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ABSTRACT

Using a CdZnTe sample detector, a variety of diagnostic tools are applied, so as to assess the crystal characteristics and to compare these to the X-ray response measured with synchrotron radiation. Correlations are found, such that X-ray response degrading processes can be identified. In this respect the performance of the detector is found to be limited by both large scale defects such as some grain boundaries and also pipes and by crystal imperfections, together with impurities and other crystal defects, both at the surface and in the bulk crystal. The relatively soft CdZnTe crystals are very sensitive to improper handling, producing particularly surface damage, which in turn deteriorates the detector performance, as is rather clearly established by photoluminescence measurements.

Keywords: X-ray detectors, CdZnTe, X-ray astronomy, compound semiconductors

1. INTRODUCTION

Future X-ray astrophysics missions exploring the energy range 10 to 100 keV will require imaging solid state detectors to provide a wide field coverage with medium energy resolution and good timing and spatial characteristics. Missions currently under study for the post XMM and AXAF eras feature higher energy imaging X-ray telescopes. In parallel to the development of the hard X-ray imaging telescope technology a commensurate effort will be required to ensure that sensitive imaging detectors for the focal plane will be available.

A number of such candidate compound semiconductors are under study as the detector base material, with CdZnTe (CZT) being one of the most advanced materials. CZT has been extensively studied over the past few years. For extensive reviews the reader is referred to Schlesinger et al.¹ CZT offers the potential of low noise and large sizes with high X-ray stopping power. For example a 2 mm thick CZT crystal has a photoabsorption efficiency of $\geq 80\%$ at 100 keV. However currently the energy resolution of detectors based on CZT is inadequate for astrophysical applications. For example the measured resolution of CZT detectors is comparable to those obtainable for high pressure Xenon gas scintillation counters² (some 2% at 60 keV) and is far away from the anticipated Fano limited resolution of $\sigma_E/E_x = 235.5 * (F * w/E_x)^{0.5} = 0.8\%$, with $F=0.138$ and $w=5 \text{ eV}^3$ at $E_x=60 \text{ keV}$.

In this paper we present the first results of a programme to establish the fundamental spectroscopic limitations of CZT as a detector base material with a specific application in X-ray astrophysics over the range 10 - 100 keV. A variety of diagnostic probes have been utilized to establish the relationship between energy resolution, X-ray signal and crystal morphology. The current results are restricted to X-ray energies below $\sim 5 \text{ keV}$ so as to establish the linkage between the crystal surface and subsurface morphology and X-ray signal. Future work will probe the response deeper into the crystal at X-ray energies closer to our long term application ($\geq 10 \text{ keV}$).

2. DETECTOR FABRICATION

The crystal used in our investigations is coded B2925 and was procured from eV Products, USA. This crystal of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, with $x \approx 0.12$ and $\rho = 5.9 \text{ g cm}^{-3}$, was $5 \times 5 \times 2 \text{ mm}^3$ in size and was grown by the High Pressure Bridgman (HPB) technique. It was fabricated from boule B29. After cutting and inspecting the crystal was chemically polished in a 5% bromine/methanol solution to remove surface damage.⁴ The Au contacts were then produced by electroless deposition at the crystal manufacturer's plant, immediately after the etching.⁵

After receipt of the crystal, it was characterized by current-voltage and spectroscopic measurements. The crystal was then packaged as a detector into an evacuated aluminium housing, implementing a dedicated Peltier cooler, able to cool the detector crystal and the low noise matched FET down to $\approx -35^\circ\text{C}$. The room temperature resistivity was found to be $2 \times 10^{10} \Omega \text{ cm}^{-1}$, with ohmic contact behaviour. From α -radiation measurements the electron mobility/lifetime product was measured as $\mu\tau = 3.76 \times 10^{-3} \text{ cm}^2/\text{V}$ at room temperature. The spectral resolutions at 5.9 keV (Fe-55) and 60 keV (Am-241) were $\text{FWHM}_{5.9 \text{ keV}} = 480 \text{ eV}$ and $\text{FWHM}_{60 \text{ keV}} = 1500 \text{ eV}$, respectively, as measured at -30°C with full area illumination. The detector was considered of spectroscopic grade, but with somewhat poor peak to background ratio. All measured values are in good agreement with the literature.^{6,1} The electronics used consisted of a transistor reset preamplifier and common NIM-electronics shaping amplifier.

3. X-RAY PERFORMANCE

3.1. Experimental setup

The morphology of the CZT detector was mapped using two beamlines at the synchrotron radiation laboratory BESSY, namely the SX-700 PTB beamline and the general use KMC beamline.^{7,8} Together, these two beamlines cover the energy range 30 eV to 5.9 keV, and include the two absorption edges Cd-L_{III} and Te-L_{III} at 3.54 keV and 4.34 keV, respectively. A detector signal response map of the $5 \times 5 \text{ mm}^2$ detector area was obtained at 1.7 keV, measuring at 9×9 positions with a pitch of $500 \mu\text{m}$. In addition, two linear orthogonal scans were made at an energy of 2.5 keV with a stepwidth of $100 \mu\text{m}$. Further, an energy scan at the center of the detector was performed, measuring at the X-ray energies 1.7, 2.0, 2.5, 3.0, 3.488 & 3.588 (Cd L_{III}), 4.291 & 4.391 (Te L_{III}), 5.89 keV. In all these measurements, except those at 5.89 keV, the synchrotron beam profile was approximately gaussian, with a $\text{FWHM}_{\text{pos}} \approx 200 \mu\text{m}$. The beam was monochromatic, with the FWHM_E of the order of a few eV. The countrate was adjusted such to be low enough to avoid electronic distortions and was typically about 1 kHz. The test detector was used in the same electronic configuration as described in the section above (detector fabrication).

3.2. Spectral response maps

The low energy of the X-ray photon beam used in these experiments allows us to probe the detector response and relate this to the potential surface and sub-surface morphology of the sample. Figure 1 shows the $1/e$ penetration depth as a function of X-ray photon energy for CZT. Clearly the photoabsorption occurs not only in the first few microns in the Z direction, but the spread in this absorption point is very small. This allows also for the complete charge transport properties across the complete crystal thickness of $\sim 2 \text{ mm}$ to be examined as a function of position in the X, Y plane. Internal crystallographic features, as can be identified using such techniques as IR microscopy and photo-luminescence spectroscopy (PL), can then be correlated with the X-ray signal $G(E_x, x, y)$.

Figure 2 (a) shows a contour map of the detector signal $G(E_x, x, y)$ at $E_x = 1.7 \text{ keV}$. Spatially dependent signal variations of as much as 10%, defined as $(G_{\text{max}} - G_{\text{min}})/G_{\text{mean}}$, were observed. While a 10% signal variation may have a relatively minor contribution at 1.7 keV, it may become the dominant contribution to the energy resolution at higher energies.

The on-axis collimated response to a $200 \mu\text{m}$ diameter beam of photons from 1.7 to 4.5 keV was obtained at the center of the detector ($x=0, y=0$), which is a high signal region of figure 2 (a) at 1.7 keV. The detector signal $G(E_x)$ is shown as a function of photon energy in figure Figure 2 (b). The linearity of the detector is better than 2% over this limited energy region. The responsivity of the detector, $R = G(E_x)/E_x$, is therefore essentially constant and independent of X-ray energy. Note the mean penetration depth varies from 0.5 to $4.5 \mu\text{m}$ over the same energy range. Clearly any charge transport losses, which reduce the signal detected $G(E_x, x, y)$ due to recombination and trapping sites through the crystal does not effect R.

Figure 1. The X-ray penetration depth ($1/e$) in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, with $x=0.12$, as function of X-ray photon energy. The L_{III} absorption edges of Cd and Te are also indicated. Note all X-ray measurements reported here probe the first 5 μm of the crystal and its subsurface structure.

The effect of sub-surface defects and charge losses are best observed through measurement of the resolution, see figure 2 (c). The energy resolution does not however follow a $E_x^{1/2}$ function at lower energies.

To investigate the possibility of additional variances contributing to the spectral response function we define a spectral response quality factor $QF = (\text{Tail-Gauss}) / \text{Gauss}$, where 'Tail' is the integral of the low energy half of the measured response function after background subtraction, and 'Gauss' is the integral of the fitted gaussian response function. Effectively QF measures the skewness of the spectral response distribution at lower energies, particularly when normalized to the peak position. Those events present in the skewed part of the distribution are possibly events absorbed rather close to the surface, where surface trapping sites and contaminations like oxides will increase the charge loss. Figure 2 (d) shows the spectral distribution quality factor QF as a function of X-ray photon energy. Now we clearly see the effect of the Cd- L_{III} and Te- L_{III} absorption edges on the response function, indicating a surface and sub-surface damage charge loss mechanism.

The effect of such surface and sub-surface loss processes on the energy resolution can be further illustrated by a collimated 200 μm beam diameter measurement at 2.5 keV, taken in a high and a low signal region of the detector, $G(x_{high}, y_{high})$ and $G(x_{low}, y_{low})$, respectively, where the $\Delta G \approx 10\%$. Figure 3 shows the spectral distribution functions for (a) $G(x_{low}, y_{low})$ and (b) $G(x_{high}, y_{high})$. In the low signal region the energy resolution has degraded from 20 to 29% (~ 500 to 725 eV). Simultaneously the low energy tail became more intense, indicating a different charge loss between the two regions, due to different sub-surface damage or bulk properties.

To investigate further the spatial frequencies over which these variations in $G(E_x, x, y)$ occur, two orthogonal scans were performed at 2.5 keV with a resolution of 100 μm and shown in 4 (a,b). This further aids the identification of variations in $G(E_x, x, y)$ with specific crystal defects (see next section). It is clear that major changes in signal are seen in these scans and will be identified with specific regions of the crystal in the next section.

The inserts in figures 4 (a) and (b) show histograms of the detector signal for the high signal areas (i.e. disregarding discontinuities) for the X- and Y-scan, respectively. The fluctuations there, on a spatial scale of 100 μm to 1 mm, are as low as a few 0.1%, and never exceed 1%. Thus the poor energy resolution seen in figure 3 (b) of $\sim 20\%$ at 2.5 keV for a highly collimated beam (200 μm diameter) are due to a rather uniform (at a resolution of 100 μm) crystal properties extending over larger areas (few mm in size). Of course the crystal might well be very non-uniform on a microscopic scale.

Figure 2. (a) Contour plot of detector signal $G(E_x, x, y)$ as function of position. The contours are linearly spaced, with a dynamic range of 80 to 90. The peak to valley compared to the mean is $\sim 10\%$. The map corresponds to the complete detector crystal size of $5 \times 5 \text{ mm}^2$. The X-ray probe energy was 1.7 keV, which has a mean penetration depth of only $0.7 \mu\text{m}$, while the beam size was $200 \mu\text{m}$ diameter. Cubic interpolation was used to generate the image. (b) The detector signal linearity of a high signal region $G(E_x, 0, 0)$ of $200 \mu\text{m}$ diameter as a function of X-ray photon probe energy. The signal is remarkably linear with energy to within $\leq 2\%$. (c) The energy resolution of the same region as a function of photon energy. The $E_x^{-0.5}$ relation is also shown as a solid line, indicating the worsening resolution towards lower energies due to electronic noise and possibly fluctuations due to trapping of charge carriers near the surface. (d) The energy distribution quality factor (see text) as a function of X-ray photon energy for the same $200 \mu\text{m}$ diameter region. The L_{III} absorption edges of Cd and Te are also indicated. The quality factor appears to be related to the $1/e$ depth of the photons, possibly indicating losses during charge transport due to traps and recombination centers.

Figure 3. The X-ray spectra in low (a) and high (b) signal areas, taken with a collimated 200 μm diameter monochromatic beam of 2.5 keV.

Figure 4. The signal variations at 2.5 keV in two orthogonal scans across the detector (a): X-scan, (b): Y-scan. The images on the left show the location of the scans, superimposed on SEM images of the detector crystal. The inserts show histograms of detector signal distribution for the high signal areas (i.e. in the 'flat' areas, away from crystallite boundaries or pipes). Note that the uniformity in these 'flat' areas is about 1%.

Figure 5. Optical (Nomarsky) micrograph of the test sample, $5 \times 5 \text{ mm}^2$ in size. The surface roughness is partly due to the removal process of the the Au coating. The spot in the upper left corner is a marker, the large (4.5 mm diameter) circular feature was made during the production of the detector. Note a 'pipe' in the upper left quadrant, running horizontally for about 1 mm.

4. CRYSTAL MORPHOLOGY AND STRUCTURE

After the completion of the X-ray mapping, the detector was dismantled and its Au electrodes were removed with adhesive tape followed by a brief (few seconds) polishing step by immersion in Br-methanol.

4.1. Optical microscopy

Figure 5 shows a Nomarski micrograph of the complete detector crystal and reveals pipes, scratches, surface structure and some examples of non-uniform etching. Note a pipe is a structure, which is often observed in HPB CZT. The pipes are longitudinal crystal defects, parallel to the crystal axis, and are probably voids, which are known to be sometimes filled with a precipitate. Clearly such pipes seriously affect the charge transport across the crystal.

4.2. IR-transmission

To investigate other potential defects deeper in the detector, IR microscopy has been utilized. Figure 6 shows an IR transmission image of the complete detector crystal, probing directly through the crystal. The pipe detected in the optical image is weakly observed, while the lower left pipe is more intense and is located in the bulk of the crystal. Figure 7 shows a high resolution image of this pipe. Both pipes are about 1 mm long.

Also other features in the IR image, like the mark in the upper left corner, the circular feature of 4.5 mm diameter, and some point defects and scratches on the front surface, correlate with the optical image. The correlations with the X-ray response, particularly with the detector signal, are discussed later.

4.3. X-ray and SEM topography

Synchrotron x-ray topography (SXT) is a technique for investigating the crystal structure. As a non-destructive method it can be used, together with those described above, to study the key crystallographic properties of the

Figure 6. The IR transmission measurement shows the mark in the upper left corner and scratches, mainly located on the back surface. Two pipes are visible: the one seen also in the optical image in the upper left quadrant, and another, more pronounced one, in the lower left corner.

Figure 7. Detail IR transmission image, showing the lower pipe, about 1 mm long and 30 μm wide. The detector response may well be deteriorated by the presence of such pipes (voids in the crystal, sometimes filled with precipitates).

Figure 8. Mosaic of synchrotron X-ray reflection topographs from the three main grains of the test sample. A gap was left for clarity, therefore the image scale on this figure is different from the others showing the complete crystal. The topographs of four small grains are not shown.

sample. In particular the mosaic crystal structure and orientation can be investigated over dimensions from $100\ \mu\text{m}$ to $10\ \text{mm}$.⁹

The sample was exposed with white x-ray beam from a HASYLAB bending magnet source having the incidence angle to the sample surface of 6 degrees. The storage ring DORIS III parameters were typically 4.43 GeV electron energy, with a current of 70 mA. The Bragg reflections taking place in the crystal lattice are recorded on a high-resolution x-ray film (Kodak type R) placed perpendicularly to the incident beam at the distance of 80 mm behind the sample. In this geometry only a thin layer of the sample surface is imaged. Several Laue patterns of topographs, one from each crystallite or grain, are recorded on the film during a single short exposure of 1 second. Figure 8 shows a reconstructed topograph of the sample, indicating that three major crystallites are present. The figure has been assembled in "jigsaw puzzle" fashion from the photographically enlarged mini-topographs of each crystallite, in the same way as described by Stephanson et al.¹⁰

The vertical oval-shaped white areas both on the left and on the right side of the sample originate from the high-voltage pins used as electric contacts in the detector measurements. The thin lines in the figure 8 are images of scratches on the sample surface. The grain boundaries between the minor crystallites, appearing as white stripes in figure 8, are sharp and planar. Similar structure is also seen in many other samples. This suggests that these boundaries are very coherent, i.e. defect free, and preferred ones.

In figure 9 an SEM image of the sample is shown, taken with 30keV electrons. Clearly, conventional SEM picks out the major crystallite boundaries, showing the shape and size of each crystallite (each typically few mm in size). As seen in figure 4, the crystallite boundaries seen in the SEM image may well be a key factor governing the variations of $G(x,y)$.

4.4. X-ray correlation with crystal morphology

The main crystal features, crystallite boundaries and pipes, are shown in figure 10, overlayed onto a greyscale map of the detector signal measured at 1.7 keV. The main crystallite boundaries coincide well with low values of $G(E_x, x, y)$

Figure 9. The SEM image, taken at 30 keV, shows the same main crystallite boundaries as detected in the X-ray reflection topography image of figure 8. Also visible is an anomalous area in the upper right corner, possibly caused by edge effects and crystal conductivity irregularities.

as do the two pipes. High signal regions, however, also exist on this signal map and do not appear correlated with any features observed in the microscope images described above. Presumably the overall signal variation is governed by additional charge transport loss mechanisms deep in the crystal. It is also worth noticing, that at the coherent grain boundaries there is no major change in the detector signal.

4.5. Photoluminescence

To investigate further the potential charge transport loss mechanisms in the crystal, a set of photoluminescence spectra (PL) were obtained. These spectra provide information on the electronic structure of the crystal and the trapping or recombination centers present. A He-Ne laser and an Ar^+ ion laser were used as the excitation sources. The laser spot on the sample had a diameter of $\sim 300 \mu\text{m}$, similar to the X-ray beam dimension. The sample was cooled to $\sim 13 \text{ K}$. A number of samples have been measured both 'as cut' and polished so as to establish benchmark spectra for our detector sample. The sample B2925 shows a peak located at 1.664 eV, which is connected to a neutral donor bound exciton (D^0X) transition. A small hump around 1.65 eV is attributed to a neutral acceptor-bound exciton A^0X . The peak at 1.62 eV is probably due to a donor-acceptor pair transition (DAP), with its first phonon replica DAP-1LO at 1.595 eV. The dominating feature of PL spectra of unetched samples is the surface defect related broad maximum located at energies from 1.48 to 1.58 eV.

PL spectra were obtained at a few points along the center horizontal axis of the sample crystal. At a position 0.75 mm (position 'A') from the left edge, a non-uniformity was discovered. Figure 11 shows a large, broad maximum at 1.55 eV in the PL spectrum of the sample position 'A' (solid line). This peak, located 130 meV below the bandgap peak, is thought to result from excitons bound to extended defects, e.g. dislocations or stacking faults, probably resulting from surface damage. Figure 11 also shows, for comparison, the average PL spectrum measured elsewhere on the sample (position 'B') as dashed line. Position 'A' is probably identical with the location of the electric contact spring used during the X-ray detector measurements.

It also was found that the PL spectrum of a scratch on the sample and of an electron-irradiated crystal area were similar to that of the sample position 'A'. A detailed description and analysis of the PL spectra measured from a

Figure 10. The key crystal morphology overlaid on the grey scaled detector signal $G(E_x, x, y)$ at $E_x = 1.7$ keV. The bright white corresponds to a maximum signal, while the black is a minimum signal. The range is $\sim 10\%$, the grey scale is linear.

Figure 11. Photoluminescence spectra at two locations on the sample. 'A' is an anomalous region near the mechanically damaged area of the electric contact spring location used during the X-ray performance measurements, and 'B' is an average area. The insert shows the positions 'A' and 'B' on the X-ray reflection topography image. At position 'A' the sample surface was stressed and damaged by handling (electrode connection point).

large number of CZT detector crystals is presented in reference.¹¹

5. CONCLUSIONS

We have shown, that significant changes in the signal of the detector occur as a function of position on the detector. Low signal regions can be correlated with gross crystal morphology features, such as crystallite boundaries and voids (pipes). Other regions of low signal have been identified using PL spectra, and have been associated with sub-surface defects or trapping sites deep in the crystal.

Appart from gross crystal morphology features, the spatial variations in the detector signal at a spatial scale of 100 μm to 1 mm do not account for the observed poor energy resolution. The signal variations on this scale within a crystallite contribute insignificantly to the energy resolution. It seems, that deep trapping centers in the bulk crystal currently constrain the detector energy resolution.

While the detector signal appears highly linear with energy, the spectral response distribution broadens and becomes skewed towards lower energies, as a result of charge loss either to surface trapping sites or to sub-surface dislocations or impurities. This photon energy dependent effect is associated with the mean photoabsorption depth in the crystal.

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