Direct Observation of influence of secondary-phase defects on CZT Detector Response

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ABSTRACT

Commercial detector-grade cadmium zinc telluride (CZT) crystals still suffer from various types of extended defects, e.g., dislocations, micro-grains, grain boundaries, and Te-rich secondary phases. Most of these defects cannot readily be identified and characterized using conventional techniques, though they are believed to be the dominant factor causing non-uniformity in the detector response. In this work, we revealed and characterized these secondary-phase defects in CZT crystals by employing multiple advanced techniques, e.g. X-ray diffraction topography, micro-scale X-ray response mapping, chemical etching and infrared microscopy. We then evaluate the detector performance of the crystals by recording high spatial-resolution raster scans of the charge collection and spectral response. We directly correlated the influence of the secondary-phase defects on the performance of the detector responses. The experimental results exhibit clear evidence of the undesirable effects of extended defects on the performance of commercial CZT radiation detectors.

PACS: 81.05.Dz ; 61.72.Ff

Keywords: A1. Defects, A1. Characterization, A1. Etching, A1. High resolution X-ray diffraction, B1. Cadmium compounds, B2. Semiconducting Cadmium compounds.

1. Introduction

In recent years, cadmium zinc telluride (CZT) detector technology has gained popularity in applications of nuclear security, medical imaging, and high-energy physics [1-5], because of its ambient-temperature operation, compact size, and promising energy resolution. However, the widespread usage of CZT detectors remains limited by the low yield of high-quality, detector-grade crystals and their associated cost. Over the past decade, many problems related to crystal defects have been identified pertaining to the performance of CZT crystals, and reductions of these defects have taken the technology to a more advanced stage [6-7]. Now large-volume, high-resistivity CZT single crystals can be produced, but there is a wide variability in their performance due to structural defects e.g., dislocations, sub-grains, Te inclusions, and Te-rich secondary phases. These defects are primarily generated during crystal growth or post-growth treatments (e.g., ingot cool-down or post-growth annealing) [8-9]. Most of these defects are neither readily identified nor easily characterized by conventional techniques, so the defects in these crystals are often overlooked, although they are usually the root cause of the degraded performance of the detectors.

Some of the defects (e.g., grain boundaries and twins) are easily identified during initial screening, which helps to select acceptable crystals for fabricating into devices. However, some other known defects, e.g. micro-twins, sub-grains and dislocations, are not readily visible by the conventional screening techniques; nevertheless, they can have significant impact on the device performance. To identify them, additional techniques are needed, including chemical etching, x-ray diffraction topography, and transmission electron microscopy.

In this work, we employed a collection of advanced experimental techniques to reveal the nature of extended defects and determine their concentrations in commercially available detector-grade CZT crystals. We carried out a series of experiments using high spatial resolution X-ray diffraction mapping and different chemical etching methods to assess the density and network of dislocations, strain fields and other crystallographic defects. In addition, we conducted

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high spatial resolution charge-collection mapping [10] using a highly-collimated synchrotron x-ray beam to determine a precise nature of the remaining defects in the detectors. The roles of different specific crystalline defects were identified by correlating the signatures with the detector responses. The results revealed clear evidence of undesirable effects of the extended defects on performance of CZT radiation detectors.

2. EXPERIMENT

We employed commercially available detector-grade as-grown and annealed CZT crystals grown by Bridgman method and Traveling Heater Method (THM). We have characterized the presence of dislocations, sub-grains, and other secondary-phase defects of both type of crystals and evaluated detector performance of one planar and one pixelated detector. The samples were mechanically polished using a fine-grade alumina powder, followed by chemo-mechanical polishing with a 2% Bromine solution. We used a hydrofluoric acid (HF) based selective etchant [11] to reveal the dislocation-related defects on (111B) oriented surfaces. The etched surfaces were investigated, and images were registered using an optical microscope. We also exploited alternative technique, white beam X-ray diffraction topography to reveal the sub-grains and other secondary-phase defects in the crystals and for correlating the microstructure with our characterization data on carrier trapping. Afterwards, we carried out high spatial-resolution raster scanning to map the charge-collection properties of the CZT planar and pixelated detectors. We took advantage of a synchrotron X-ray source that affords us a spatial resolution as low as 10 μm and tunable x-ray energy to determine the fine details of the role of existing crystalline defects on the charge-transport properties in fabricated detectors. The detectors were mounted on a standard brass holder in which a gold-plated spring contact held the detector against a beryllium window that also acted as the cathode. During x-ray response scanning, the cathode side of each detector was irradiated by a collimated x-ray beam. The brass holder was connected to a preamplifier, and the whole unit was placed on a three-dimension translation stage capable of sub-micron resolution, allowing us to obtain repeatable raster scans with high precision. For each irradiated point of the raster scan, a pulse-height spectrum, corresponding to the excited area was recorded through a multi-channel analyzer and stored for further processing. The data were analyzed and displayed as 2-D maps. Energy spectra were also obtained with an Am-241 sealed radioactive source.

3. RESULTS AND DISCUSSIONS

3.1 Dislocations and sub-grains

Dislocations and sub-grain boundaries are present in CZT crystals regardless of the growth technique. These defects are primarily generated during crystal growth and post-growth treatments, and are not easily revealed by conventional techniques due to their dimensions and characteristics. It is important to reduce the size and concentration of defects in the crystals for trading off with the acceptable detector performance. We employed multiple techniques, e.g. white beam x-ray diffraction and selective etchants, to characterize these defects. **Fig. 1** displays dislocation etch-pits on the etched surface of an as-grown BM grown crystal. The shape and pattern of the etch pits in the images are, in fact, commonly arranged in linear patterns like the one illustrated in **Fig. 1a**. **Fig. 1b** shows a reconstructed image by tracing out individual etch pits using software we developed to quantify the concentration of the pits. The reproduced image shown in **Fig. 1b** replicates the original etch pits, and the estimated etch-pit density (EPD) is in the range $10^3 - 10^4 \text{ cm}^{-2}$. Usually the dislocation density in CZT crystals are larger than $5 \times 10^4 \text{ cm}^{-2}$ and in Si crystals is less than $1 \times 10^3 \text{ cm}^{-2}$ [12]. A high-magnification SEM image shows the typical shapes and sizes of dislocations (**Fig. 1c**). The etch pits reveal the exit points of the dislocations, and their linear associations represent dislocations that are aligned along the sub-grains extends their network into the crystal bulk often assimilated in virtual walls[13-16] that act as trapping centers for charge carriers while drifting towards the electrodes and eventually, degrade the detector performance. However, it is not easy to identify them either with selective etching process as they have limited reactivity other than 111A or 111B planes or any other conventional method. We employed a high spatial resolution X-ray diffraction mapping technique [17] to reveal these dislocations through other crystallographic orientation. We selected a mirror-like cleaved surface as the surface planarity is critical for this measurement to minimize the background reflected noise that may overwhelm the actual signals. We obtained a raster scan of X-ray diffraction with 10- μm spatial resolution of a selected $2 \times 1\text{-mm}^2$ area on the surface and recorded the diffraction images at each points (**Fig. 2c**) and reproduced the orientation and intensity images. **Fig. 2a** displays the perfectly orientated with only $\sim 0.03^\circ$ variation. A low index pole picture shown in **Fig. 2b** indicates

the surface orientation to (011). From intensity image shown in **Fig. 2d**, it can be seen that the dislocation line appeared on the crystal surface that extended from the top surface to the deeper into the bulk. The pixel intensity of some of the areas was recorded high likely due to different reflectivity of the sample surface.

There are also star-shape dislocation clusters (also called punching defect) found in THM grown annealed CZT crystals. The characteristics of these punching defects are different than the six-pointed Cd inclusions reported elsewhere [18-19]. They usually formed during the post-growth annealing in a Cd overpressure at temperatures higher than Te melting point [20]. Cd atoms interact with Te inclusions during annealing and dissolve into CdTe matrix and resulting in an empty corona and strain surrounding area of the interaction point. On the other hand, Cd inclusions are generated during the crystal growth at a certain condition with excess Cd and randomly distributed into the CZT matrix. Punching defects are usually invisible in infra-red light unlike the Cd- inclusions. Selective etching revealed these defects on crystal surface as shown in **Fig. 3a**. We measured the size and concentration of the features, and generated a model [21] to simulate their impacts on detector performance. Here, we employed X-ray diffraction mapping technique to determine their shapes and structures. A raster scan was carried out with a 10- μm step, where each position generates multiple diffraction images. All the images from different coordinates and angles were recorded and compiled to produce a complete image of the selected area of the crystal. **Fig. 3b** shows the intensity map of the feature acquired from the high spatial resolution fluorescence raster scan. The compiled 2D images of the features at different orientations are shown in **Fig. 3c-h**, where the star-shaped defects appeared variable shapes from different orientations and the strain field surrounding the defects extends to volumes larger than the actual defect size. It is likely that the impact of such punching defects is much larger than their actual size which is consistent with the results reported by F. Sheng et al. [22].

3.2 Impact on Device Performance

Our model demonstrated that star-shaped features substantially reduce the detector's photopeak efficiency [21]. In order to record an experimental evidence of impact of these defects on detector performance, we carried out experiments to observe directly the influence of these defects on detector performance. We selected an 8x8 pixelated CZT detector shown in inset of **Fig. 4a** and captured an X-ray diffraction image of the detector area which clearly revealed the defects contained in the detector crystal as shown in **Fig. 4a**. We chose a 2x2 pixel area, which contains defects including a large visible defect at bottom-left pixel, and conducted a 10- μm step raster scan for mapping charge collection using a highly collimated 26-keV synchrotron X-ray beam. **Fig. 4b** shows the charge-collection map of four pixels, where each pixel size is 4mm². It can clearly be seen that more than 50% charge loss occurs in the pixel with a large star-shaped defect which can be the direct evidence of the detrimental effect of punching defects on detector performance. Like the other secondary-phase defects, these features also act as a trapping center and trapped the charge carriers surrounding area while they drifted toward the electrodes which reduce the photopeak efficiency of the projected detector's active area. Therefore, the non-uniformity in detector response over the large active-area of the detector was reflected at the charge collection mapping image produced by high-spatial resolution raster scan. The severity of the influence is less in thick detector ($\geq 5\text{mm}$) than in thin ones. In addition, the point of interactions is closer to the defect has higher impact than ones further away from their downstream pathway. Nevertheless, this experimental result provides direct evidence of the detrimental role of the star-shaped features, consistent with our simulation results. It is essential to remove these defects in order to improve the performance of fabricated detectors.

Furthermore, to observe the impact of such defects on spectral response, we selected a 15x15x5mm³ CZT crystal that contained secondary phase-defects. The texture of the crystal was revealed on surface by selective etchant beforehand to choose the region of interest precisely. After reprocessing the etched crystals, Au-contact with a guard-ring was deposited one at a defective region and another at a defect-free region. Guard-ring was used to minimize the interference of induced charge from outside the detector's active area. The optical image of the surface texture at the active detector areas and the corresponding detector responses are shown in **Fig. 5a**. We recorded pulse height spectra individually from each contact area. In pulse height spectra shown in **Fig. 5b**, it can be seen that the photopeak efficiencies within the defective region are noticeably reduced, and the peak-to-noise ratios for the lower energy peaks are also degraded compared to the response within the clear regions. Such non-uniformity and associated degradation occurs in a manner that is not easily detected by observing only the energy resolution of the photo-peaks.

4. Conclusions

We revealed dislocation wall, punching defects and associated strains in the commercially available detector-grade CZT crystals, and determined their precise shapes and locations using a unique X-ray diffraction mapping technique. We demonstrated the experimental evidence by directly measuring the detector performance over the defects, which help to make one-to-one correlation to the impact of the specific defects on detector performance. The experimental results suggest that both dislocation walls and punching defects trap charge carriers resulting in non-uniformity in detector response over the large active-area of detector, which was replicated in the charge collection mapping image produced by high-spatial resolution raster scan. Further studies are needed to reduce these defects by altering the growth and/or annealing process, thereby increasing the yield of high-quality crystals.

Acknowledgement

This work was supported by U.S. Department of Energy, Office of Defense Nuclear Nonproliferation Research and Development, DNN R&D. The manuscript has been authored by Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The United States Government retains, and the publisher, by accepting the article for publication, acknowledges, a world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for the United States Government purposes.

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FIGURE CAPTIONS

Fig. 1. (a) Optical image of an etched CZT surface. Dislocation etch-pits appeared on [111] oriented surfaces, and some are aligned along the sub-grains, which extend into the bulk; (b) Reconstructed image of fig. 2b used to determine the dislocation density. (d) High-magnification SEM images show clearly the shape and size of the dislocations

Fig. 2. (a) A cleaved surface of a CZT detector crystal. (011) orientated surface is almost homogeneous with only $\sim 0.03^\circ$ variation across sample. (b) Cartoon of a low index pole figure that indicates the surface orientation. (c) Diffraction images collected at each point over the scan area for generating the area image. (d) X-ray micro-diffraction mapping image of a $2 \times 1 \text{ mm}^2$ area of a CZT crystal. Dislocations revealed on this surface.

Fig. 3. (a) An optical image of an etched surface of a CZT annealed crystal. Star-shaped dislocation clusters are appeared on the surface. (b) 2D intensity map was collected by using X-ray diffraction raster scan. (c-h) images of the features at different orientations

Fig. 4. (a) X-ray micro-diffraction image of a CZT pixelated detector (detector shown in inset). Image depicted the star-shaped punching defects randomly distributed in the CZT crystals. (b) High spatial resolution charge-collection map of a 2×2 pixel (marked area) with a visible defect in one of the voxels. Significant charge losses are evident due to the presence of the large star-shaped punching defect.

Fig. 5. (a) Optical image of the etched surface of a $20 \times 20 \times 5 \text{ mm}^3$ CZT crystal. The distribution of the defects appeared on the surface. Spectral measurements were taken in the clear and defective regions of the crystal. (b) Spectral responses were acquired individually from the clear and defective regions. Degradation can be observed in the photopeak counts and peak-to-noise ratio from volumes with a higher concentration of defects.

Fig. 1

Fig. 2

Cleaved CZT surface oriented to (011)
with a 0.03° variation

Micro-diffraction
raster scan mapping

Fig. 3

Fig. 4

Fig. 5