"Analysis of grain boundaries, twin boundaries, and Te precipitates in CdZnTe grown by high-pressure bridgeman method" by J. R. Heffelfinger, D. L. Medlin, and R. B. James

This paper elucidates the microstructures of a commercially available polycrystalline CdZnTe material by the use of light and electron microscopies. The introduction is excellent and the paper is clearly written. Figures are clear, except possibly for Fig.4 a), which can easily be made clearer by having a marked boundary around the Te precipitate.

There are several interesting new findings reported, including finding that a Te precipitate is actually single crystalline and takes on hexagonal structure closely aligned with the surround CZT matrix. It was not clear whether the precipitates are amorphous, polycrystalline, or single crystalline. Detailed analysis of the electron diffraction results and cross correlation of the methods used enable the authors to reach credible scientific conclusions.

Further work in the future enabling statistical statement would be interesting, if the result could be correlated with growth conditions, material composition, and strain .

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ANALYSIS OF GRAIN BOUNDARIES, TWIN BOUNDARIES AND Te PRECIPITATES IN $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ GROWN BY HIGH-PRESSURE BRIDGEMAN METHOD

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ABSTRACT

Grain boundaries and twin boundaries in commercial $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, which is prepared by a high-pressure Bridgeman technique, have been investigated with transmission electron microscopy, scanning electron microscopy, infrared-light microscopy and visible-light microscopy. Boundaries inside these materials were found to be decorated with Te precipitates. The shape and local density of the precipitates were found to depend on the particular boundary. For precipitates that decorate grain boundaries, their microstructure was found to consist of a single, saucer-shaped grain of hexagonal Te (space group $P3_121$). Analysis of a Te precipitate precipitates by selected-area diffraction revealed the Te to be aligned with the surrounding $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grains. This alignment was found to match the (111) $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ planes with the (1 $\bar{1}$ 01) planes of hexagonal Te. Crystallographic alignments between the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grains were also observed for a high-angle grain boundary. The structure of the grain boundaries and the Te/ $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ interface are discussed.

INTRODUCTION

$\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ is a leading material for the application of room-temperature gamma-ray spectrometers. $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ possesses the necessary material properties of high bulk resistivity, good photoconductivity and acceptable electron and hole transport, that are required to fabricate gamma-ray detectors. Production of large-volume $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ material is currently hindered by the presence of chemical and structural inhomogeneities, such as grain boundaries, twin boundaries, inclusions and precipitates.[1,2] Although the effect of these inhomogeneities on device performance is still poorly understood, mounting evidence suggests that defects, such as grain boundaries, affect the electrical transport properties inside the material.[3] The local effect of the grain boundaries, and the precipitates associated with them, may act to channel charge along certain paths inside the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, and thus, create a device where the electrical transport properties are anisotropic. In order to gain insight on how these defect structures affect device performance, the structural and chemical nature of grain boundaries and twin boundaries in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ are explored.

Commercially available $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ is typically manufactured using a high-pressure Bridgeman (HPB) technique.[4] In this method, a large over-pressure of an inert gas (typically Ar) is used to inhibit the evaporation of the charge material. Material prepared by this method has a polycrystalline microstructure with grains on the order of centimeters in size. In order to grow material by this method, several complications must be addressed. Perhaps one of the most challenging growth dilemmas is that of the retrograde solubility in the Cd-Te phase diagram.[5-7] As the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ boule is cooled, Te and/or Cd precipitate out of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ lattice. The chemistry of these precipitate is determined by whether the starting material is rich in Te or Cd. Precipitates tend to decorate internal boundaries, such as grain boundaries and twin boundaries inside $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$. The composition and distribution of the precipitates have been previously studied for CdTe and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ materials grown by either HPB or Bridgeman techniques.[2,8,9] Post-growth annealing treatments of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ boule has been used to reduce the number and concentration of precipitates, but the effect of annealing on the electrical properties of the material has yet to be determined.[10-12] In this study, Te precipitates have been investigated for their microstructure and crystallographic alignment with the surrounding $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ matrix. By analyzing the shape, alignment and internal microstructure of the Te

precipitates, valuable insight into the mechanisms of their formation and their effect on the surrounding $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ lattice can be made.

EXPERIMENTAL

Polycrystalline $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ material, manufactured using HPB techniques, was obtained from commercial suppliers for analysis. This material was grown from a Te-rich charge with a nominal zinc concentration of 10%. An Ar over pressure was used to suppress the loss of Cd from the melt. Parameters related to the growth and cooling rates were not disclosed by the manufacturer. $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ samples were characterized using visible-light microscopy (VLM), transmission infrared-light microscopy (IR), scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (XEDS) and transmission electron microscopy (TEM). Prior to examining by VLM, IR and SEM, $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ samples were polished using one-micron alumina slurry and a felt cloth. Although this procedure produces a surface with noticeable scratches, no chemical alteration of the surface is expected to occur. TEM samples were prepared using conventional dimpling and ion milling techniques. A JEOL 840 SEM operating at 15 keV and equipped with a beryllium-window, Noran XEDS detector were used for SEM and XEDS analysis. A JEOL 1200EX operating at 120 keV and equipped with a Tracor Norton 5500 XEDS were used for TEM and XEDS analysis. A JEOL 4000EX operating at 400 keV was used for high-resolution TEM analysis.

RESULTS AND DISCUSSION

Precipitation of Te at grain boundaries and twin boundaries in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$

The surface of polished $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ shows visible evidence of grain boundaries, twin boundaries and precipitates. Fig. 1 is a pair of VLM images showing a grain boundary (Fig. 1a) and a twin boundary (Fig. 1b). Such boundaries can be seen in the VLM due to the anisotropic polishing of the alumina slurry. Here, grains of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ polish at different rates depending on their relative orientation to the surface. Likewise, precipitates of a different phase and chemistry from that of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ will also be visible at the surface. Precipitates, which decorate the grain boundary and twin boundary in Fig. 1, are seen to protrude out the surface. This observation suggests that the Te polishes at a slower rate than the surrounding $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$. A three dimensional perspective of the distribution of Te precipitates can be acquired using IR imaging. Fig. 2 shows a transmission IR image of a grain boundary, which is the same boundary as seen in Fig. 1a. A schematic representation of the viewing direction and distribution of Te precipitates is seen next to the image in Fig. 2. The fact that $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ is transparent to IR light allows for analysis of internal defects, such as precipitates, voids and cracks that act to either scatter or absorb the IR light. Fig. 3a is a secondary-electron SEM image of a Te precipitate that has intersected the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ surface. The Te precipitate was located along a grain boundary (i.e. the same grain boundary that is seen in Fig. 1a and Fig. 2). The chemistry of the Te precipitate was probed with XEDS inside the SEM. Fig. 3b and 3c show XEDS spectra from the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ matrix and the Te precipitate. Light elements, such as oxygen, were not detected in the XEDS spectra due to the use of a beryllium-window XEDS detector. Constituents, other than the three starting materials of Cd, Te and Zn, were not detected by XEDS in the SEM.

The precipitation of Te from the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ matrix is due to a retrograde solubility in the phase diagram, as described earlier. Grain boundaries and twin boundaries act as low-energy nucleation sites for the precipitation of Te. For this reason, the grain boundaries and twin boundaries contain a higher density of precipitates than the bulk $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$. In general, grain boundaries were observed to have a higher density of precipitates than the twin boundaries. This observation suggests that the barrier for nucleation of a Te precipitate at a grain boundary is generally less than that for the twin boundary. The distribution of Te precipitates at grain boundaries was also seen to vary between different grain boundaries. Thus, as the character of the grain boundary changes the barrier for nucleation also changes. Some of the grain boundaries were found to be completely free of Te precipitates, while regions where grain boundaries met (i.e. triple junction) were found to contain some the highest concentration of precipitates. Often, these triple junctions contained a continuous precipitate or a wire of Te. If the wire were to

Fig. 1
a) VLM image of a grain boundary decorated by Te precipitates.
b) VLM image of a twin boundary decorated by Te precipitates.

Fig. 2 a) IR transmission image showing the distribution of Te precipitates at a grain boundary.
b) Schematic illustration of the sample seen in Fig. 2a.

Fig. 3 a) Secondary-electron SEM image of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ surface along a grain boundary. This image shows a Te precipitate that has intersected the surface. b) XEDS spectrum from the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ matrix. c) XEDS spectrum from the Te precipitate.

transverse the entire detector, the defect may cause a short circuit path and would be particularly harmful to device performance. Specific sites along twin boundaries were also observed to act as preferential nucleation sites. As seen in Fig. 1b, precipitates were observed to preferentially form on jogs of the twin boundary. In $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ the common twinning plane is that of the (111) plane. Jogs along the twin boundary would change the interface between the twinned regions from the (111) plane to some other plane, such as a (11 $\bar{2}$) plane. The corner where the two twinning planes meet apparently acts as a low energy site for nucleation. An observation of this occurrence is shown in Fig. 1b.

The shape of the Te precipitates was found to depend on their location. In general, precipitates that were located either along twin boundaries or in the bulk of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ tended to have a faceted polyhedra shape. By faceting onto specific planes of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ lattice, the interfacial energy between the precipitate and matrix can be minimized. Precipitates that form along grain boundaries were found to have a saucer shape, as seen in Fig. 2 and Fig. 3. As will be shown in the following section, the interface between the Te and the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ is different for the two sides of the grain boundary. The shape of the Te/ $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ boundary will thus depend on the alignment between the two phases.

Microstructure and alignment of Te precipitates

The microstructure, phase and crystallographic alignment of the Te precipitates were characterized using the TEM. Fig. 4 is a bright-field TEM image. This image shows a Te precipitate that is located along a grain boundary in the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$. Selected-area diffraction patterns that were taken from the precipitate were consistent with the Te having a hexagonal crystal structure (space group $P3_121$). This is the room-temperature and atmospheric pressure phase for Te. X-ray diffraction studies of Te precipitates in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ have previously reported the presence of a high-pressure Te phase.[11] The microstructure of the precipitate consisted of a single grain of Te that contained voids and dislocations. Voids in the precipitate may arise from trapped gasses inside Te or a volume change of the Te as it cooled. The interface between the Te precipitate and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ was sharp with no apparent amorphous or tertiary phase layer at the interface. Chemistry of the precipitate was explored using XEDS. Spectra from the precipitate and the matrix are shown in Fig. 4b and 4c. The Al and Cu signals seen in these spectra are artifacts from the microscope and the washers used to mount the TEM sample. A noticeable oxygen peak is present in the spectra taken from the precipitate. This increased oxygen signal may be the result of the formation of a tellurium oxide layer on the surface of the precipitate or an increased amount of oxygen in the Te precipitate as compared to the bulk $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$. A small Fe peak was also observed from the Te precipitate. Fe has been previously reported as a contaminate in small concentrations in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ materials.[13]

The Te precipitate was found to be aligned with the surrounding $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grains. Fig. 5 is a selected-area diffraction pattern taken from the precipitate and one of the adjacent $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grains. This patterns was taken along the [11 $\bar{2}$] zone axis of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and shows the (111) planes of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ to be aligned closely with the (1 $\bar{1}$ 01) Te planes. The mismatch in lattice spacing between these two planes is a mere 7%. Alignment of planes that are closely matched in lattice spacing would be a way for the system to minimize the interfacial energy between the precipitate and matrix. Other alignments between the Te precipitates and the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ were observed. Details of these alignments and their implications on the morphology of the Te/ $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ interface will be a topic of a future research.

Character of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grain boundaries

An important question in the study of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ is whether the high-angle grain boundaries contain a secondary phase at the interface. A secondary phase may have significant effects on the electrical properties of the boundary. Obviously, Te has been identified as a secondary phase, but these precipitates are assumed to be localized. To verify whether the interface between the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grains is sharp, high-resolution TEM was used to characterize a high-angle grain boundary. Fig. 6 is a high-resolution TEM image of a $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grain boundary. This image shows lattice fringes from the planes of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grains. Each grain has a different orientation with respect to the electron beam and thus, the two grains appear to have quite different

Fig. 4 a) Bright-field TEM image of a Te precipitate and the Cd_{1-x}Zn_xTe matrix (c). from the Te precipitate (b) and the Cd_{1-x}Zn_xTe matrix (c).

Fig. 5 Selected-area diffraction pattern showing the alignment between the Te and Cd_{1-x}Zn_xTe This pattern is seen along the [112] Cd_{1-x}Zn_xTe axis and shows the alignment of the (111) Cd_{1-x}Zn_xTe planes with the (1101) Te planes.

Fig. 6 High-resolution TEM image of the Cd_{1-x}Zn_xTe grain boundary.

lattice spacing. The importance of this picture is to illustrate that the two $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grains are in close contact with each other (within ~ 1 nm). A certain amount of overlap of the two grains can be seen in Fig. 6. No secondary or amorphous phase was observed at the grain boundary. The grain boundary was not associated with a particular plane of either grain of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and had a meandering character. Selected-area diffraction found the $\langle 110 \rangle$ type direction of one $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grain to be closely parallel to the $\langle 110 \rangle$ type direction of the other $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grain. The observed alignment and interface structure between the grains was characterized for only one grain boundary. Other grain boundaries will certainly have different alignments and dissimilar structures at the interface. Future research will work to understand the correlation between grain boundary alignment and the density of precipitates observed at the interface.

CONCLUSIONS

Commercially available $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, grown by the high-pressure Bridgeman (HPB) method, has been characterized for its microstructure and internal precipitates. Grain boundaries and twin boundaries were found to be decorated with Te precipitates. Specific sites along the grain boundaries and twin boundaries were seen to act as preferential nucleation sites (i.e. triple junctions of grain boundaries and jogs in the twin boundaries). TEM analysis found the Te to form with a hexagonal crystal structure (space group $P3_121$), which is the room temperature and pressure phase. The Te was aligned with the (1101) Te planes nearly parallel to the (111) $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ planes of an adjacent grain. For regions of the grain boundary that are located at a relatively far distance away from the Te precipitate, the grain boundary was found to be relatively sharp (within ~ 1 nm in width). No secondary or amorphous phases were observed at the grain boundary interface.

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REFERENCES

1. R. B. James, T. E. Schlesinger, J. Lund, and M. Schieber, in Semiconductors and Semimetals Vol. 43, edited by T. E. Schlesinger and R. B. James (Academic Press, San Diego, CA 1995) pp. 335-381.
2. J. R. Heffelfinger, D. L. Medlin, H. Yoon, H. Hermon and R. B. James, in Hard X-ray and Gamma-ray Detector Physics, Optics and Application, edited by R. B. Hoover and F. P. Doty (SPIE Proc. 3115, Bellingham, WA, 1997) pp. 40-50.
3. F. P. Doty, J. P. Cozzatti and J. P. Schomer, in Hard X-ray and Gamma-ray Detector Physics, Optics and Application, edited by R. B. Hoover and F. P. Doty (SPIE Proc. 3115, Bellingham, WA, 1997) pp. 51-55.
4. F. P. Doty, J. F. Butler, J. F. Schetzina, and K. A. Bowers, *J. Vac. Sci. Technol.* **B10**, 1418 (1992).
5. M. Hage-Ali and P. Siffert, in Semiconductors and Semimetals Vol. 43, edited by T. E. Schlesinger and R. B. James (Academic Press, San Diego, CA 1995) pp. 219-257.
6. F. T. J. Smith, *Met. Trans* **1**, 617 (1970).
7. D. DeNobel, *Philips Research Publications* **14**, 361 (1959).
8. R. D. S. Yadava, R. K. Bagai and W. N. Borle, *J. Electr. Mat.* **21**, 1001 (1992).
9. D. J. Williams, in Properties of Narrow Gap Cadmium Based Compounds, edited by P. Capper (INSPEC, Exeter, England 1994) pp. 510-515.
10. H. R. Vydyanath, J. Ellsworth, J. J. Kennedy, B. Dean, C. J. Johnson, G. T. Neugebauer, J. Sepich, and P.-K. Liao, *J. Vac. Sci. Technol.* **B10**, 1476 (1992).
11. T. S. Lee, J. W. Parks, Y. T. Jeoung, H. K. Kim, C. H. Chun, J. M. Kim, I. H. Park, J. M. Chang, S. U. Kim and M. J. Park, *J. Electr. Mat.* **24**, 1053 (1995).
12. N. V. Sochinskii, E. Diegues, U. Pal, J. Piqueras, P. Fernandez, A. F. Agullorueda, *Semi. Sci. Tech.* **10**, 870 (1995).
13. S. Sen and J. E. Stannard, in Semiconductors for Room-Temperature Radiation Detector Applications, edited by R. B. James, T. E. Schlesinger, P. Siffert and L. Franks (Mater. Res. Soc. Proc. 320, Pittsburgh, PA 1993) p. 391.

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