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CRYSTALLOGRAPHIC AND METALLURGICAL
CHARACTERIZATION OF
RADIATION DETECTOR GRADE CADMIUM TELLURIDE
MATERIALS

CJ. JOHNSON*, E.E. EISSLER*, S.E. CAMERON*, Y. KONG**, S. FAN**,
S. JOVANOVIC** AND K.G. LYNN**

*eV PRODUCTS, div. of II-VI Incorporated, 375 Saxonburg Boulevard,
Saxonburg, PA 16056

**Brookhaven National Laboratory, Department of Physics,
Upton, NY 11973

ABSTRACT

Radiation detector grade CdTe crystals are characterized by several crystallographic and metallurgical techniques including infrared microscopy, dislocation etch pitting and X-ray diffraction. Results are presented for a set of 50 detectors fabricated from an ingot produced by the High Pressure Bridgman method. Data on the temperature dependence of leakage current and pulse height analysis are presented, along with measurements of room temperature charge transport properties. Attempts to relate crystal structure to detector performance will be discussed.

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INTRODUCTION

The performance of cadmium telluride (CdTe) and cadmium zinc telluride (CdZnTe) materials as room temperature radiation detectors is mainly limited by charge transport properties. These properties depend critically on the quality of crystals that can be grown. The purpose of this work is to investigate macro- and micro-structure relationships to charge transport characteristics and device performance. We have initiated this effort with the binary alloy CdTe and will progress to the ternary CdZnTe at a later date. Our ultimate objective is to better understand crystal growth and device fabrication, which in turn will support more predictable manufacturing and practical application of CdTe/CdZnTe radiation detectors.

In the present work, we grew a CdTe crystal (HPA008) by the High Pressure Bridgman (HPB) method. Crystallographic and metallurgical properties of the as-grown ingot and cut slices were characterized using optical microscopy, laser back reflection orientation, infrared (IR) microscopy, dislocation etch pitting and X-ray diffraction. A total of 51 detectors was fabricated from three slices and the performance of 50 units was evaluated (1 detector was broken prior to testing). Results of IV characterization, pulse height analysis and charge transport studies are under investigation in search of structure/performance correlations.

IR microscopy has previously been used to identify numerous inclusions and precipitates in CdTe materials, particularly in the study of substrates for HgCdTe epitaxy [1,2]. Dislocation etch pitting has been extensively developed for this same application and some correlation has been established between specific dislocation features and epitaxial HgCdTe IR detector performance [3]. Previous studies of CdTe/CdZnTe crystallinity by X-ray reflection or transmission topography and by X-ray double crystal rocking curve measurements have identified a number of structural defects but correlations to device performance have been elusive [4,5]. We intend to focus these characterization techniques, primarily applied to IR substrates in the past, on the assessment of CdTe/CdZnTe radiation detector materials.

This paper is a report on work in progress. Eventual full commercial development depends on success in understanding,

controlling and tailoring defects induced during CdTe/CdZnTe crystal growth and device fabrication.

EXPERIMENTAL DETAILS

Crystal Growth

Ingot HPA008 was grown by the high pressure Bridgman (HPB) method [6] in one of two HPB furnaces operated by eV PRODUCTS. The elemental Cd and Te used were of the highest purity available (advertised as >6-9's and specified by eV as "vendors best"). The 3 kg ingot was grown under an overpressure of 100 atm. in a purified and coated graphite crucible during a start-to-finish growth cycle of 30 days.

Crystallographic and Metallurgical Characterization

After assessing the macroscopic grain structure, a section that could be oriented to yield slices with significant {111} areas was selected. Pre-slicing orientation to within 15 arc minutes was accomplished using HeNe laser back reflection techniques and post slicing orientation accuracy of better than 15 arc minutes were verified by the same method.

The following methods were used to characterize the sample.

- 1). IR microscopy which allows for opaque inclusions and/or precipitates to be mapped, photographed and dimensionally measured down to a size limit of 1 to 2 microns.
- 2). The Nakagawa etch pitting procedure [7], utilized to identify dislocation patterns on {111} A-faces, is appropriate for assessing densities to levels of $>10^6/\text{cm}^2$.
- 3). X-ray diffraction measurements are performed using a Philips Model **** laboratory generator having a Cu target. The 8 keV, CuK(a) X-rays are collimated by reflection from either a highly perfect Si first crystal for topography or InSb first crystal for double crystal rocking curve (DCRC) examination.

Detector Fabrication Methods

All slicing and dicing during fabrication of detectors was performed using a diamond inside diameter saw. Br:MeOH etching (5% Br) was employed to remove surface and/or edge damage left by sawing. In every etching step, a minimum of 25 microns was removed. When mechanical/chemical polishing preceded etching, a thickness in excess of 100 microns was removed.

Gold contacts were applied by the electroless AuCl method [8]. Care was taken to minimize the time delay from final surface etching to electroding in an attempt to prevent oxidation. It is recognized that the electroding process is potentially highly variable and operator dependent, hence attention has been paid to details such as the freshness of the AuCl solution and the time allowed for the solution to be in contact with the CdTe surface. Efforts have also been made to thoroughly clean all detector surfaces after electroding in order to remove residual salts and/or other products of the electroless process.

Detector Characterization

Current-voltage (IV) plots have been generated on PC driven test stations over the range from -100 to +100 volts. All 50 of the detectors produced for this study were 0.2 cm thick, thus field strengths for our IV testing ranged from -500 V/cm to +500 V/cm.

Pulse height analysis (PHA) screening was conducted at field strengths in the 1000 V/cm range. Other PHA testing ranged over applied fields from 50 to 6000 V/cm.

Figure 1 shows the setup for transient charge response measurement. LED pulses with wavelength of 660nm and rise time <30 nsec, or alpha-particles from an ^{241}Am source, were used for exciting electron-hole pairs at the grounded electrode as shown. Temperature cycling was conducted in an environmental chamber in ambient conditions. Depending on the polarity of the biased electrode, either electrons or holes will be drifted across the detector. The transient charge response is recorded by a digital storage oscilloscope connected to the output of the charge-sensitive preamplifier. All measurement and data acquisition processes are automated and averaged for at least 100 pulses. Analysis of transient charge response provides information on the transport properties of the charge carriers. For example, the bias dependent

charge collection contains information on $(\mu\tau)$ product, and carrier mobilities can be determined by differentiation of the transient charge response.

While it is relatively straightforward to measure electron transport properties, difficulties can arise in the quantitative characterization of hole transport. The most important contributing factors are related to low hole mobility value and large trapping/recombination probabilities. In the present study, the detector thickness was 2 mm for electron measurements and 0.5 mm for hole measurements and bias fields range up to 6000 V/cm. Also, we note that the detector is in series with the leakage resistor of the detector bias supply, the voltage drop across this leakage resistor is less than 5% at $T=40^\circ\text{C}$ and should have negligible effects on the actual detector bias below this temperature in our measurement.

RESULTS AND DISCUSSION

Grain Structure and Detector Layouts

A section of ingot HPA008 used in this work was oriented and sliced to yield $\{111\}$ surfaces over 30% to 70% of individual slice areas. The $\{111\}$ regions correspond to the brighter areas on the slice EPD macro photos of Figure 2. Also, Figure 2 shows the layout of the detectors fabricated and studied in this work. Note that 13 detectors are $\{111\}$ single crystals, 25 are partial $\{111\}$ single crystals and 8 are randomly oriented single or polycrystals. In the following, detectors are denoted as shown in Figure 2, e.g. "Detector D5-11".

Detector IV Characteristic and Am241 Spectrum Screening

Figure 3 displays three IV characteristic (IVC) types which we found in our sample set. We have labeled them according to the shape of the IV curve as Types I, L, and D respectively for Increasing, Linear and Decreasing resistance characteristics. Two trends were noticed when the detectors were sorted according to these type definitions. First, the apparent resistivity decreased for Types I, L and D from near E11 to low E10 to mid E9 ohm-cm respectively. Second, Type I detectors tended to display good Am241 spectra with low noise thresholds, Type L units showed poor

photopeaks and higher noise thresholds and Type D detectors yielded no photopeaks and significantly higher noise thresholds. Figure 4 shows the strength of this correlation. Note that 82% of our "high resolution" detectors were Type I's, 55% of the "poor resolution" detectors were Type L's and 80% of the "no photopeak" detectors were Type D's.

Figure 5 displays correlation statistics for IVC Type versus Ingot Location. Note that there is a strong correlation between the number of Type I detectors and location expressed as distance above ingot bottom (first to freeze end). That is, 85% of the units located 2 cm above the bottom are Type I's and 0% of the units located 6 cm above the bottom are Type I's. Conversely, the percentages of Type L and Type D units increase monotonically from 15 and 0 percent respectively at the 2 cm location to 50% each at the 6 cm location. This data may indicate that some impurity or other performance controlling defect is monotonically increasing or decreasing along the ingot axis.

Figure 6 shows the IV characteristics versus Slice Number statistics. No significant correlation is indicated with the exception of the small percentage of Type L units in Slice 3. The slices were cut nearly parallel to the ingot axis, thus this result is not unexpected given the distributions shown in Figure 5. That is, all three slices contained material from locations 2 cm to 5 or 6 cm above ingot bottom.

IR Microscopy

Figure 7 displays the morphologies of precipitates and inclusions found in the ingot. The typical triangle size is from 20 to 30 microns. The ovals tend to be in the 5 to 10 micron range. The 10 to 15 micron sized "staple" shaped precipitates are unusual in our experience. We have never observed this shape in either CdTe or CdZnTe material grown for epitaxial substrate applications by the sealed quartz ampoule, vertical Bridgman method (data base contains over 4000 ingots), therefore it may be unique to HPB processed material. Extended "line segment" inclusions are 5 to 15 microns wide and from 1 to 15 nm in length. The nature of these is not yet understood, but some of them may be voids formed during solidification and sometimes referred to as "metallurgical piping".

Figures 8 and 9 show the maps of precipitates and inclusions in Slices D3 and D6 respectively. Note the strong tendency for triangles and ovals to occur on or near grain boundaries. Also, the line segments all occur in the last to freeze end of the slices where we showed higher populations of Type L and Type D detectors. The orientation notes in Figures 8 and 9 refer only to the {111} region of each slice. The orientations of the peripheral grains were not determined.

Dislocation Etch Pitting

A macro photo of the Nakagawa etch pitted A-face side of Slice D3 is shown in the center of Figure 10. The macro photo is overlaid with a grid showing the location of the 12 detectors fabricated from this slice. Only the brighter area, corresponding to the A-face of the central grain, is pitted by the Nakagawa etch procedure. Higher magnification photographs of specific features reveal a variety of defects, ranging from uniform $4\text{E}4/\text{cm}^2$ EPD areas, to graded EPD bands, to high ($>1\text{E}6/\text{cm}^2$) EPD areas near certain grain boundaries. Two interesting features shown are the crossed slip line patterns and the crystallographically oriented dislocation punchouts around precipitates.

Figure 11 displays the analogous EPD features of Slice D6. One additional pattern seen in this slice is the major fault running across Detector D6-19 and terminating in massive tangles at the grain boundary in the lower left region of Detector D6-20. Also, cellular patterns are evident in the region containing Detectors D6-12 and D6-15. Slice D6 EPD values range from $8\text{E}4/\text{cm}^2$ to $>1\text{E}6$.

X-ray Diffraction

Our X-ray diffraction study to date has included only a detailed analysis of Detector D3-6 as shown in Figure 12. Note that this detector is a Type I unit showing high Am^{241} energy resolution as represented by a 4% FWHM of the 59.5 keV photopeak. As recorded on the topograph, this detector contains a number of structural defects including an area populated with cellular dislocation tangles and a series of slip lines oriented along {111} planes which are inclined to the {111} surface. Notice also the strong subgrain boundary beyond which the tilt of the lattice is enough to destroy

the Bragg diffraction condition, creating a completely dark region on the topograph.

Four 2x2 cm² areas were selected for DCRC measurements as shown in Figure 12. All four of the resulting rocking curves indicate considerable lattice disruption by their shouldered or multipeak character. A perfect CdTe lattice should yield a rocking curve FWHM of 8 to 9 arc seconds for the {333} reflection and diffraction conditions utilized. Note however that the upper two areas do show significantly better structure than the lower two areas. The upper left quadrant of the detector appears on the topograph to have the cleanest structure and the lower right is probably the most disturbed. A follow up experiment we plan to conduct is to quarter this detector and attempt a detector performance to crystal structure correlation on a smaller scale.

IV Characteristics versus Temperature

IV characteristics have been measured for sample D6-7 within the temperature range -60 to 40 C, as shown in Figure 13. While the increasing resistance behavior dominates over this temperature range, there is some difference below T=20 C at -200 V detector bias, where decreasing resistance behavior is observed. In order to further probe this deviation, our studies will be extended to larger negative biases. Also, the IV curves will be examined with appropriate models to extract useful parameters relating to metal-semiconductor contacts and bulk crystal properties.

Also shown in Figure 13 is the logarithmic of the detector resistance at various temperatures. Fitting of the data gives rise to an activation energy of 0.75 eV between 0 to 60 C, and 0.25 eV between -60 to 0C, where possible impurity effects are increasingly important.

PHA versus Temperature

Figure 14a shows a three dimensional plot of pulse height analysis versus temperature for CdTe detector D6-7 using gamma-rays from Am241. A conducting rubber is put in between the Am241 source and the detector surface, thus alpha particles and low energy X-rays will be stopped or attenuated before they are

detected. It will be the 59.5 keV gamma-ray peak that is of main interest in our studies. In figure 14a, A drastic reduction in pulse height is found below -25 C, as is also indicated in Figure 14b. The percentage FWHM, representative of the resolving ability of this detector is found to be optimum at around -20C, where the peak-to-valley ratio is also maximized. The temperature dependence observed here can be associated with defect trapping properties which affect the lifetime of carriers, and carrier mobility and other material temperature dependent properties. In that respect, combined study with thermally stimulated current (TSC) and other techniques will provide a more quantitative interpretation of our observations. We note here that polarization effect appears below about -25 C, the PHA spectra in figure 14 are taken when there are negligible time dependence in the detector performance. Detailed polarization study will be reported elsewhere.

Charge Collection versus Bias

Figure 15a shows detector bias dependent collection of electrons and holes under LED illumination between -60 to 40 C for sample D6-7. The signal amplitudes at 200 V bias are plotted in Figure 15b as a function of temperature for both electrons and holes. For electrons, the optimum charge collection is achieved at around -20C, in agreement with the PHA measurement shown in Figure 14. The maximum collectible charge decreased by about a factor of two when the temperature reached -60C. However, the hole signal reaches a maximum value between 0 and -20C, and the signal amplitude is reduced by almost an order of magnitude at -60C, indicating possible deep trap characteristics for holes in this temperature range. The decrease in electron and hole collectible charge with increasing temperatures above $T=0^{\circ}\text{C}$ is associated with the decrease of the carrier mobilities. It should be pointed out that the polarization effect below -25 C will affect the measurements and introduce deviations from an ideal Hecht relation.

Charge Transport Properties

Figures 16 and 17 show the evaluation of $\mu\tau$, μ and τ values for electrons and holes from the transient charge technique previously discussed for sample D6-7. One hundred transient charge pulses are recorded and averaged for each bias voltage at room

temperature to obtain a value for the maximum collectible charge. The result thus obtained is fitted to Hecht relation with two free parameters, i.e., the maximum collectible charge, Q_0 , and $\mu\tau$ product as indicated in the figures. The obtained $\mu\tau$ product for electrons is 6×10^{-4} cm²/V. For holes, Q_0 is fixed at the electron value when extracting the $\mu\tau$ product, and consequently, the fit for holes will be less than ideal. Nevertheless, the obtained value, 3×10^{-5} cm²/V, agrees with previous studies [ref.X]. The differentiated electron pulse compares well with simple transient current response with no detrapping effects, hence its FWHM is taken to be the transit time of the electrons. Measurements with biases ranging from 50 V to 200 V yield an electron mobility value of 1050 cm²/V.S, giving rise to an electron lifetime of about 0.57 micro-sec. The wave form for holes in Figure 17 is less well defined for the purpose of obtaining the transit time, compared with that for electrons, because of the presence of detrapping effects. Nevertheless, by taking the FWHM of the differentiated charge response as the transit time, a mobility value of 45 cm²/V.S is consistently obtained for detector biases between -100 to -300 V. We note here that if trapping is severe, the FWHM of the current pulse will be artificially decreased, thus the hole mobility obtained here will represent an upper limit for the actual value. The resulting hole lifetime from the evaluated $\mu\tau$ and μ values is 0.67 microsec, comparable to the value found for electrons.

Detector Performance Features

Figure 18 shows the Am241 spectrum for Detector D3-2 at three different bias field strengths. The character of these spectra is different from all others shown in this paper in that these three were recorded with a Be window on the detector enclosure rather than an Al window. Our intent here is to document the degradation in resolution and noise threshold as the bias field is decreased. It is clear that the resolution at 59.5 keV has decreased from 4.4% to 8.5% in response to a decrease in the field from 1000 V/cm to 250 V/cm. It can also be seen that the Np X-ray structure from 14 to 21 keV far less resolved at a bias field of 250 V/cm than at 1000 V/cm.

In order to investigate the operating stability of Type I detectors, we placed this same detector on a 100 hr test under continuous irradiation by an Am241 source and continuous bias at a field strength of 1000V/m. The results are shown in Figure 19. It

can be seen that the performance changed only minimally during the test, indicating that short term stability of Type I detectors is satisfactory. Long term detector stability is currently under investigation and will be reported elsewhere.

CONCLUSIONS

We have investigated CdTe high pressure Bridgman grown radiation detector grade materials and fabricated a set of 50 detectors from one 3 kg ingot. Detectors have been classified into three groups based on their IV characteristics; Types I, L and D for Increasing, Linear and Decreasing Resistance characteristics, respectively. We found that Type I correlates strongly with high photopeak resolution and low noise threshold, Type L with poor photopeak resolution and higher noise threshold and Type D with no photopeak resolution and noise threshold >25 keV. In the type-I detectors, the resolution of HPA008 detectors is typically 4-5% FWHM at the 60 keV gamma-ray energy, indicating that high quality detectors can be fabricated by the high pressure Bridgman method.

A significant correlation also exists between detector type and ingot location measured as distance above the first to freeze.

No clear relationships have yet been established between detector performance and specific crystallographic and metallurgical defects studied by optical and IR microscopy, dislocation etch pitting and X-ray diffraction. Directions for continuing studies are however indicated by progress to date.

Measurements of Type I, HPB grown CdTe detectors demonstrate excellent 100 hours stability and attractive low bias performance. The charge transport characteristics of a set of detectors were studied and found to be consistent with previous literature values. However, an interesting decrease in the pulse height and transport properties occurred at approximately -20 C for both holes and electrons. Data presented on pulse height analysis, charge collection and charge transport properties indicate an advance in the quality of HPB CdTe radiation detectors. Further work will be carried out in extracting quantitative information about material properties from charge transport and related techniques.

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REFERENCES:

[X] see, e.g., E. Sakai, Nucl. Instru. Meth. 196, 121-130, (1982).

TRANSIENT CHARGE TECHNIQUE SETUP

Fig 1

EPD Macrophotos of Three {111} Oriented Slices Showing 51 Detector Layout

Slice D3

4 - {111} Singles
8 - Partial {111} Polys

12

Slice D5

5 - {111} Singles
8 - Partial {111} Polys

4 - Unoriented
17

Slice D6

4 - {111} Singles
9 - Partial {111} Polys

4 - Unoriented
22

Total 51

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IV Characteristic & Am241 Spectrum Screening Three Types

I = Increasing R

and

High Resolution:
FWHM = 4% @ 59.5 keV
Low Noise:
Threshold = 7 keV

Detector D3-2
@ 1000 V/cm

L = Linear

and

Poor Photopeak:
FWHM = 16% @ 59.5 keV
Higher Noise:
Threshold = 15 keV

Detector D6-4
@ 1000 V/cm

D = Decreasing R

and

No Photopeak
Very High Noise:
Threshold > 25 keV

Detector D3-8
@ 1000 V/cm

Correlation of IVC Types and Photopeak Character

Correlation of IVC Types and Ingot Location

Correlation of IVC Types and Slice Numbers

Fig 2

Morphologies of Precipitates in CdTe Ingot HPB008

Triangles & Small Ovals

HPA008-D6

Triangles and Ovals

HPA008-D5

Line of Staple Shapes

HPA008-D4

Line Segment

HPA008-D5

Map of Precipitates in Slice HPA008-D3

Map of Precipitates in Slice HPA008-D6

11/3/0

Etch Pitting Results for Slice HPA008-D3

Etch Pitting Results for Slice HPA008-D6

X-ray Diffraction Measurements of HPB CdTe Detector D3-6 (1 x 1 x .2 cm³; I-Type; Ili Res w/4% FWHM @ 59.5 keV)

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IV Characteristics of 1x.7x.2 cm³ HPB CdTe Detector D6-7

IV Temperature Dependence

$$E_a = \begin{cases} 0.75\text{eV} & 0 \text{ to } 60^\circ\text{C} \\ 0.25\text{eV} & -60 \text{ to } 0^\circ\text{C} \end{cases}$$

Fig. 14

Detector D6-7 Pulse Height Analysis from -60 to 40°C **(1x.7x.2 cm³ HPB CdTe @ 200V bias)**

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Electron & Hole Signal versus Bias from -60 to 40°C (1x.7x.2 cm³ CdTe Detector D6-7 with LED Excitation)

Room Temperature $\mu\tau$, μ and τ for Electrons (HPB CdTe Detector D6-7, $1 \times 7 \times 2 \text{ cm}^3$)

$$Q = Q_0 \mu \tau V_B / d^2 [1 - \exp(-d^2 / \mu \tau V_B)]$$

$$\mu = d^2 / T_R V_B$$

V_B : bias; d : thickness;

T_R : transit time

$$\begin{aligned} \mu \tau &= 8 \times 10^{-4} \text{ cm}^2 / \text{V} \\ \mu &= 1050 \text{ cm}^2 / \text{V} \cdot \text{sec} \\ \tau &= 0.57 \mu\text{s} \end{aligned}$$

Room Temperature $\mu\tau$, μ and τ for Holes (HPB CdTe Detector D6-7, $1 \times 7 \times 0.05 \text{ cm}^3$)

$$Q = Q_0 \mu \tau V_B / d^2 [1 - \exp(-d^2 / \mu \tau V_B)]$$

$$\mu = d^2 / T_R V_B$$

V_B : bias; d : thickness;

T_R : transit time

$$\begin{aligned} \mu\tau &= 3 \times 10^{-5} \text{ cm}^2/\text{V} \\ \mu &= 45 \text{ cm}^2/\text{V} \cdot \text{sec} \\ \tau &= 0.67 \mu\text{s} \end{aligned}$$

Detector Performance versus Bias for Detector D3-2

Material: High Pressure Bridgman (HPB) CdTe
Size: 1 x 1 x 0.2 cm³
Detector Window: 0.25mm Thick Be

Results of 100 hr Test of Detector D3-2 (Continuous Bias @ 1000 V/cm)

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