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Tellurium precipitates in (Cd,Mn)Te:V crystals: Effects of annealing

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***Abstract*– We suggest that (Cd,Mn)Te is a suitable material for fabricating gamma- and X-ray detectors [1]. Our investigations, reported here, are focused on producing high-quality (Cd,Mn)Te crystals with high resistivity (10^9 Ω-cm) by the Bridgman method.**

As-grown, undoped (Cd,Mn)Te crystals are typically p-type, signifying that they contain excess Cd vacancies (acting as acceptors), accumulated during growth. Doping with vanadium atoms, which function as compensating centers, results in a semi-insulating material (Cd,Mn)Te:V. Properly annealing the platelets in cadmium vapors at uniform temperature reduces the number of cadmium vacancies, and lowers the level of the vanadium doping required for compensation.

We found that annealing in cadmium vapors not only decreases the concentration of the native cadmium vacancies but also improves the crystal's quality. Infrared observations of the interior of the samples show that annealing in a temperature gradient perpendicular to the platelet has an additional effect, viz., the tellurium precipitates migrate towards the side where the temperature is higher.

We demonstrate, with IR pictures of monocrystalline (Cd,Mn)Te:V platelets cut parallel to the (111) crystal planes, the influence on tellurium inclusions and precipitates of various conditions of annealing in cadmium vapors.

INTRODUCTION

X-ray and gamma-ray detectors have wide applications in security and medical diagnostics. Although CdTe and (Cd,Zn)Te are the material customarily used, recently, (Cd,Mn)Te was proposed as a potentially better material for the detectors. In our previous paper [1] we discussed some of its advantages.

Among the major benefits of using (Cd,Mn)Te rather than of (Cd,Zn)Te are its better homogeneity, monocrystalline blocks in the crystal, and the smaller amount of the second cation that must be added. Moreover, what is important for cutting the platelets, the twins in (Cd,Mn)Te spread across the whole crystal.

Among the defects that occur in the CdTe-based crystals are point defects, linear defects (dislocations), planar defects (such as twinning), tellurium precipitates and inclusions. All of them influence the transport of current carriers in the material.

Cadmium vacancies (V_{Cd}), which are characteristic of tellurium-based materials like CdTe grown by the Bridgman method, deserve special attention. The presence of cadmium vacancies, which act as acceptors, lead to p-type crystals. They are the reason why as-grown Bridgman crystals have low resistivity ($\approx 10^1 \div 10^3$ Ω·cm). To decrease their concentration, and thus increase resistivity, the crystals are annealed in Cd vapors.

The proper annealing procedure not only increases the resistivity, but also, as we show later, improves the materials crystalline quality, reducing the number of dislocations and tellurium precipitates.

Tellurium precipitates are undesirable in crystals intended for detectors as they are local regions of completely different physical properties, including resistivity, and energy gap. In this communication, we report the findings from the two different methods of annealing in the Cd-

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vapors: annealing at uniform temperature, and annealing in a temperature gradient. Vydyanath et al. [2], [3] proposed a method of eliminating tellurium precipitates in CdTe and (Cd,Zn)Te crystals, and a mechanism explaining this method. Some of our results, discussed herein, confirm the applicability of their ideas to (Cd,Mn)Te.

Experimental details

Research on growing cadmium manganese telluride (Cd,Mn)Te crystals doped by vanadium at the Institute of Physics, Polish Academy of Sciences (IP PAS) focuses on Bridgman growth from the melt [1], [4]. A dopant is used to obtain high-resistivity ($\rho \geq 10^9$) material for fabricating X- and gamma-ray detectors.

Observations with infrared (IR) microscopy, measurements of the density of dislocations (by etch pit density-EPD), and mapping of the resistivity are undertaken on mechanically or mechano-chemically polished (Cd,Mn)Te samples.

Ingots are cut parallel to the twinning planes, which are revealed by etching in HF:HNO_3:acetic acid solution [5]. The (Cd,Mn)Te (111) wafers are mechanically polished with a 20÷30 μm powder and mechano-chemically polished on rubber covered with a mixture of bromine (4 ml), methanol (125 ml), and glycol (75 ml). For EPD measurements, we etch the platelets, after mechano-chemical polishing, in the EAg-2 solution, following Inoue et al. [6]. On selected crystal surfaces (e.g., parallel to the (111) or (110) crystal planes), the etch pits have a characteristic shape and can be easily observed (and counted) under an optical microscope.

To assess the influence of the annealing regime on the properties of (Cd,Mn)Te crystals, we placed the platelets from the as-grown material, together with a piece of pure cadmium, in quartz ampoules and put them into the furnace (Fig. 1). The ampoules are evacuated with a high-vacuum pump and closed with a quartz plug. A few platelets are placed inside the ampoule; they are supported by a special quartz holder. The crystallographic direction [111] of the platelets is parallel to the ampoule's axis. For annealing at uniform temperature, we usually ensure that the tellurium (B) sides face the bottom of the ampoule (the rounded end). For annealing in a temperature gradient, we maintain the bottom of the ampoule at a higher temperature. For investigating the migration of the tellurium precipitations, either the tellurium (B) or cadmium (A) sides are directed towards the bottom of the ampoule (where the temperature is higher). As shown in Fig. 1, thermocouples monitor the temperatures at the ends of the ampoule.

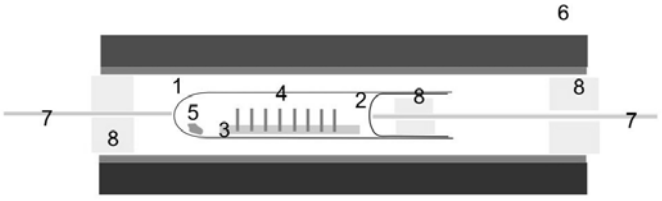

Fig. 1. Quartz ampoule with samples inside the furnace. 1 – quartz ampoule, 2 – quartz plug, 3 – quartz holder for samples, 4 – samples, 5 – pure cadmium, 6 – heater, 7 – thermocouple, 8 – thermal insulation.

Since we applied two annealing procedures to the crystal platelets, we placed the ampoule in two different positions with respect to the furnace and its temperature characteristics.

These two locations, for annealing at nearly uniform temperature and in the gradient of temperature, are depicted in Figs. 2 and 3, respectively.

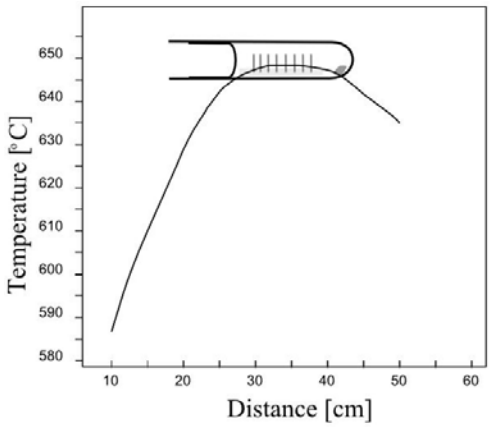

Fig. 2. Temperature profile of the furnace and position of the ampoule during annealing at nearly uniform temperature.

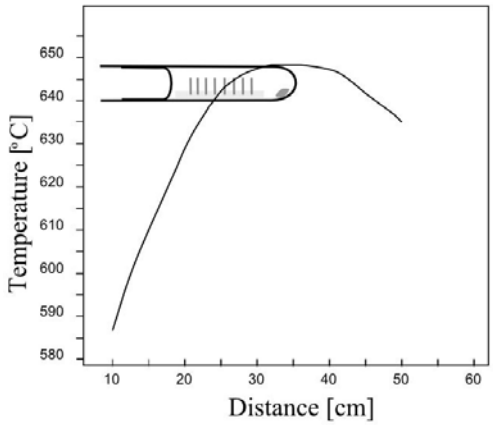

Fig. 3. Temperature profile of the furnace and position of the ampoule during annealing in the temperature gradient.

During annealing at uniform temperature, the cadmium vapors in the ampoule are saturated. The annealing process has three steps: we maintain the temperature at 650 ºC for about 100 hours, then lower it, first to about 450 ºC, and later to 250 ºC. Thereafter, the sample is left to cool to room temperature.

During annealing in the temperature gradient, the cadmium vapors are unsaturated and their pressure is determined by the temperature at the cooler end of the ampoule. In this annealing process we maintained a temperature of 650 ºC for about 100 hours, and subsequently lowered the temperature. The magnitude of the temperature gradient is about 3~5 ºC/cm.

Experimental results and discussion

Cadmium vacancies and resistivity.

Annealing in the cadmium vapors at uniform temperature decreases the concentration of the cadmium vacancies in the material, and thus increases resistivity. After annealing in the temperature gradient, we observed an increase in the material's resistivity. Presumably, the V_{Cd} concentration is lower than before annealing.

Table 1 lists the resistances of undoped (Cd,Mn)Te samples before and after annealing at uniform temperature.

TABLE I
RESISTANCE OF UNDOPED (CD,MN)TE SAMPLES BEFORE AND AFTER ANNEALING AT UNIFORM TEMPERATURE.

$Cd_{0.73}Mn_{0.07}Te$ No. 4538 No. Sample	Resistance between identical electrodes [Ω]	
	Unannealed	Annealed at uniform temperature
1	$7.0 \cdot 10^4$	$2.7 \cdot 10^6$
2	$6.7 \cdot 10^4$	$4.7 \cdot 10^5$
3	$8.6 \cdot 10^4$	$1.8 \cdot 10^6$

The resistivity map of the sample (from the same crystal ingot) after annealing at uniform temperature is given in Fig.4. (Such a map could not be made before annealing, as the resistivity was too low (< 10^5 Ω cm) for the apparatus to quantify the resistivity).

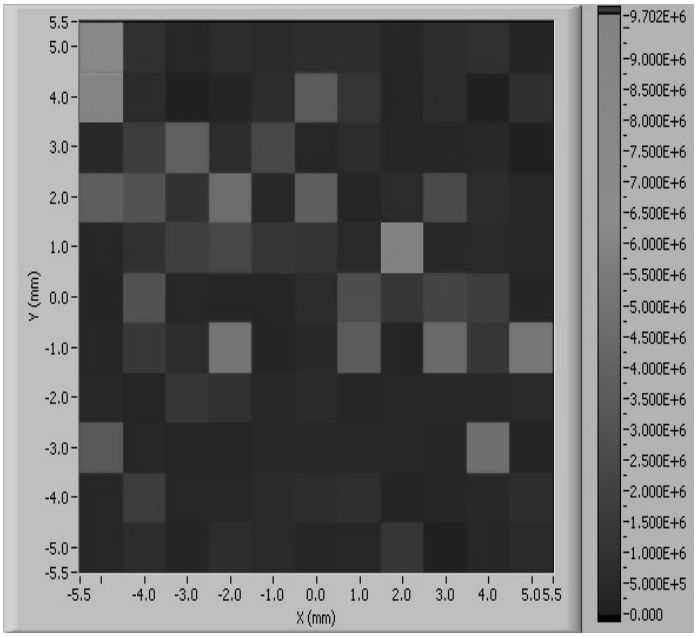

Fig. 4. Mapping of the resistivity by Time-Dependent Charge Measurement, TDCM (with the "Eu-ρ-scan" from EURORAD) of an undoped (Cd,Mn)Te crystal No. 4538, annealed at uniform temperature.

Resistivity increases of about two orders-of-magnitude were observed after annealing due to the reduction in the concentration of cadmium vacancies.

Density of dislocations.

We measured the density of dislocations (determined as EPD) in samples from the same crystals that we used to investigate the density of tellurium precipitates (described in the next section). Table II gives the results.

A decline in dislocation density was observed on both faces of the (Cd,Mn)Te crystal plates after annealing at uniform temperature and in the temperature gradient.

Tellurium precipitates.

Two types of tellurium precipitates are distinguishable in the (Cd,Mn)Te crystals -- small ones (diameter 2 - 8 μm) and large ones (diameter 15- 0 μm). The IR measurements of the density of the tellurium precipitates were carried out for the crystal platelets before and after annealing in the temperature gradient. Table III shows the findings.

TABLE II
DISLOCATION DENSITIES (EPD) IN THE (CD,MN)TE CRYSTALS BEFORE AND AFTER ANNEALING

Crystal	Sample	EPD [cm^{-2}]			
		Unannealed		Annealed	
		A face (Cd)	B face (Te)	A face (Cd)	B face (Te)
$Cd_{0.94}Mn_{0.06}Te$:V ($5\cdot10^{16}$ cm^{-3})	4503_2+	$2.5\cdot10^3$	$6.7\cdot10^4$	$1.5\cdot10^2$	$9.0\cdot10^3$
$Cd_{0.94}Mn_{0.06}Te$:V ($5\cdot10^{16}$ cm^{-3})	4503_2-	$5.6\cdot10^5$	$5.7\cdot10^5$	$1.0\cdot10^3$	$3.5\cdot10^4$

$Cd_{0.94}Mn_{0.06}Te$:V ($5\cdot10^{16}$ cm^{-3})	4503_5-	$7.5\cdot10^{4}$	$4.5\cdot10^{4}$	$1.8\cdot10^{3}$	$2.8\cdot10^{4}$
$Cd_{0.94}Mn_{0.06}Te$:V ($5\cdot10^{16}$ cm^{-3})	4512_8	$1.7\cdot10^{5}$	$1.4\cdot10^{5}$	$7.0\cdot10^{5}$	$4.5\cdot10^{4}$
$Cd_{0.94}Mn_{0.06}Te$:V ($5\cdot10^{16}$ cm^{-3})	4513_1	$9.2\cdot10^{4}$	$3.0\cdot10^{4}$	$3.5\cdot10^{3}$	$1.8\cdot10^{4}$
$Cd_{0.91}Mn_{0.09}Te$:V ($1\cdot10^{16}$ cm^{-3})	4519_9	$5.8\cdot10^{4}$	$4.3\cdot10^{5}$	$1.3\cdot10^{5}$	$3.4\cdot10^{5}$
$Cd_{0.91}Mn_{0.09}Te$:V ($1\cdot10^{16}$ cm^{-3})	4520_c	$4.8\cdot10^{5}$	$4.9\cdot10^{5}$	$4.4\cdot10^{5}$	$8.8\cdot10^{5}$
$Cd_{0.91}Mn_{0.09}Te$:V ($1\cdot10^{16}$ cm^{-3})	4520_d	$8.2\cdot10^{5}$	$2.4\cdot10^{5}$	$2.1\cdot10^{5}$	$7.4\cdot10^{4}$
$Cd_{0.95}Mn_{0.05}Te$:V ($3\cdot10^{16}$ cm^{-3})	4527_a	$5.0\cdot10^{3}$	$2.4\cdot10^{4}$	$1.0\cdot10^{3}$	$1.1\cdot10^{4}$

TABLE III
DENSITY OF THE TELLURIUM PRECIPITATES ON THE (111) CADMIUM AND (111) TELLURIUM SURFACES BEFORE AND AFTER ANNEALING IN A GRADIENT OF TEMPERATURE.

Te precipitates density, given per cm^2 (focal length of IR microscope is 100 μm)					
Crystal	Sample	Unannealed		Annealed	
		A face (Cd)	B face (Te)	A face (Cd)	B face (Te)
$Cd_{0.94}Mn_{0.06}Te$:V ($5\cdot10^{16}$ cm^{-3})	4503_3+	$1.7\cdot10^{3}$	$3.3\cdot10^{3}$	$5.0\cdot10^{2}$	$1.1\cdot10^{3}$
$Cd_{0.94}Mn_{0.06}Te$:V ($5\cdot10^{16}$ cm^{-3})	4503_3-	$2.3\cdot10^{3}$	$1.9\cdot10^{3}$	$8.0\cdot10^{2}$	$9.0\cdot10^{2}$
$Cd_{0.94}Mn_{0.06}Te$:V ($5\cdot10^{16}$ cm^{-3})	4512_9	$1.0\cdot10^{4}$	$0.4\cdot10^{3}$	$0.8\cdot10^{3}$	$1.3\cdot10^{4}$
$Cd_{0.94}Mn_{0.06}Te$:V ($5\cdot10^{16}$ cm^{-3})	4513_2	$5.3\cdot10^{4}$	$1.8\cdot10^{4}$	$1.1\cdot10^{4}$	$1.2\cdot10^{4}$
$Cd_{0.91}Mn_{0.09}Te$:V ($5\cdot10^{16}$ cm^{-3})	4519_2	$1.3\cdot10^{3}$	$1.0\cdot10^{3}$	$2.0\cdot10^{3}$	$2.2\cdot10^{3}$
$Cd_{0.91}Mn_{0.09}Te$:V ($1\cdot10^{16}$ cm^{-3})	4519_5	$1.4\cdot10^{3}$	$4.3\cdot10^{3}$	$2.5\cdot10^{3}$	$1.6\cdot10^{3}$
$Cd_{0.91}Mn_{0.09}Te$:V ($1\cdot10^{16}$ cm^{-3})	4519_9	$2.9\cdot10^{3}$	$2.7\cdot10^{3}$	$1.3\cdot10^{3}$	$1.7\cdot10^{3}$
$Cd_{0.91}Mn_{0.09}Te$:V ($1\cdot10^{16}$ cm^{-3})	4520_b	$7.3\cdot10^{3}$	$0.8\cdot10^{3}$	$0.7\cdot10^{3}$	$2.6\cdot10^{3}$
$Cd_{0.91}Mn_{0.09}Te$:V ($1\cdot10^{16}$ cm^{-3})	4520_c	$2.2\cdot10^{3}$	$2.0\cdot10^{3}$	$1.3\cdot10^{3}$	$1.6\cdot10^{3}$
$Cd_{0.91}Mn_{0.09}Te$:V ($1\cdot10^{16}$ cm^{-3})	4520_d	$5.8\cdot10^{3}$	$1.8\cdot10^{3}$	$3.4\cdot10^{3}$	$1.9\cdot10^{3}$
$Cd_{0.95}Mn_{0.05}Te$:V ($3\cdot10^{16}$ cm^{-3})	4527_1b	$7.0\cdot10^{2}$	$9.0\cdot10^{2}$	$4.0\cdot10^{2}$	$4.0\cdot10^{2}$
$Cd_{0.95}Mn_{0.05}Te$:V ($3\cdot10^{16}$ cm^{-3})	4527_1a	$2.2\cdot10^{3}$	$2.0\cdot10^{3}$	$1.8\cdot10^{3}$	$1.8\cdot10^{3}$

In summary, the following are the changes after annealing in the temperature gradient:

1. Usually, the density of tellurium precipitates was reduced.

2. This reduction is more significant at the side of the platelet where the temperature was a little lower.

3. There are fewer of the largest precipitates, so only the smaller precipitates are seen.

We investigated the distribution of tellurium precipitates along the temperature gradient on the cleaved surfaces parallel to the [111] direction (parallel to the ampoule's axis). Before annealing, the crystal exhibited a homogenous distribution. .After annealing, the density of tellurium precipitates near the lower-temperature side of the platelet was less than that near the side, 2 mm away, with the higher temperature.

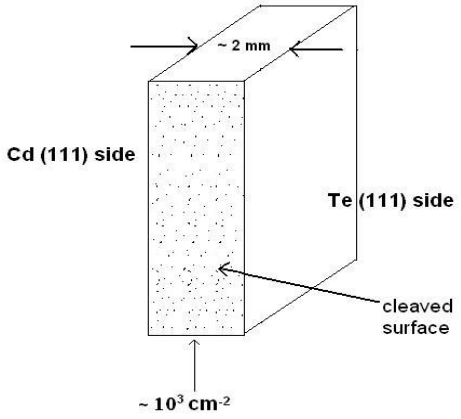

Fig. 5. Cleaved surface of the platelet before annealing.

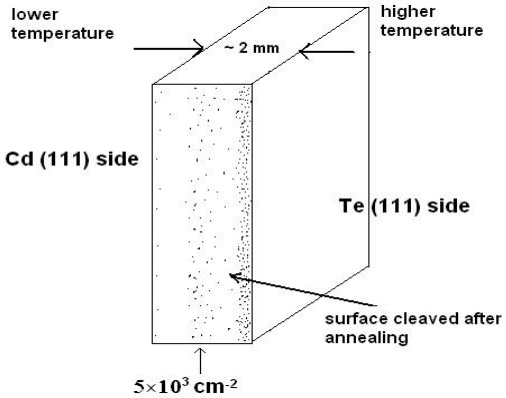

Fig. 6. Cleaved surface of the platelet after annealing in the temperature gradient.

Two different mechanisms are responsible for eliminating tellurium precipitates during annealing in the temperature gradient: the thermo-migration of precipitates, and the in-diffusion of Cd. At the temperature of annealing, i.e., ~ 650 C, the tellurium precipitates are in liquid state and in the presence of a temperature gradient they move in the direction of this gradient (Fig. 7).

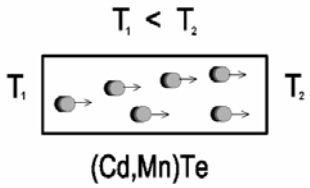

Fig. 7. Thermal migration of Te precipitates in the direction of temperature gradient (after [2] and [3]).

While the large tellurium precipitates are eliminated by annealing in the temperature gradient, the fine precipitates cannot be eliminated this way. Rather, extended annealing in the cadmium vapors at uniform temperature is required to remove them effectively, that is, the in-diffusion of cadmium from its vapors. This process converts tellurium precipitates into CdTe or (Cd,Mn)Te, and is more effective in the surface regions of the crystal. Because of the larger distance over which the cadmium ions must diffuse to deeper regions in the bulk the diffusing cadmium atoms appear later and in smaller quantity. To obtain the high-resistivity (Cd,Mn)Te crystals for detector applications, a long annealing time in cadmium vapors at uniform temperature is essential.

Conclusions

We explored two techniques of annealing (Cd,Mn)Te crystals in cadmium vapors: annealing at uniform temperature and annealing in the temperature gradient. Both reduce the concentration of Te precipitates. The large tellurium precipitates can be eliminated by annealing in the temperature gradient; the tellurium precipitates melt and migrate in the temperature gradient. Smaller precipitates are eliminated by extended annealing at uniform temperature due to the in-diffusion of cadmium, i.e., by the same technique as is used to obtain high resistivity in the crystals.

Acknowledgments

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