Characterization of Low-Defect $Cd_{0.9}Zn_{0.1}Te$ and CdTe Crystals for High-Performance Frisch Collar Detectors

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***Abstract*—Low dislocation density, high-purity, and low inclusion concentration $Cd_{0.9}Zn_{0.1}Te$ (CZT) and CdTe crystals were grown by a vertical Bridgman technique using in-house zone refined precursors. The grown crystals were sequentially processed using optimized chemo-mechanical processes to fabricate planar and Frisch collar detectors. Infrared transmission and scanning electron microscopy studies have shown that EIC grown CZT and CdTe crystals have significantly lower Te inclusions and defect densities than commercially available spectrometer grade crystals. The charge transport properties (electron and hole mobility-lifetime products, $\mu\tau_e$ & $\mu\tau_h$) of various detectors have been evaluated by Hecht analysis. The detectors have been tested for spectral response using 59.5 and 662 keV γ-ray sources. The CZT detectors with planar electrodes showed 2.6% FWHM at 662 keV. By adding a Frisch collar, the detectors' spectra improved significantly. The Frisch collar detectors proved to be very promising for assembling large-area arrays with excellent energy resolution at relatively low manufacturing cost.**

***Index Terms*—$Cd_{0.9}Zn_{0.1}Te$, CdTe, Frisch-collar, low defect density, semiconductor detectors.**

I. Introduction

THERE have been increasing demands for high-performance nuclear spectrometers for isotope identification in various areas, especially for homeland-security applications. As proven by the recent case of contamination of a major commercial airliner with radioactive materials, there is increasing need for highly efficient large-area radiation detectors for airport security and border crossing check points. Among many candidate materials for gamma-ray detectors, CdTe and $Cd_{0.9}Zn_{0.1}Te$ (CZT) are the most promising, due to their room temperature operation, high average atomic number ($Z \sim 50$), wide bandgap (≥ 1.5 eV at 300 K), and high density (~ 5.8 g/cm^3) [1]. Scintillator detectors combined with photomultiplier tubes are not able to provide as good of an energy resolution as CdTe and CZT detectors because of their high electron-hole pair generation energies (≤ 50 eV). Si and Ge detectors need cooling to liquid-nitrogen temperature due to high leakage currents from their low bandgap energy (E_g). For these reasons, CdTe and CZT have been the primary semiconductor materials used as room-temperature x-ray and gamma ray detectors for medical imaging, space astronomy, environmental monitoring, and national security applications [2]–[4].

However, CZT crystal growth by the high-pressure Bridgman (HPB) method results in low yields of the nuclear spectrometer grade crystals and also small crystal sizes. The HPB growth technique has the associated problems of easy formation of defects such as dislocations, Te inclusions, cracks, and non-uniform zinc composition. According to previous studies, Te inclusions and precipitates resulting from the growth process and retrograde solid solubility of CdTe system are attributed to affecting the leakage current of a detector and distorting the carrier transport in CdTe and CZT devices [5]. Te-rich regions of the crystals can be easily identified by infrared transmission microscopy. Defect formation in the crystal is significantly affected by mass and heat transport phenomena during the crystal growth operation [6], [7]. In order to address these issues, we have grown CZT and CdTe crystals from zone-refined precursors using a modified vertical Bridgman technique based on numerical modeling and simulation of the transport process during growth. The grown crystals were sequentially processed using chemo-mechanical polishing and surface etching. Then, the crystals were characterized by IR microscopy and scanning electron microscopy (SEM). Planar and Frisch collar detectors were fabricated from various locations of the ingots. Finally, the charge transport properties and spectral responses of the planar and Frisch collar detectors for ^{241}Am (59.5 keV) and ^{137}Cs (662 keV) sources have been evaluated.

II. Experimental

A. Crystal Growth

We have used a modified vertical Bridgman growth method to produce spectrometer-grade CdTe and CZT single crystals with a high yield [7]. Using numerical modeling and simulation of global heat transfer and thermal elastic stresses, the temperature distribution in the furnace, the flow patterns, and the interface shapes were predicted and experimentally verified. The thermal stresses caused by the non-uniform temperature distribution were also calculated and examined. Based on simulation

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and modeling results, CdTe and CZT crystals have been grown from stoichiometric amounts of in-house zone-refined precursor materials. For CdTe growth, the crystals were grown under controlled Cd overpressure. The details of simulation and modeling as well as the crystal growth conditions are described in our previous reports [7], [8].

B. Crystal Processing and Characterization

After crystal growth, several CdTe and CZT wafers (up to $10 \times 10 \times 10\ \mathrm{mm}^3$) were cut from the ingots using a low-speed diamond-impregnated wire cutter (South Bay Technology). The wafers were lapped and polished successively by emery powder, aluminum oxide powder, and diamond paste of various grain sizes down to 0.25 μm. The final polishing was carried out chemo-mechanically for about an hour with an alkaline silica gel. The final etching of the polished wafers was carried out by applying five to six times the following cycle: 1.0% Br_2-methanol dip for 60 s, ultrapure methanol rinse, 0.5% Br_2-methanol dip for 30 s, new methanol rinse, final drying by blowing pure nitrogen. The processed wafers appeared bright, shiny, and had a good surface finish. IR microscopy images were taken at Brookhaven National Laboratory (BNL) to characterize Te inclusions and their distributions within the processed crystals, and SEM pictures were taken at EIC to calculate the etch pit density of the crystals using an Everson etchant [9].

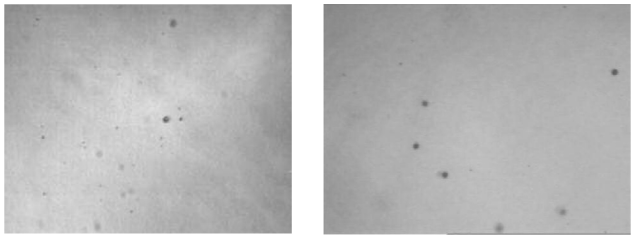
C. Detector Fabrication and Characterization

After surface processing, wafers were used for evaluating the physical, optical, and electrical properties of the CdTe and CZT crystals as well as for planar ($10.9 \times 10.1 \times 1.9\ \mathrm{mm}^3$) and Frisch collar ($5 \times 5 \times 10\ \mathrm{mm}^3$ and $6.1 \times 4.2 \times 6.4\ \mathrm{mm}^3$) detector fabrication. For both types of detectors, gold contacts (60–90 nm) were deposited on the two opposite faces of the detectors with DC sputtering using metal masks. The Frisch collar detectors were fabricated at Kansas State University (KSU) by following the procedure described in [10]. Nuclear detection measurements were carried out at room temperature by irradiating CdTe and CZT detectors with $^{241}\mathrm{Am}$ (59.5 keV) and $^{137}\mathrm{Cs}$ (662 keV) sources. For nuclear detection spectra measurement at EIC, we have used the same setup described in our previous report [7].

III. Results and Discussion

A. Material Characterization

After the crystal growth, we have obtained CdTe and CZT ingots with ≥ 2.5-cm diameter and up to 10-cm length. In order to characterize the stoichiometry of the grown crystals, energy dispersive analysis by x-rays (EDAX) was used. The EDAX results for four CdTe wafers cut at various axial positions along the ingot showed reasonably uniform stoichiometry ($\pm 0.5\%$ atomic). For EDAX spectra on five axial CZT wafers, there were about 5% deviations from stoichiometry of Zn at the top and bottom portions of the ingot but less than $\pm 0.1\%$ at the center. XPS analysis of the chemical compositions of CdTe and CZT crystals showed similar results.



(a) (b)

Fig. 1. IR microscope images of (a) CdTe and (b) CZT wafers. The average Te inclusion size was $\sim 10\ \mu$m for CdTe crystal and $\sim 8\ \mu$m for CZT crystal. Dark spots show Te inclusions.

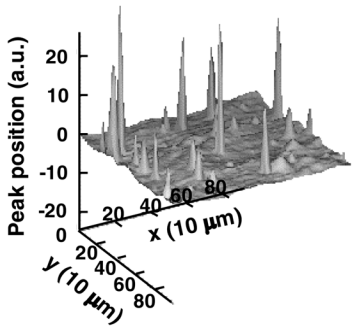


Fig. 2. Two dimensional x-ray mapping of a CZT detector, which shows the Te inclusion distribution. The scan was performed with a 30-keV beam with 10 μm$\times$ 10 μm size.

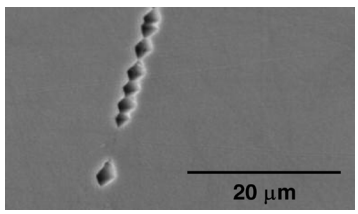


Fig. 3. Scanning electron microscope picture of etch pits on a CZT crystal after Everson etching.

Following the stoichiometry analysis, the crystals were evaluated by an IR transmission microscope to characterize Te inclusions distributions. It is reported in the literature that Te inclusions adversely influence the detector because they degrade the crystal with increased leakage current and deteriorated the x-ray and γ-ray spectral response [5], [11]. Thus, it is ideal to minimize Te inclusions for better detector performance.

Fig. 1 shows the IR images of the processed CdTe and CZT wafers. The dark spots in the pictures show the Te-rich regions. The small size and low density of Te inclusions in the crystals indicate good quality of the crystals for high-resolution nuclear detectors. The Te inclusions distribution in the CZT wafers were further characterized by 2D x-ray scans at the National Synchrotron Light Source at BNL. Fig. 2 shows the 2D x-ray mapping of a CZT crystal. A 30 keV monochromatic beam with a $10\ \mu\mathrm{m} \times 10\ \mu$m size was used for scanning a 1 mm $\times$ 1 mm area of a CZT crystal. For CZT, the absorption length of the 30-keV photon is ~ 0.3 mm. Thus, the beam is sensitive to defects in the near-surface region of CZT. In Fig. 2, the flat regions show a uniform device response, whereas the peaks show the locations of

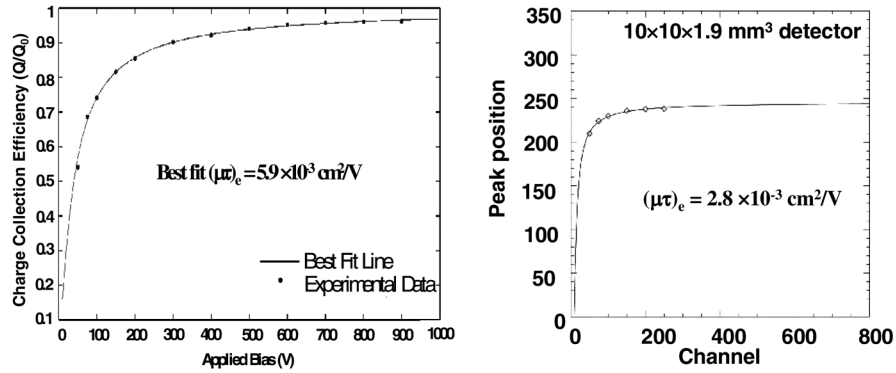


Fig. 4. (a) Electron $\mu\tau$ product of a CZT detector measured at S.M.A.R.T. Laboratory, KSU and (b) at BNL. Similar results were obtained at EIC Laboratories, Inc.

the inclusions in CZT and their associated charge loss. Because the Te inclusions deteriorate the spectral response of detectors, we can evaluate the uniformity and quality of the crystals for detector applications by this non-destructive method [5].

In addition, etch-pit densities (EPD) were measured by taking scanning electron microscope (SEM) pictures of the wafers after Everson etching. The EPD analysis showed an etch pit density to be $\leq 3 \times 10^4\ \mathrm{cm}^{-2}$ for CZT and $\leq 5 \times 10^4\ \mathrm{cm}^{-2}$ for CdTe, confirming the good crystal quality [12]. Fig. 3 shows the SEM image of etch pits formed on a CZT wafer after Everson etching. Both IR and SEM studies have shown that EIC-grown CZT and CdTe crystals have lower Te inclusions and defect densities than commercially available spectrometer-grade crystals, which show potential for fabrication of high-resolution and high-efficiency nuclear detectors.

B. Device Characterization

Using the detectors fabricated by the steps described in the experimental section, the current-voltage (I-V) characteristics were measured to estimate the bulk resistivities. From these measurements, the leakage current, which adversely affects detector quality by increasing noise, was quantified. For both CdTe and CZT detectors, the leakage currents were very small (5–8 nA at $-1000\,V$). From the linear regression of the dark I-V curves, the electrical bulk resistivity was estimated to be $\sim 1.5\times 10^{10}\Omega\cdot\mathrm{cm}$ for CdTe and $\sim$ 2-5 $\times\ 10^{11}\Omega\cdot\mathrm{cm}$ for CZT. From the I-V measurements, the operational voltage ranges of the detectors were determined, and the charge transport properties of electrons and holes were evaluated by measuring pulse positions at different bias voltages.

By changing the polarity of the applied bias, the mobility-lifetime product $(\mu\tau)$ for electrons [Fig. 4(a) and (b)] and holes were estimated using Hecht analysis [13]. In order to see the effect of zone-refining, the CZT crystals grown from 6 N purity precursor materials were also evaluated. The $^{241}\mathrm{Am}$ source was used for the $\mu\tau$ product measurements. The results are summarized in the Table I.

From the table, the CdTe and CZT crystals grown from zone-refined precursors showed $(\mu\tau)_e = 2 \times 10^{-3}$ and 3–6 $\times 10^{-3}$, respectively. These results confirm the effectiveness of ZR to improve crystal transport properties. From the results, the CdTe has advantage in the more balanced electron and hole transport properties, whereas the CZT has an order of magnitude higher resistivity. Moreover, by comparing materials' properties of different purity precursors, it is evident that using zone-refined precursors is beneficial because of the higher resistivity and superior charge transport properties.

TABLE I
COMPARISON OF CHARGE TRANSPORT PROPERTIES OF ELECTRONS AND HOLES

Parameters	CdTe (EIC's ZR Precursors)	$Cd_{0.9}Zn_{0.1}Te$ (6N Purity Vendor Precursors)	$Cd_{0.9}Zn_{0.1}Te$ (EIC's ZR Precursors)
Resistivity (Ω·cm)	1.5×10^{10}	$\sim5\times10^{9}$	$\sim2\text{-}5\times10^{11}$
Electron μτ product (cm^2/V)	2×10^{-3}	$\sim10^{-3}$	$3\text{-}6\times10^{-3}$
Hole μτ product (cm^2/V)	8×10^{-5}	2×10^{-5}	$4\text{-}6\times10^{-5}$

The pulse height spectra were measured for planar detectors of CdTe and CZT fabricated from the middle portions of the grown ingots. Fig. 5 shows the detection spectra of single-element CdTe and CZT detectors. For the CdTe detector, a negative bias of -600 V was applied, and an $^{241}\mathrm{Am}$ source was used as a nuclear source. Fig. 5(a) clearly shows the 60 keV peak of the $^{241}\mathrm{Am}$ with an energy resolution of $FWHM = 6.2\%$ with clearly visible lower energy x-ray peaks. For the CZT detector, a negative bias of -1800 V was applied, and a $^{137}\mathrm{Cs}$ source was used. The CZT data were taken at BNL. Fig. 5(b) shows a sharp 662-keV energy peak of $^{137}\mathrm{Cs}$ with $FWHM = 2.6\%$. The digital pulse analysis was carried out at BNL and is shown in Fig. 6. Fig. 6 (left) shows the amplitude on the output signal versus rise-time, and Fig. 6 (right) shows the corresponding pulse-height spectrum. In Fig. 6 (left), the line at channel number 200 illustrates electronic noise. From the figure, the total energy deposition curve is broad and gets broader with rise time. This broad distribution is explained by the presence of Te inclusions [14].

Furthermore, Frisch collar detectors were fabricated and tested at KSU [Fig. 7(a)]. The detector performance was compared for the planar and Frisch collar configurations from the same boule. Fig. 7(b) shows the pulse-height spectra of

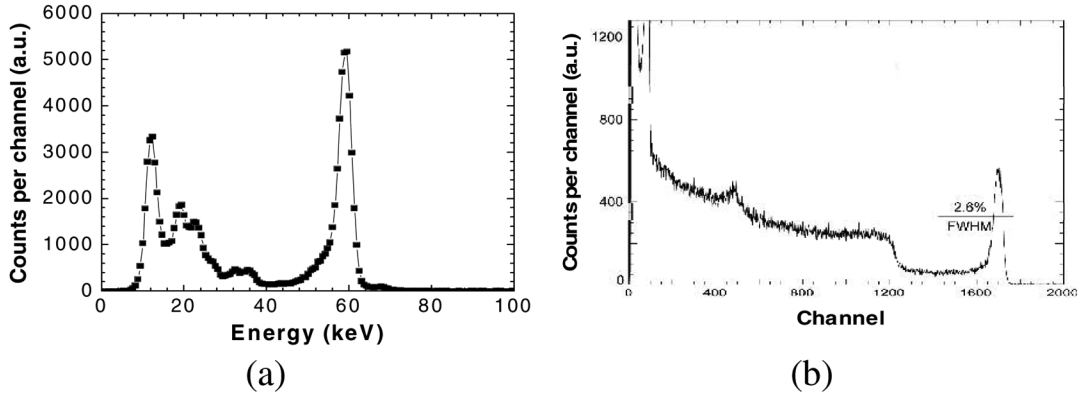


Fig. 5. Pulse-height spectra of (a) CdTe detector (Dimension: 6.9 mm × 6.9 mm × 4.8 mm, source: ^{241}Am, bias: -600 V, shaping time: 1 μs) and (b) CZT detector (Dimension: 5 mm × 5 mm × 10 mm, source: ^{137}Cs, bias: -1800 V, shaping time: 1 μs, measured at Brookhaven National Laboratory).

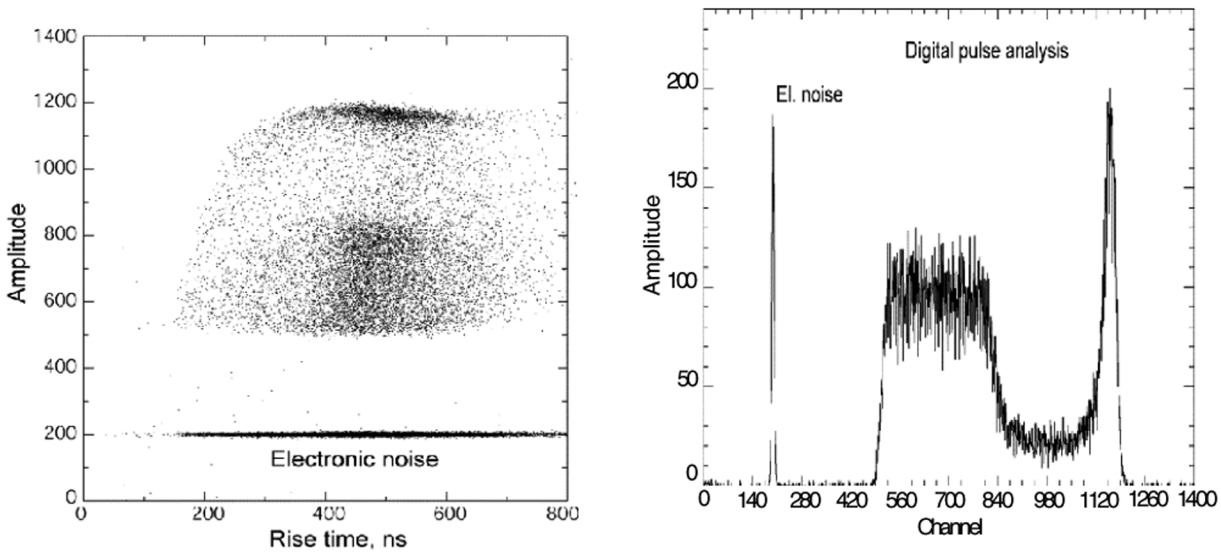


Fig. 6. Total energy deposition curve for a CZT detector (left); corresponding pulse-height spectrum (data measured at BNL) (right).

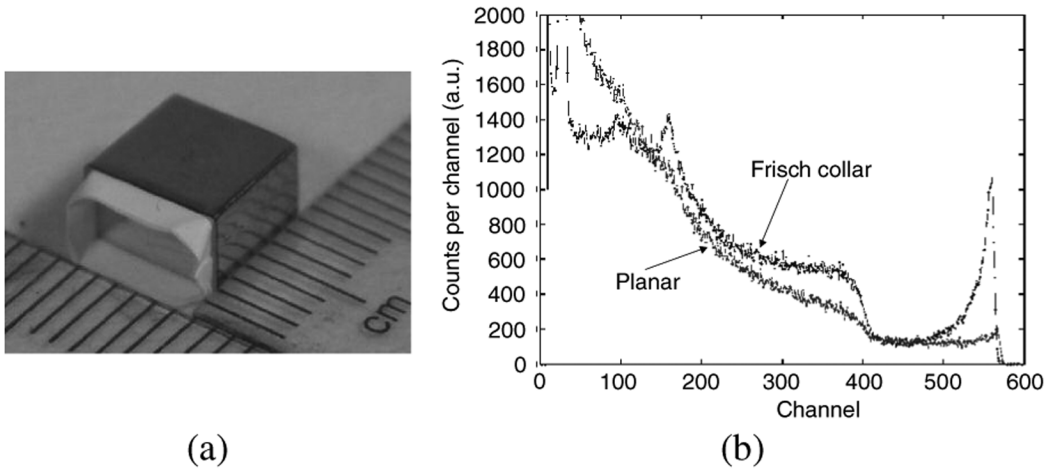


Fig. 7. (a) Digital picture of a Frisch-collar detector fabricated at Kansas State University. (b) Comparison of the pulse-height spectra of CZT planar and Frisch-collar detectors. (Dimension: 6.5 mm × 4.5 mm × 6.5 mm, source: ^{137}Cs, bias: -1000 V, shaping time: 1 μs, measured at Kansas State University).

planar and Frisch-collar detectors at -1000 V irradiated by a ^{137}Cs source. The result shows that the addition of Frisch collar improved the detection spectrum significantly. For planar detectors at 662-keV, the energy resolution measured was 7.8%, whereas the energy resolution improved significantly to 2.8% with Frisch collar configuration. The Frisch collar detectors are very promising for assembling large-area arrays with outstanding energy resolution at relatively low manufacturing

cost. By characterizing crystals from the entire ingot, we have obtained over 50% yield of the spectrometer-grade quality crystals.

IV. Conclusion

We have grown low defect density and high-quality CdTe and CZT crystals by using high-purity ZR precursors and improved heat and mass transport during crystal growth. The Frisch-collar detectors fabricated from the EIC-grown crystals showed very promising results for assembling large-area arrays with good energy resolution at relatively low cost.

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