Defect depth profiling of CdZnTe using high-energy diffraction measurements

M.S. Goorsky,[a] H. Yoon,[a] M. Ohler,[b] K. Liss[b]

[a] Department of Materials Science and Engineering
University of California, Los Angeles
Los Angeles, California 90095-1595

[b] European Synchrotron Radiation Facility
B.P. 220, F-38043 Grenoble Cedex, France

ABSTRACT

We utilized monochromatic high energy synchrotron x-rays (100 keV) to perform transmission diffraction measurements on bulk cadmium zinc telluride ($Cd_{1-x}Zn_xTe$, x ~ 0.1) crystals used for room temperature radiation detectors. The high-energy measurements assess the crystalline properties throughout the thickness (2-3 mm) of the structures and we determined - in combination with standard high-resolution diffraction measurements - that most defects propagate through the width of the sample. Maps of both composition and crystalline quality were generated using both the high energy and standard diffraction sources and a clear correlation was observed for both composition variation and for mosaic structure. In some cases, up to twenty individual peaks are observed in a rocking curve with a beam size of 100 x 100 μm^2 which allows for a determination of the crystallite size. This experiment represents the first time in which transmission high-energy x-ray diffraction techniques have been applied to examine the crystal quality of $Cd_{1-x}Zn_xTe$ used in nuclear radiation detector applications. The technique allows one to measure the bulk structural properties of thick (mm's) crystals and the technique is particularly useful because these crystals are used as bulk devices. Hence, this enables one to perform a proper analysis of the relationship between the structural defects (present in the bulk) and the detector performance.

Keywords: High energy diffraction, CdZnTe, radiation detectors, x-ray diffraction

INTRODUCTION

Cadmium zinc telluride ($Cd_{1-x}Zn_xTe$) grown by the high pressure Bridgman method[1] can be used to fabricate high performance room temperature operating nuclear radiation (i.e., high energy) detectors. Gamma-ray cameras employing this material as the sensing element are becoming commercially available in the United States. However, non-uniformities in both crystalline perfection and zinc composition throughout the grown crystal result in correspondingly unpredictable device performance. This clearly limits the production yield, imposing a barrier to successful commercialization of detectors based on this materials system.

The CdZnTe detectors typically consist of a slab of "single crystal" material which is on the order of several millimeters thick. Photo-carriers generated in the bulk of the sample are collected at electrodes at the surfaces. Recombination of carriers at defects within the crystal as well as non-uniform electric fields caused by macroscopic defects can reduce the efficiency of these detectors. Therefore, it is important to develop techniques that provide crystallographic information throughout the bulk of the wafer. Our earlier analysis using low energy (8 keV, Cu kα) radiation from both the front and backside of a sample confirmed that many crystallographic defects tended to propagate through the thickness of the detector, but those x-ray techniques were highly insensitive to crystallographic defects which were contained within the crystal.[2]

Structural defects such as mechanical cracks, twins, grain and tilt boundaries, and dislocations all lower the crystalline perfection of the material, and have been identified as major yield-limiting sources for CdZnTe high energy detectors.[2] Our aim is to further assess the bulk structural perfection through the use of transmission high-energy x-ray diffraction and to directly correlate these results to detector efficiency. The key aspect to this approach is that the nondestructive nature of this experiment will allow us to measure both the structural perfection and the detector response on

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exactly the same spatial location on the crystal. In the initial phase of this study, we focus on the first part of this issue: determining the feasibility of applying high energy radiation diffraction experiments to the study of crystalline perfection and zinc mole fraction over large areas of bulk CdZnTe crystals. Future studies will aim to correlate the diffraction measurements with electrical measurements. For example, the energy levels used for the high-energy radiation measurements ($\approx$ 100 keV in this case) are comparable to the gamma-ray energies. This makes it feasible to simultaneously generate diffraction measurements and detector response measurements.

High-energy x-ray diffraction techniques are beginning to play an important role in the analysis of the bulk properties of materials. The absorption length for most materials in the 100 keV range is in the millimeter to centimeter range, so studies of thick structures are more accessible than with other techniques. Given these high absorption lengths, diffraction measurements that utilize these high energies are transmission measurements. It is well known that high resolution double axis (or double crystal) diffraction measurements in reflection are limited in their application to materials perfection. One reason for this limitation is that the double axis measurements integrate scattered intensity over a wide arc representing the Ewald sphere. This intensity integration convolutes broadening effects that are related to lattice tilting – such as mosaic spread – and to strain distributions. Therefore, the resolution of the technique is limited. To overcome this limitation, triple axis diffraction measurements have become more widely utilized. In the triple axis arrangement, a crystal is placed after the sample in the diffracted beam path. This "analyzer" crystal acts as a "slit" which narrows the arc of the Ewald sphere over which the diffracted intensity is gathered. For example, in a typical low energy (Cu kα radiation) double axis diffraction measurement, the detector aperture typically represents a few tenths of a degree of the Ewald sphere. With an analyzer crystal, the arc of the Ewald sphere is reduced to a few arc seconds. Comparable measurements using high energy and transmission mode represent a much more recent development[34] and have not been applied to many semiconductor materials.

Alternative methods to the high-energy diffraction measurements include gamma ray diffraction and standard (low energy) x-ray diffraction. Gamma ray rocking curves, for example, have been used to assess bulk structural perfection of HgI$_2$ crystals,[5] but the technique suffers from low intensity that is typically available using standard gamma-ray sources. Low energy x-ray diffraction techniques (e.g., standard x-ray tubes such as Cu or Ag targets), although much more readily available than the synchrotron sources which are required for the high energy measurements, are predominantly used in the reflective mode and probes only the "surface" (i.e., ~ a few microns of near the top surface). Although this technique has been demonstrated to be useful for structural analysis[6] of CdZnTe bulk samples, transmission high-energy x-ray diffraction is foreseen to be more relevant.

EXPERIMENT

Sample Description

The samples were (111) oriented single crystals of 1-10 cm^2 area and thickness of ~ 2-3 mm. These crystals were cut from a polycrystalline ingot of ~ 10 cm diameter, ~ 15 cm length, grown by the high-pressure vertical Bridgman method. The surface orientation of the primary grain(s) was determined using Laue back reflection measurements and Cu kα radiation prior to the high-energy measurements. Cd$_{1-x}$Zn$_x$Te has a cubic zincblende crystal structure, and the lattice parameters of CdTe and ZnTe are 6.4812Å and 6.1026Å, respectively. The composition of the sample crystals is nominally x=0.1 which corresponds to a lattice parameter of about 6.4433Å.

High and low energy diffraction measurements

The transmission high-energy x-ray diffraction setup of the beamline ID15A at the European Synchrotron Facility is ideally suited for high resolution high-energy diffraction measurements. We utilized the double axis and the triple axis diffraction modes that uses a monochromator to select the desired incident energy and an analyzer crystal (for the triple axis mode) to define the diffracted beam. Silicon (511) analyzer and monochromator crystals are employed. The incident beam is limited by secondary slits of the beamline. (220) reflections from the samples were used for all measurements. The diffractometer ω and 2Θ axes are interferometer controlled with sub arc-second resolution. The monochromator is placed in a lead tank with a 10 x 10 mm^2 aperture. Also, long steel collimators with 5 mm apertures are used i) between the monochromator and sample, ii) sample and analyzer crystal, and iii) analyzer crystal and detector in order to reduce the background scattering. Under these conditions, the background is typically less than a count per second. The sample stage

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also translates. Combined with special aperture optics which limit the beam size to the sample of approximately 100 μm × 100 μm, mapping of the rocking curve width (ω-scan or rocking curves to determine crystalline perfection / mosaicity) and detector position (lattice parameter) provides for determination of the materials properties of the CdZnTe samples as a function of position. Figure 1 below shows the schematic of the types of crystallographic defects that are typically observed from high resolution rocking curve scans. Figure 1(a) shows the rocking curve associated with a perfect crystal. Fig. 1(b) shows the rocking curve of a crystal with localized small scale (on the order of arc-seconds) tilts among different regions of the illuminated crystal or a mosaic-type structure. Fig. 1(c) shows the diffraction pattern of two distinct misoriented grains within the region illuminated by the x-ray beam. The high-energy incident radiation also provides for a very different scattering geometry than typically occurs with laboratory source x-ray diffractometers. For example, for a 3mm thick crystal, the transmission value at 100keV (λ = 0.124Å) is approximately 7%. The corresponding Bragg angles – assuming $Cd_{0.9}Zn_{0.1}Te$ crystal for a (220) reflection – is θ_B=1.56°.

The high-energy measurements are complemented by high-resolution low energy (Cu kα1; 8 keV) x-ray diffraction measurements performed in a reflection [(111) or (333)] geometry. For these measurements, triple axis reciprocal space mapping is performed using a modified Bede D3 diffractometer with silicon (111) monochromating crystals and a (220) four bounce analyzer crystal. With a minimum beam size of about 1 mm × 1 mm and sample stage translation, both the variation in crystalline perfection and in the zinc mole fraction (as determined by absolute lattice parameter measurements) were mapped to provide for comparison with the results from the high energy transmission diffraction measurements. As noted above, we previously showed that mechanical cracks in the material are found to act as conductive "shorting paths", indicated by excessive leakage currents and reduced charge (electron) collection measured along these cracks. Reduced charge collection is also obtained across grain boundaries and in regions with poor crystallinity (as quantified by higher rocking curve full width at half maximum (FWHM), indicating that these regions serve as carrier recombination sites.[2]

(a)   (b)   (c)

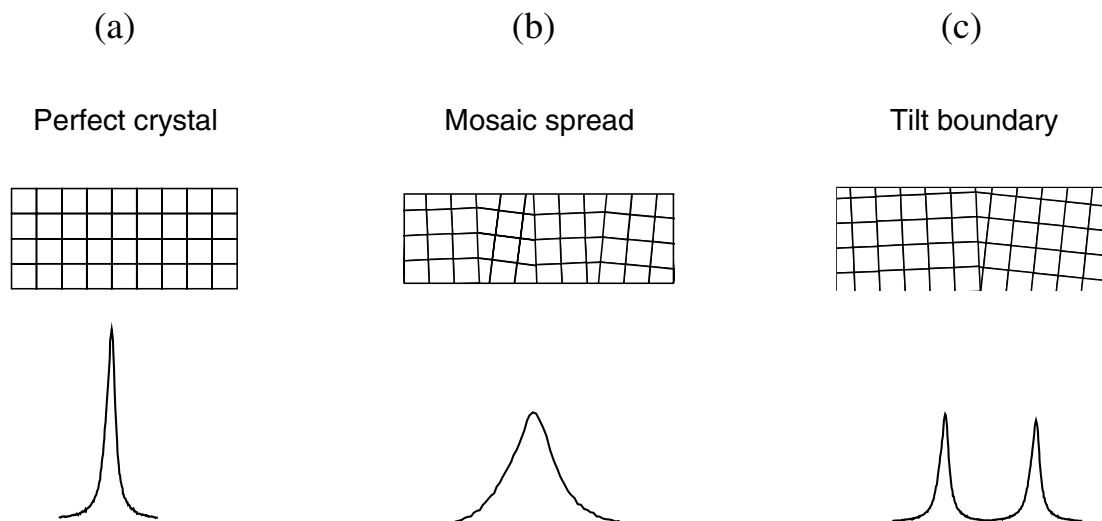Perfect crystal   Mosaic spread   Tilt boundary

Figure 1. Crystalline perfection and the related rocking curve. (a) A single narrow peak represents perfect crystal. In these measurements, the minimum width for both the high and low angle measurements is on the order of four arc-seconds. (b) Mosaic crystal with small regions (with respect to the beam size) that are tilted by small amounts (with respect to the beam divergence) produce a rocking curve which is broadened as compared to the rocking curve for the perfect crystal. (c) A low angle tilt boundary is represented by distinct "perfect crystal" rocking curves.

RESULTS AND DISCUSSION

Figure 2 shows representative double axis high-energy diffraction scans to demonstrate the crystallinity variation of a $Cd_{1-x}Zn_xTe$ crystal. Fig 2(a) shows a rocking curve width for a highly perfect region of the sample. In this case, the FWHM is about 8 arc seconds and shows a single slightly broadened peak with a shoulder on the right (high angle) flank. Fig. 2(b) shows a rocking curve from a lower crystalline region of the sample. In this case, the FWHM is about 45 arcsec and the presence of several peaks is clear, although many of the peaks are not distinct. Nonetheless, one can generate a map of crystalline quality as a function of position through a series of rocking curve scans. Figure 3 shows a contour plot with

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FWHM values ranging from 1 to 45 arc seconds. In this case, the beam aperture was about 100 μm × 100 μm and the measurements were taken at one mm steps; each square represents the step size and not the aperture size in this figure. Some crystal regions are apparently of high quality while others contain mosaic structure and small angle tilt boundaries. As mentioned above, however, the peak width from a double axis measurement includes broadening effects related to tilt (mosaic structure, curvature, etc.) and strain (lattice parameter variations). Triple axis measurements are required to separate these effects, but these measurements clearly demonstrate that the high-energy diffraction techniques are sensitive to variations in the properties of CdZnTe.
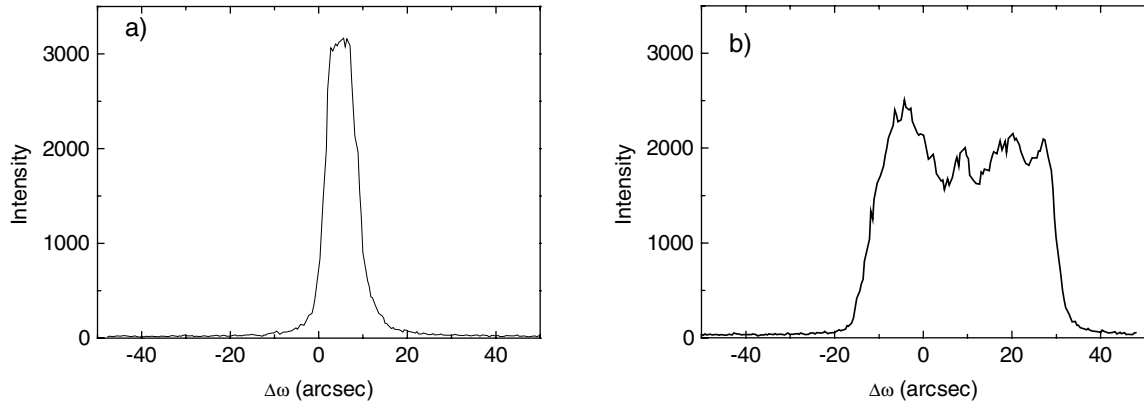

Figure 2. Representative double axis rocking curves from a high crystalline quality region (a) and a low crystalline quality region (b).
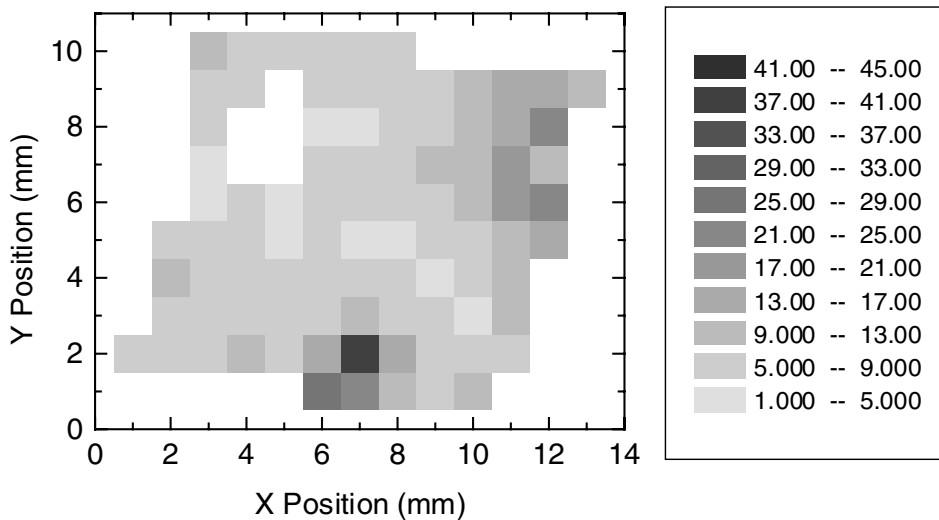

Figure 3. Rocking curve or ω-map showing the double axis high energy transmission rocking curve width as a function of position across a 10 mm × 10 mm CdZnTe sample.

An important aspect of the high-energy measurements is to compare triple axis high-energy diffraction ω-maps with those generated using standard low energy reflection measurements. Figure 4 provides such a comparison using a typical sample. Figure 4(a) shows a triple axis ω-map that was generated using the standard laboratory source equipment in reflection. It can be seen that – for this irregularly shaped crystal – there are regions of both high and low crystalline quality. Two regions of reduced crystalline quality are clearly observed near in the upper – middle portion of the sample and near the lower left portion of the sample. Previous results[7] also demonstrated that these regions also showed (i) a higher threading

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dislocation density and (ii) a lower μ·τ product determined by separate electrical measurements. Figure 4(b) shows the ω-map generated by determining the FWHM from the high energy diffraction measurements in transmission. It is very interesting to note that the regions that exhibited lower structural quality in the low energy reflection measurements show similar trend in the high energy measurements. Thus, the high-energy diffraction measurements exhibit the same properties as the low energy diffraction measurements and that – for this sample – there are no extended defects embedded within the volume of the detector.
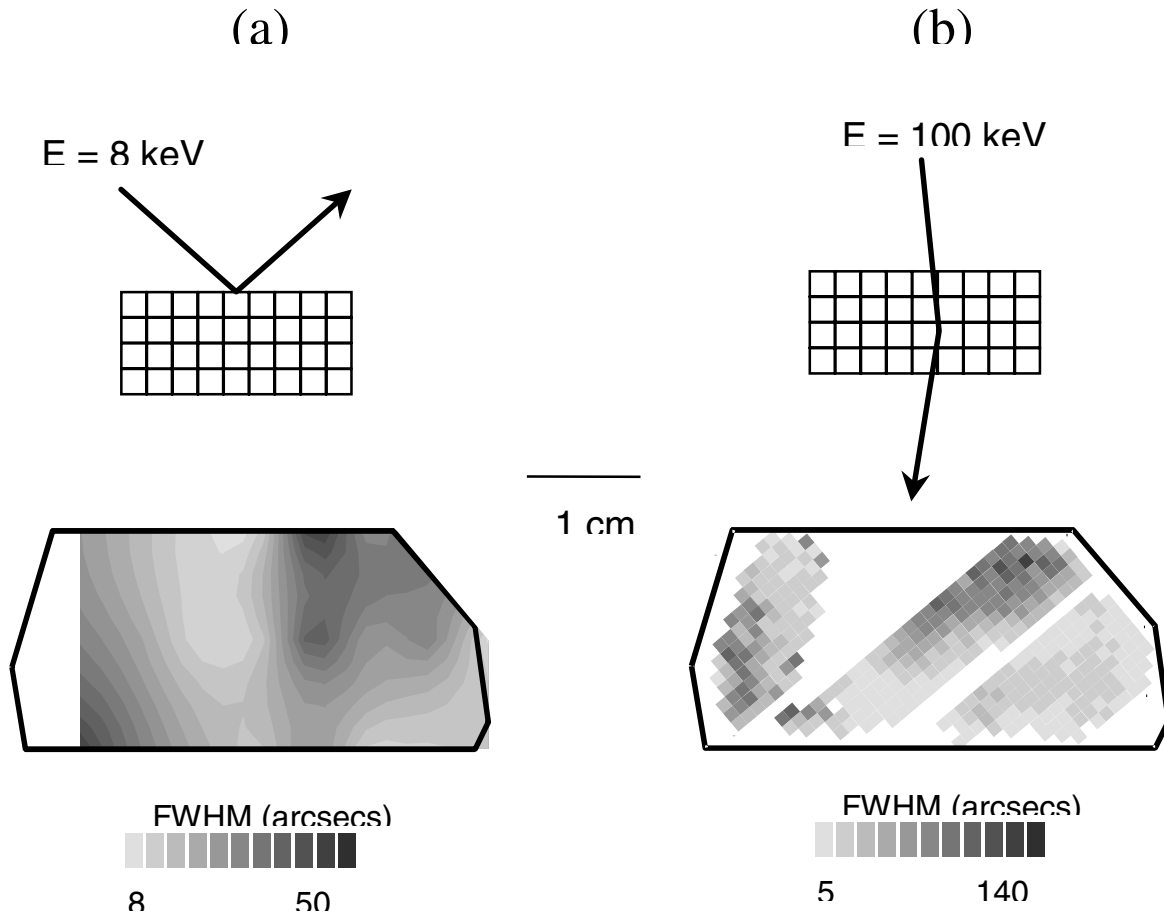

Figure 4. Comparison of ω maps for (a) standard triple axis diffraction measurements and (b) high-energy diffraction measurements.

Triple axis diffraction measurements separate strain effects and tilt effects. Therefore, it should be possible to determine the lattice parameter of the structures as a function of position using the high energy diffraction technique. We have already demonstrated that the technique can be applied to low energy diffraction measurements and have converted the change in the detector position ($2\Theta_B$) or the lattice parameter to a zinc mole fraction. In that case, the detector position had been calibrated with a silicon reference crystal, so absolute 2Θ values and hence, absolute lattice parameter and zinc compositions could be determined.[6] For these samples, there is a significant zinc concentration variation along the sample. These pieces were nominally cut along the growth direction. The segregation coefficient of Zn in CdZnTe is not unity and therefore, one would expect a variation in zinc composition along the sample. Figure 5(a) shows the zinc segregation determined using the standard low energy measurement varies from about 10% zinc near the first-to-freeze portion of the crystal to about 5% a few cm away. A small set of lattice parameter measurements was generated using high-energy transmission. In this case, the detector position was not calibrated, so only relative changes in the detector position (and hence lattice parameter and zinc mole fraction) could be determined. Over the smaller lateral range covered using the high

energy triple axis apparatus, the corresponding Zn change determined by the low angle measurement was about 2.5% Zn. In the case of the high-energy measurements, the detector position changed by about 35 arc seconds over this same range. Given the radiation wavelength and (2,2,0) reflection, this angular change corresponds to a zinc composition change of 2.0% which confirms that the high energy diffraction measurements can indeed be used to determine the change in composition as well as variations in crystalline quality.
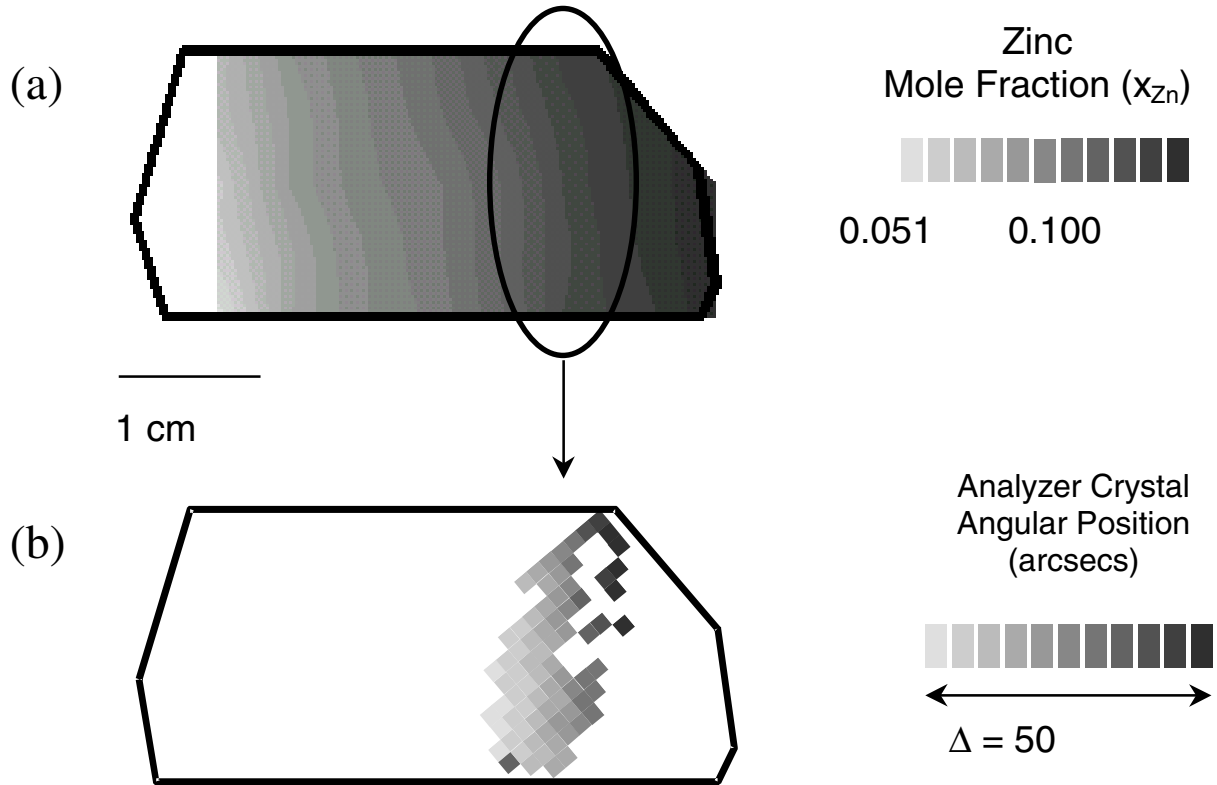

Figure 5. (a) Zinc composition variation across the sample determined using standard low angle triple axis diffraction. (b) Change in the detector position $(2\Theta_B)$ as a function of sample position.

SUMMARY

We have demonstrated that high energy (100 keV) transmission diffraction measurements in a triple axis diffraction arrangement can be used to assess the crystallographic properties of CdZnTe crystals that are used for radiation detection devices. The results from the high energy diffraction measurements match those from typical low energy reflection measurements. In the triple axis mode, maps of rocking curve widths and lattice parameter measurements (zinc mole fraction) showed the same trends in both cases. These results are important as they set the baseline for crystallographic measurements in this system. The next goal is to take advantage of the high energy source that is used for the diffraction measurements to simultaneously generate detector response measurements. This type of measurement will be the focus of future studies in this materials system.

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