) spectroscopy to characterize the change of defect-related levels in CZT. Fig. 12 plots the PL spectrum before and after the annealing. Two interesting features were found. Firstly, a very sharp donor-acceptor pair (DAP) peak appeared, which was not resolvable in the as-grown crystal. Secondly, the D band increased obviously after the annealing. As mentioned, the resistivity of as-grown CZT is very high ($5.4 \times 10^{11} \Omega\text{-cm}$), which means a full charge compensation was established in the crystal. In this case, most of dopant In atoms will exist in the neutral form of Cd vacancy-donor complex $(V_{Cd}-2In_{Cd})^0$. The Cd-vapor annealing introduced extra Cd atoms, which occupied those Cd vacancy sites originally occupied by In atoms. As a result, the acceptor complex $(V_{Cd}-In_{Cd})^-$ and the donor In^+ were formed accordingly, as shown in equation (1).

This is consistent with the decrease of resistivity after the annealing. The extra donor In^+ also increased the amount of DAP and strengthened DAP compensation, which was confirmed by the presence of the sharp DAP peak. Actually, we even observed the longitudinal optical (LO) phonon replicas of the DAP peak, (DAP-LO), on the right shoulder of the D

band after the annealing. Meanwhile, as the so-called A center, the complex $(V_{Cd}-In_{Cd})^-$ composed the D band together with DAP-LO peak. Extra $(V_{Cd}-In_{Cd})^-$ complex and extra In^+ both contributed to the increase of the intensity of D band.

Fig. 12. PL spectrum of a CZT crystal before and after the annealing at 700°C under Cd overpressure. The measurement temperature was 4.3K.

4. SUMMARY

We investigated the effects of post-growth annealing of CZT. Our experimental results show that the annealing in Cd vapor reduces the density of Te inclusions, while a large temperature gradient promotes the migration of small-size Te inclusions. Simultaneously, annealing lowers the density of dislocations. However, the only-Cd-vapor annealing lowers the resistivity, which may be caused by the introduction of extra Cd. We plan to adopt subsequent Te-vapor annealing to recover the resistivity after removing Te inclusions.

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