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Material and Detector Properties and Cadmium Manganese Telluride (CdMnTe) Crystals Grown by the Modified Floating-Zone Method

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Material and detector properties of cadmium manganese telluride ($Cd_{1-x}Mn_xTe$) crystals grown by the modified floating-zone method

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Abstract:

We demonstrated the material- and radiation-detection properties of cadmium manganese telluride ($Cd_{1-x}Mn_xTe$; x=0.06), a wide-band-gap semiconductor crystal grown by the modified floating-zone method. We investigated the presence of various bulk defects, such as Te inclusions, twins, and dislocations of several as-grown indium-doped $Cd_{1-x}Mn_xTe$ crystals using different techniques, viz., IR transmission microscopy, and chemical etching. We then fabricated four planar detectors from selected CdMnTe crystals, characterized their electrical properties, and tested their performance as room-temperature X- and gamma-ray detectors. Our experimental results show that CMT crystals grown by the modified floating zone method apparently are free from Te inclusions. However, we still need to optimize our growth parameters to attain high-resistivity, large-volume single-crystal CdMnTe.

Keywords: CdMnTe, Te inclusions, dislocations, IR transmission, spectral response, mobility-lifetime product.

Introduction:

Recently Cadmium Manganese Telluride (CMT) has emerged as a promising material for room-temperature X- and gamma-ray detectors [1-4] because it offers several potential advantages over CdZnTe. Among them are its optimal tunable band-gap, ranging from 1.7-2.2 eV, and its relatively low content (<5%) of Mn, compared to that of Zn in CdZnTe (10%) that assures a favorable band-gap range. Another important asset is the segregation coefficient of Mn in CdTe that is approximately unity compared to 1.35 for Zn in CdZnTe [5], so ensuring the homogenous distribution of Mn throughout the ingot; accordingly, a large-volume stoichiometric yield is attained. However, some material drawbacks primarily related to the growth processes, such as twins, dislocations, and Te inclusions, impede the production of large single crystals with high resistivity and a high mobility-lifetime product. Twins and grain boundaries are identified easily and can be screened out in selecting single crystals for fabricating radiation detectors. In contrast, Te inclusions and dislocations that extend throughout the bulk material can only be traced by IR transmission microscopy and other advanced methods. They trap only small fractions of the charge from the electron clouds, but, at high concentrations, such defects collectively introduce significant fluctuations in the devices' responses. Here, we report

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on our observations of material defects in CdMnTe (CMT) materials grown via the modified floating zone method. We characterized various defects, e.g., Te inclusions, twins, and dislocations in such crystals grown by the floating-zone method using advanced techniques, viz., white-beam x-ray reflection topography, IR transmission microscopy, and chemical etching. Thereafter, we fabricated some detectors from carefully selected CdMnTe crystals, characterized their electrical properties, and tested their performance as room-temperature X- and gamma-ray detectors.

Results and discussion:

A detector's properties, like high resistivity, good mobility-lifetime, homogeneity, and crystalline perfection, are highly dependent upon the technology of crystal growth and the purity of source materials. Considering anticipated growth-related issues based on our knowledge of CdZnTe, we introduced a floating-zone method to grow our crystals. Its specific advantage is that we can control the temperature gradient at the solid-liquid interface at the front of growing crystal, so preventing Te merging into the single crystals.

1) Crystal growth

We grew several CMT ingots before with different In-doping, and characterized their properties [6]. We modified the conventional floating zone method and used quartz ampoule to hold the Cd, Zn and Te zone liquids; thereafter we called it modified floating zone (MFZ) method. We synthesized 7N-grade CdTe and 6N-grade MnTe in a 19-mm-diameter vacuum-sealed quartz ampoule and then melted the synthesized material at 1035°C at a velocity of 200 mm/hr in a three-zone tube furnace. Afterwards, we mounted the pre-melted ingot rod in a quartz tube in a NEC floating-zone machine. The pre-melt ingot rod was grown at 0.5 mm/hr in 1bar H_2 atmosphere with a Te-rich melt zone. The temperature gradient at the front of the solid-liquid interface was kept high to control the assimilation of excess Te into the grown ingot.

In this study, we grew a CMT ingot with In-doping of 15% after considering the outcomes of our previous growth experiments. Fig. 1 displays a typical In-doped ingot that was grown by this modified floating zone method. We cut and extracted three wafers radially from the head, middle and tail areas of the ingot. We examined the wafers under an infrared (IR) microscope to observe and to register the Te inclusions and other bulk defects. In optical images of the chemically etched wafers, we noted that twins started to grow at the beginning of the ingot, but mostly had disappeared around its middle part. However, more grains developed towards the tail of the ingot. The CMT crystals have higher tendency to generate twins compared to CZT crystals due to their higher bond-ionicity [7-8]. Seemingly, the growth parameters for CMT crystals still not fully optimized. We need more focus on the growth parameters and post-growth cooling process.

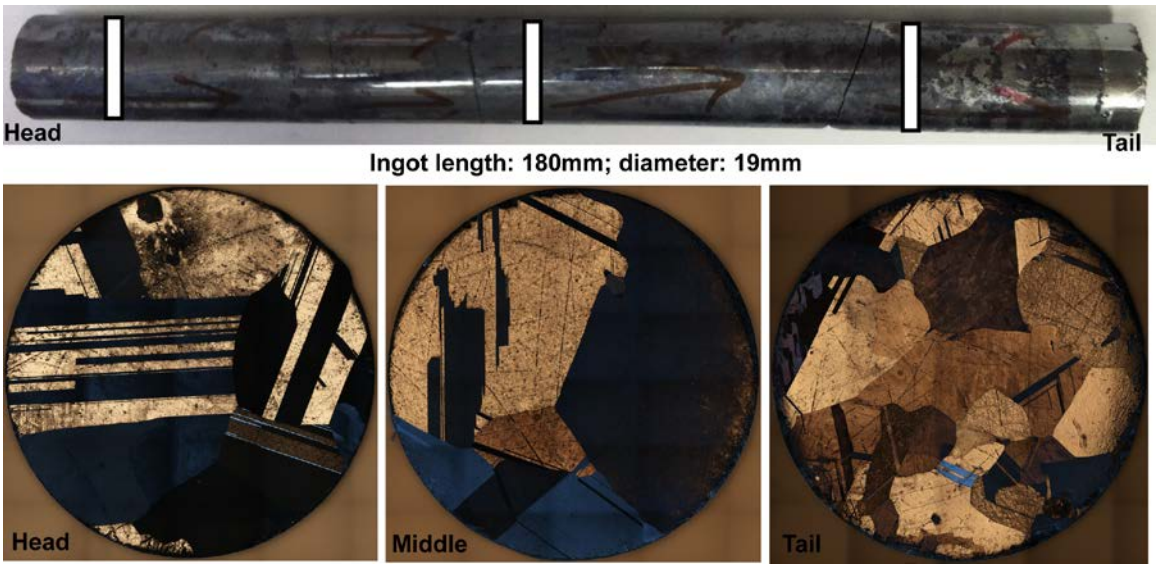


Fig 1. (Top) Image of CMT ingot grown by the modified floating zone method. (Bottom) Optical images of three wafers sliced from head, middle and tail parts of ingot. Twins and grains are clearly depicted at chemically etched wafers.

2) Material characterization

We examined two wafers from first-to-freeze and last-to-freeze under IR transmission microscopy. In the IR images of two wafers shown below, we note that a few Te inclusions were concentrated mostly along the grain boundaries and around the edge of the wafer, most of the areas of the wafers apparently are free from Te inclusions. We note that crystals grown by the modified floating-zone method contained about 10^3 to 10^4 orders of magnitude less concentrations of Te inclusions compared to those reported in CMT and CZT crystals grown by the Bridgman method [9-10].

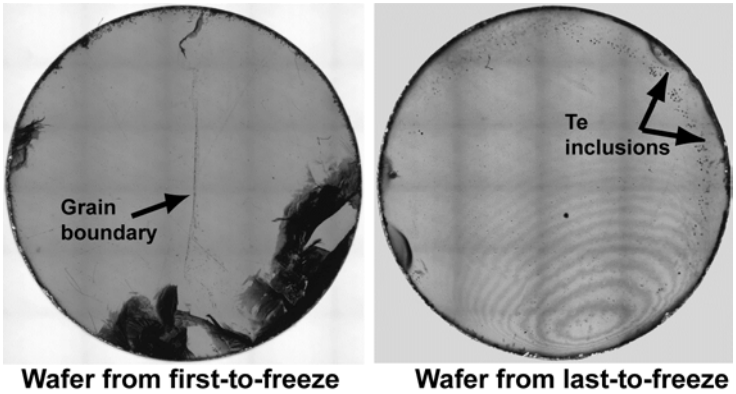


Fig 2. IR transmission microscopic images of two CMT wafers obtained from first-to-freeze and last-to-freeze part of the growth ingot. Most of the areas of both wafers are free from Te inclusions.

Chemical etching is a direct method for assessing the distribution and density of crystallographic dislocations. Once a dislocation line intersects the surface, the associated strain field locally increases the relative susceptibility to suitable etching solutions resulting in geometrical pits in that area. We used HF-based chemical etchants to reveal the dislocation-related etch pits on CMT crystal's surfaces. Fig. 3 (a) shows that the wafer has two domains and several twins have formed across the area shown. In Fig. 2(b), dislocation etch pits are clustered in a linear-and cellular-pattern. The estimated etch pit density (EPD) is in the range of 10^3 - 10^5 cm^{-2} in a single crystal. We observed similar or higher concentrations of dislocation defects in other CMT crystals, as reported elsewhere [11].

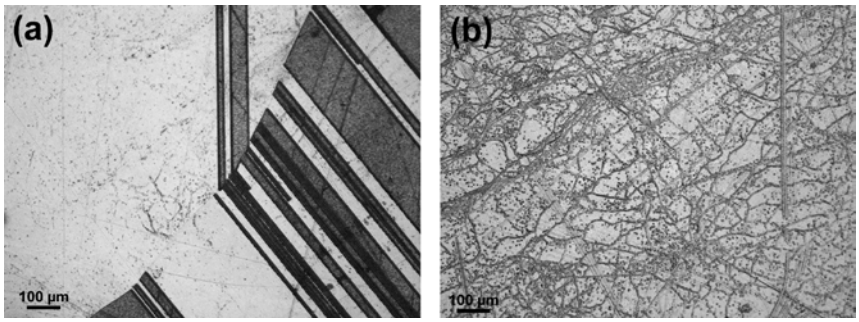


Fig 3. Images of chemically etched CMT surfaces. (a) Grain boundary, several twins, and a low concentration of etch pits were generated in certain areas of the crystal. (b) High concentration of dislocations etch pits were revealed, appearing in linear- and cellular- patterns. The estimated density of etch pits ranged from 10^3-10^5 cm^{-2}.

2) Detector fabrication and testing

We fabricated four planar-type detectors (D1, D2, D3 and D4) from selected CMT crystals with two different contact configurations (Au-CMT-Au and Pt-CMT-In/Ti) and tested their performance. We recorded the gamma-ray responses of D1, D3 and D4 detectors but not D2 due to its high leakage current. We determined their leakage currents from current-voltage measurements using an I-V probe, and calculated that the resistivity of the CMT crystals lies in the range of 10^8 -10^9 Ω-cm. We tested the detectors using gamma-ray sources and extracted a mobility-lifetime value that was in the range of $6x10^{-4}$ -$1x10^{-3}$ cm^2/V from the best fit to the Hecht equation. Figure 4 plots the current-voltage measurement of different detector configurations, pulse-height spectra, and the mobility-lifetime value. Table-I shows the pictures of four planar detectors and their properties.

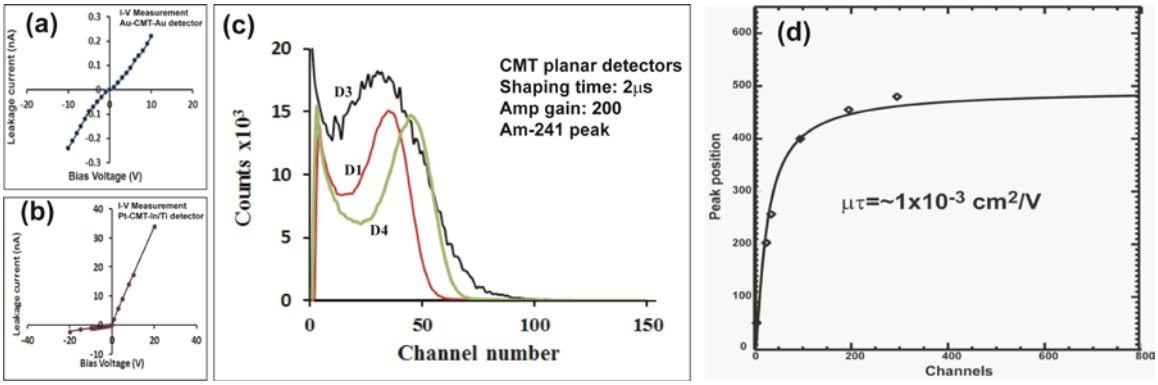
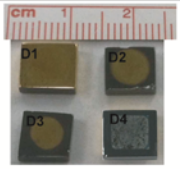


Fig 4. (a,b) Plot of current-voltage measurements of Au-CMT-Au and Pt-CMT-In/Ti planar detectors. The resistivity was calculated from the slope of the curve. (c) Am-241 gamma spectra recorded from three CMT planar detectors, and (d) The Hecht plot. The mobility-lifetime value was extracted from the best fit. The highest value $1x10^{-3}$ cm^2/V was recorded for floating zone grown CMT crystal.

Table-I: Detector properties

Sample ID	Contact configuration	Dimension	Max. applied Bias (V)	Resistivity (ohm-cm)	Product cm^2/V
D1	Au-CMT-Au		60	$8x10^9$	$1x10^{-3}$
D2	Au-CMT-Au		20	$2x10^8$	-
D3	Au-CMT-Au		50	$6x10^8$	$2x10^{-4}$
D4	Pt-CMT-In/Ti		100	$4x10^9$	$6x10^{-4}$

Conclusions:

Our experimental results indicate that our crystals grown by the modified floating-zone method are mostly free from Te inclusions, which is a notable achievement for CMT crystals and also for other similar crystals like CZT. However, the resistivity of the crystals is in the range of 10^8 -10^9 Ω-cm which is about 1-2 orders lower than the ideal range for a good detector. We believe that it can be increased by optimizing the doping concentration. The crystals contain higher number of twins and dislocations that must be reduced. The mobility-lifetime value, one of the major properties of a radiation detector is in the range of $6x10^{-4}$-$1x10^{-3}$ cm^2/V, about 1-2 orders less than that of high-quality CZT detector (10^{-2} cm^2/V). From our experience, we need to focus our corrective actions on optimizing the growth parameters and doping concentration to produce high-resistivity large-volume CMT single crystals for good radiation detectors.

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